SYNTHESIS AND POLYMERIZATION OF DIAZABUTADIENE AND AZASTYRENE DERIVATIVES

A Doctoral Thesis

by

Akihito Hashidzume

Submitted to

the Graduate School of Science, Osaka University

February, 1997

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February, 1997

橋爪章仁

Akihito Hashidzume

Contents

Chapter 1

General Introduction

Chemistry of the Compounds Containing the C=N Double Bond.[1] The C=N double bond is considered to be an intermediate between C=C and C=O double bonds in many respects. While the C=O double bond is inevitably a terminal bond, C=C and C=N double bonds can be internal bonds in chains or rings. Furthermore, both the nitrogen atom in C=N and the oxygen atom in C=O possess lone pairs of electrons. There are, however, analogies among these three: they all have two electrons in π orbitals. Some typical physicochemical properties of these three double bonds are listed in Table 1. On the basis of the data in Table 1, we can conclude that the C=N double bond is intermediate in some properties between the C=C and C=O double bonds.

As expected, compounds containing the C=N double bond undergo various types of reactions, such as addition, cyclo-addition, substitution, and cleavage; reactions being similar to those compounds containing the C=C or C=O double bond.

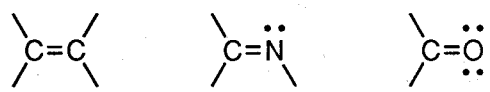
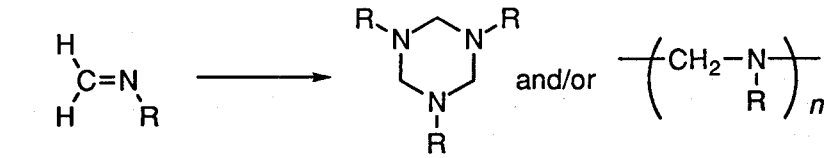
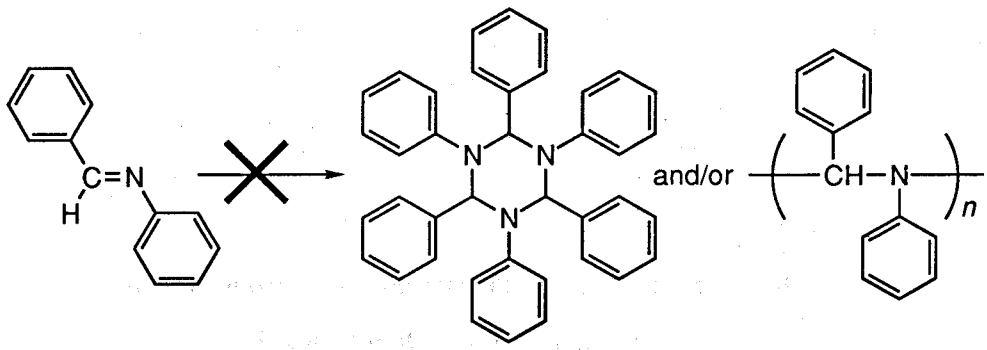


Table 1. Some Typical Physicochemical Properties of C=C, C=N, and C=O Double Bonds

	C=C	C=N	C=O
Bond Length (Å)	1.338	1.30	1.21
Overlap Integral	0.271	0.230	0.218
Dipole Moment (D)	0.0	0.9	2.3
Bond Energy (kcal/mol)	145.8	147.0	179.0

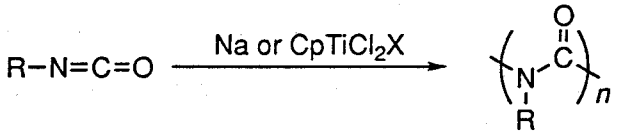
Addition Polymerization through the C=N Double Bond. There are many reports concerning the addition polymerization through C=C or C=O double bonds, and thus the properties of these polymerizations are well-known.[2] However, few papers have reported on the polymerization through the C=N double bond. Therefore, there remain many unsolved problems on the polymerization through the C=N double bond. A reason may be ascribable to extreme variations in the stability of the compounds containing the C=N double bond, imine compounds. Methylene imines are known to be stable in the vapor phase at high temperatures or in the solid phase at liquid nitrogen temperature. These compounds are polymerized or cyclic trimerized in the liquid state even at a low temperature (-140 °C).[3] At the other extreme, some imine compounds, such as *N*-benzylideneaniline, are too stable to be polymerized or cyclic trimerized,[4] although they undergo addition reaction with various compounds.[1]



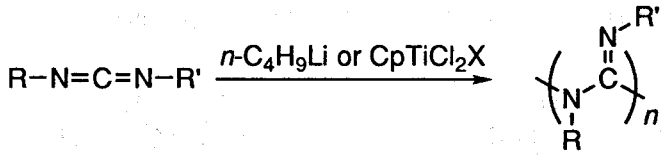


Only three classes of compounds, which can be polymerized to high molecular weight polymer ($\overline{M}$ > 10,000), have been reported so far. These are isocyanates,[5-7] carbodiimides,[8, 9] and alkanal azines.[10] Besides these exceptions, few papers have reported compounds which are polymerized through the C=N double bond.

Isocyanates have long been reported to be cyclic trimerized.[11] In 1959, Shasoua[5] first succeeded in the polymerization of isocyanates with sodium compounds. The polymers of isocyanates consist of 1-nylon units and take a helical structure in solution. Because of these unique properties, many papers have been reported on the polymerizations and the helical structure of the polymers of isocyanates.[6] Recently, Novak *et al.*[7] succeeded in the living polymerization of isocyanates.



Carbodiimides are the compounds having cumulative double bonds similar to isocyanates. In 1964, Robinson[8] first reported the polymerization of carbodiimides, and synthesized the oligomers with molecular weight of several thousands by using *n*-butyllithium. Furthermore, Robinson obtained the monomer in a quantitative yield upon pyrolysis of the obtained oligomer. Recently, Novak *et al.*[9] succeeded in conducting the living polymerization of carbodiimides and in obtaining polymers of molecular weights over 100,000. In addition, they also reported that the polymers obtained from carbodiimides took helical structures in solution and that the polymers containing chiral centers in their side chains showed high optical activity after annealing.

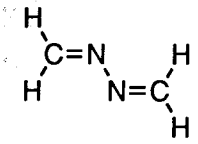


Hall *et al.*[4,12,13] investigated the polymerizabilities of the C=N double bond by using imines and 1-azabutadienes containing electron-withdrawing groups such as cyano or ester groups. Since the imines containing electron-withdrawing groups are relatively unstable, their existence was only confirmed in solution. All attempts to

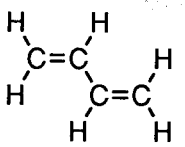
isolate the imines were unsuccessful, and only oligomers were obtained. The imines spontaneously copolymerized with *p*-methoxystyrene to give oligomers of molecular weights about 2,000.[12] However, high molecular weight polymers have not been obtained by the homopolymerization of the imines. The imines containing an aryl group at the carbon and an electron-withdrawing group at the nitrogen are stable as monomers. However, only oligomers with degree of polymerization about 8 have been obtained by homopolymerization. 1-Azabutadienes containing an electron-withdrawing or an aryl group at the nitrogen have been polymerized by anionic initiators, such as *n*-butyllithium and Grignard reagents, to form oligomers of molecular weights of several thousands.[13] The obtained oligomers were composed of 4,1- and 4,3-units, showing the participation of the C=N double bond in the polymerization.

Polymerization of 2,3-Diaza-1,3-butadiene and Its Derivatives (Azine Compounds). There are many papers concerning the chemical reactivities of 2,3-diazabutadiene derivatives.[14] However, there had been no papers on 2,3-diazabutadiene derivatives as monomers, before Kamachi *et al.*[16,17] investigated their polymerizabilities.

In 1959, 2,3-diaza-1,3-butadiene (formaldehyde azine), the simplest azine, was first prepared by Neureiter.[15] Neureiter found that the azine was stable in the vapor phase at high temperatures or in the solid phase below its melting point, and that it spontaneously polymerized in the liquid phase. However, Neureiter reported neither the details of the polymerization nor the structure of the polymer.



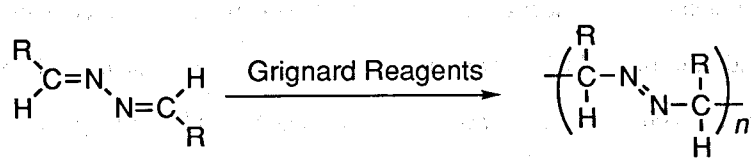
Formaldehyde Azine



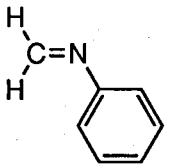
1,3-Butadiene

In 1974, Kamachi *et al.*[16] found that formaldehyde azine was stable in dilute solution in THF at room temperature under water-free conditions. They studied the polymerizability of the azine under these conditions. Although formaldehyde azine could not be polymerized with radical initiators, such as benzoyl peroxide and 2,2'-azobis(isobutyronitrile), it was polymerized with various compounds, such as anionic initiators, protic compounds, tetracyanoethylene, and chloranil. The obtained polymer was composed of both 1,2- and 1,4-units. The ratio of 1,2-units to 1,4-units was dependent on the initiator. Anionic initiators formed polymers, which were insoluble in organic solvents, composed of mainly 1,2-units (~ 90 %). The other initiators gave soluble polymers having 1,2 units of 35-50 %.

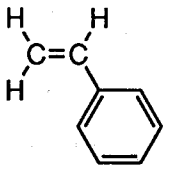
Many azine compounds substituted at 1,4-positions are stable under ordinary conditions. Kamachi *et al.*[17] focused on the polymerizability of alkanal azines (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7, ...). These azines have high anionic polymerizability, and oligomers of molecular weights about 2,000 were obtained. Furthermore, they found that these alkanal azines are polymerized by Grignard reagents to form high molecular weights polymers. The polymers were found to be composed of *trans*-1,4-units by various spectroscopies. In addition, Kamachi *et al.*[17] found that the chain transfer reaction took place at the hydrogen on the α-carbon of the C=N during the polymerization.



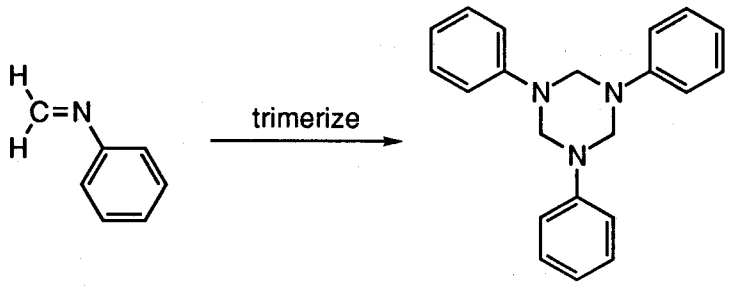
Chemical Reaction and Polymerization of Azastyrene (*N*-Methyleneaniline, MeAn). Since MeAn is a styrene analogue containing a C=N double bond, many chemists have long been interested in this compound. MeAn is known to be stable in the vapor phase and to be immediately converted to a cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine, in the condensed phase.[18]



N-Methyleneaniline
(MeAn)



Styrene



Since MeAn has never been isolated in the condensed phase, there are few studies concerning the chemical reactivity and the polymerizability of MeAn. The physicochemical properties of MeAn were investigated in its vapor phase by spectroscopic methods. The infrared (IR) spectrum of MeAn showed a sharp absorption band due to the stretching vibration of the C=N double bond at about 1700 cm^{-1}.[19] Distifano *et al.*[20] determined the ionization potentials and the electron affinities of MeAn by photoelectron and electron transmission spectroscopies (Figure 1). Ionization potentials and electron affinities of MeAn were compared with those of styrene and aniline, which were chosen as models of planar and orthogonal conformers, respectively. The authors concluded that MeAn had a planar conformation in the vapor phase because the levels of the π_A^* and the π_S^* of MeAn resembled those of styrene. Furthermore, Figure 1 shows that the π_{NC}^* of MeAn is lower than the π_{CC}^* of styrene, suggesting that MeAn has higher reactivity towards anions than styrene does. The figure also shows that the N_{1p} of MeAn is higher than the π_{CC} of styrene, suggesting that MeAn also has higher reactivity towards cations than styrene does. These results suggest that MeAn may be a good monomer for the purpose of this study.

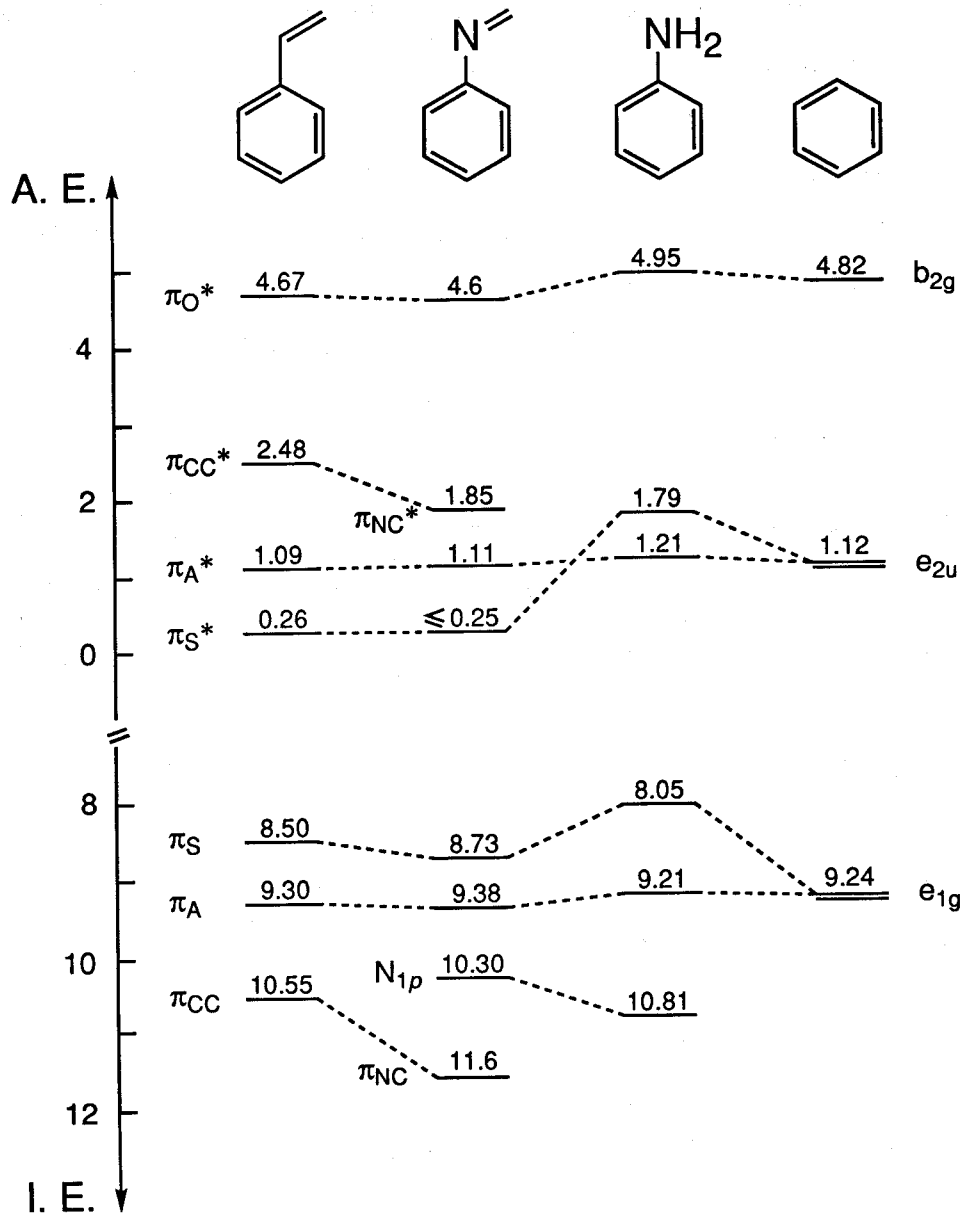
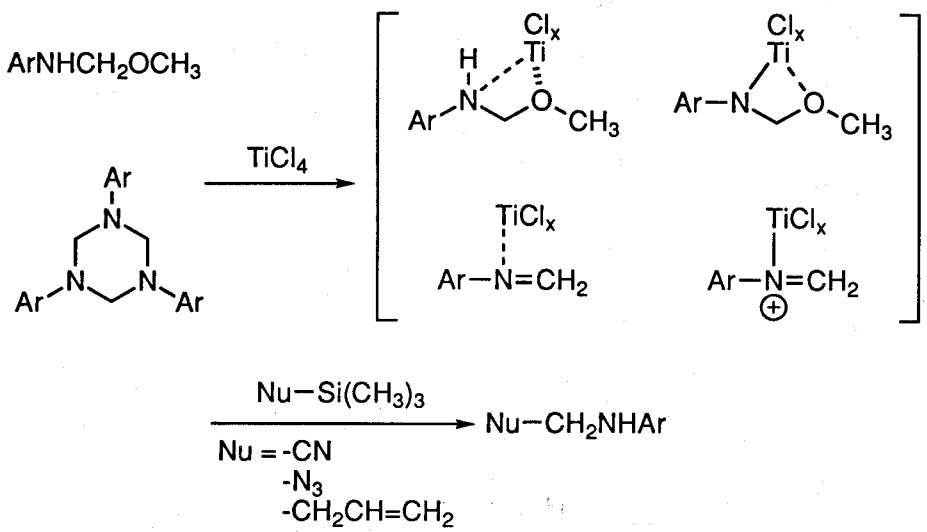


Figure 1. Ionization energies (IEs) and attachment energies (AEs) of styrene, MeAn, aniline, and benzene, as determined by ultraviolet photoelectron and electron transmission spectroscopies.[20]

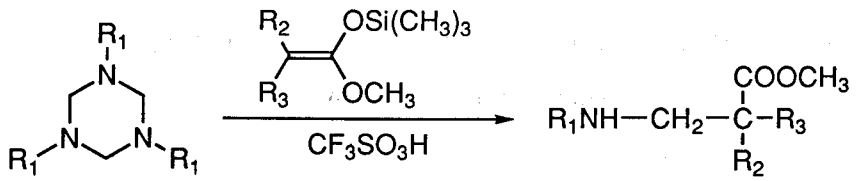
Although many chemists may have paid attention to the reactivity of MeAn because of its unique structure, only three or four groups have reported its reactions: these reactions are as follows.[21-23] Each group used chemical reactions which

produced MeAn as an intermediate in the reactions. However, no data were shown that supported the existence of MeAn. Therefore, we think that no paper has reported on the chemical reactivity of MeAn.

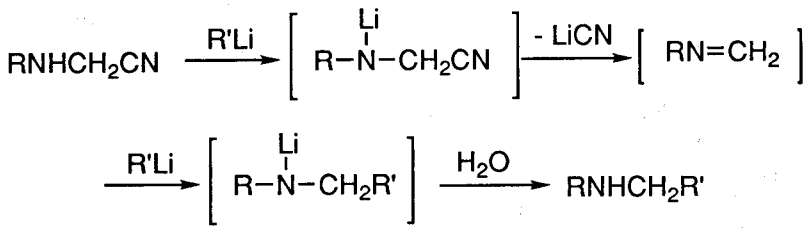
Ha *et al.*[21] prepared MeAn as an intermediate by the addition of titanium tetrachloride to *N*-methoxymethylaniline or to hexahydro-1,3,5-triphenyl-1,3,5-triazine at low temperature (-20 °C). Ha *et al.*[21] found MeAn prepared by this manner reacted with a relatively weak nucleophile, such as trimethylsilyl cyanide, trimethylsilyl azide, or allyl trimethylsilane, to form aniline derivatives.



Ikeda *et al.*[22] conducted the reaction of hexahydro-1,3,5-triphenyl-1,3,5-triazine with dimethylketene trimethylsilylacetal in the presence of trifluoromethanesulfonic acid to form β-aminocarbonate.



Overman *et al.*[23] produced MeAn by the reaction of cyanomethylaniline with an equimolar amount of *n*- or *s*-butyllithium. They prepared aniline derivatives by the reaction of MeAn with more than equimolar amount of *n*- or *s*-butyllithium.

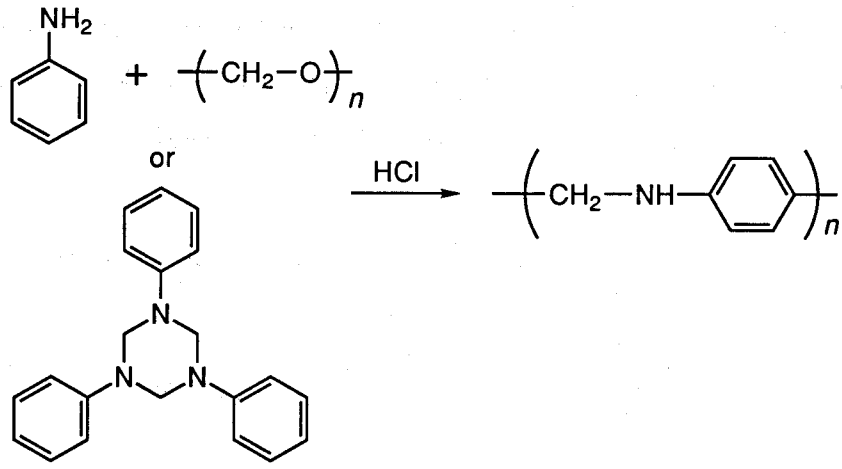


There are few papers concerning the polymerization of MeAn. No systematic studies have been performed.

Wakae *et al.*[24] reported the formation of benzene-insoluble compounds by the reaction of aqueous formaldehyde with aniline. Although they concluded that the benzene-insoluble product was polymer, they mentioned neither the molecular weight nor the structure of the polymer.

Bailey *et al.*[19] found that methyleneimines were produced by the pyrolysis of methyl allyl amines. The methyleneimines were detected by gas chromatography. However, upon collection from a gas chromatograph the methyleneimines spontaneously polymerized to low molecular weight polymers. The molecular weights of the polymers were estimated by vapor pressure osmometry to be about 300 and 1000, corresponding to trimer and decamer, respectively. The authors concluded that linear polymers were formed on the basis of the IR spectra of the polymers.

Scheele *et al.*[18] reported that a resin was obtained by the reaction of hydrochloric acid with hexahydro-1,3,5-triphenyl-1,3,5-triazine or with a mixture of aniline and paraformaldehyde. Since *p*-toluidine was obtained by the reduction of the resin, the authors concluded that the product was formed by 1,6-addition polymerization of MeAn. However, the structure of the obtained product remains unclear, because the reaction system is complicated.



As mentioned above, to our knowledge, there is no paper concerning the polymerization caused by addition of initiators to monomeric MeAn. Accordingly, its polymerizability has remained unknown.

Scope and Outline of This Thesis. This thesis consists of two parts. In ***Part 1***, the preparation and the polymerization of 2,3-diaza-1,3-butadiene derivatives (azine compounds) are described. In ***Part 2***, the preparation and the polymerization of azastyrene and its derivative are described.

As mentioned above, alkanal azine compounds (RCH=N-N=CHR, R=CH_3, C_2H_5, C_3H_7) are polymerized by Grignard reagents to form *trans*-1,4-polymers of molecular weights higher than 10,000.[10] In these polymerizations, however, chain transfer reactions take place, since the protons at the α-carbon of the C=N double bonds are eliminated by active chain ends.[10] In order to avoid the chain transfer reaction, we focused on trifluoroacetaldehydeazine (R=CF_3, TFAcAz), which has no hydrogen at the α-carbon causing the chain transfer. In **Chapter 2**, the preparation and chemical reactions of TFAcAz, a new compound, are described. The reactivity of TFAcAz was found to be different from those of alkanal azine compounds, because TFAcAz has electron-withdrawing trifluoromethyl groups. TFAcAz was readily attacked by nucleophiles, such as water, methanol, and triethylamine, which do not

react with alkanal azine compounds. When triethylamine was added to TFAcAz at room temperature (20-30 °C), a crystalline product formed. The structure of the product was investigated by elemental analysis, various spectroscopic analyses, and X-ray crystallographic analysis. Consequently, the product was found to be a cyclic dimer of TFAcAz. In addition, TFAcAz reacted with protic compounds, such as water and methanol, to form 1,2-adducts in quantitative yields.

In **Chapter 3**, the polymerization of TFAcAz is described. Only soluble oligomers were obtained by the polymerizations of TFAcAz with anionic initiators, such as *n*-butyllithium, methylmagnesium iodide, potassium methoxide/18-crown-6, and DBU. This is contrary to the expectation that the substitution of the hydrogen atoms at α-carbon with fluorine atoms suppresses the chain transfer reaction. However, polymer was obtained at -20 °C by the addition of triethylamine, which is a weaker nucleophile than the initiators above. The structure of the polymer was investigated by IR, Raman, and solid-state ^{13}C NMR spectroscopies. From these results, the polymer was found to be composed of only 1,2-units.

As described in Chapters 2 and 3, the chemical reactivity and the polymerizability of TFAcAz were different from those of alkanal azine compounds. These results suggest that the chemical reactivities and the polymerizabilities of azine compounds are remarkably dependent on the nature of their substituents. In order to confirm this, we paid attention to the azine compounds containing ester groups, which are electron-withdrawing groups. Furthermore, the azines with ester groups have no hydrogen atom on the α-carbon of the C=N double bond, which causes the chain-transfer reaction observed in the polymerization of alkanal azines. These aldehyde azine compounds containing ester groups have not previously been reported. In **Chapter 4**, the preparation, the chemical reactions, and the polymerization of *n*-butyl glyoxylate azine (R=$COOC_4H_9$-*n*, BgAz) are described. BgAz was found to be readily attacked by nucleophiles, similarly to TFAcAz. BgAz reacted with protic compounds such as alcohols to produce quantitative yields of 1,2-adducts. Furthermore, BgAz reacted with organic bases, such as DBU and triethylamine, to form oligomers. In addition,

BgAz reacted with trifluoroacetic acid to form oligomer, although TFAcAz did not react with trifluoroacetic acid. The result shows that the C=N double bonds of BgAz are more nucleophilic than those of TFAcAz.

Since alkanal azine compounds are considered to be electron-donating monomers,[16] alkanal azine compounds may be copolymerized with electron-withdrawing monomers. In **Chapter 5**, the copolymerization of acetaldehyde azine (R=CH_3, AcAz) with maleic anhydride (MAnh) is described. It was found that the copolymer was formed by addition polymerization of the one-to-one adduct of AcAz with MAnh mainly through the C=C double bonds.

In ***Part 2***, the preparation and the polymerization of azastyrene (*N*-methyleneaniline) and its derivatives are described.

Although MeAn is immediately converted to the cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine, in its condensed phase, it is known to be stable in its vapor phase.[20] The author tried to isolate MeAn in solution according to the dilution method.[16] In **Chapter 6**, the isolation, stability, and chemical reactions of MeAn are described. It was found that MeAn was stable in THF-d_8 below -40 °C. Furthermore, the existence of MeAn was confirmed in a dilute solution (~ 100 mM) even at 30 °C under acid-free conditions. In addition, a small amount of acid formed by pyrolysis was found to cause the cyclic trimerization of MeAn. Direct reactions of MeAn with nucleophiles were carried out to form aniline derivatives. In this chapter, the polymerizability of MeAn under several conditions is also described, because the conditions under which MeAn existed stably were made clear. Consequently, the author found that polymer was obtained in a relatively high yield (80-90 %) by the polymerization of MeAn in a concentrated solution (2.0-3.0 M). The structure of the polymer was investigated by elemental analysis and IR spectroscopy. The results suggested that the obtained polymer was linear and formed by addition polymerization of MeAn through the C=N double bond.

Since MeAn is immediately converted to the cyclic trimer in its condensed phase,[18-20] it is difficult to use MeAn for reactions and polymerization. Thus, the

author paid attention to 2,6-diisopropyl-*N*-methyleneaniline (DiPMAn), which had been reported to be a stable azastyrene derivative by Verardo[25] in 1985. The two isopropyl groups at the *ortho*-positions are considered to retard the cyclic trimerization of DiPMAn. In **Chapter 7**, the polymerization of DiPMAn is described, since the polymerizability of DiPMAn had not previously been reported. DiPMAn did not react with 2,2'-azobis(isobutyronitrile), which is a typical radical initiator. Although *n*-butyllithium, which is a typical anionic initiator, added to the C=N double bond of DiPMAn, no polymer was obtained because of extremely slow propagation. However, DiPMAn reacted with cationic initiators, such as trifluoroacetic acid, to give high molecular weight polymers of molecular weights higher than 10,000, under optimum conditions. The structure of the polymer was investigated by elemental analysis and IR and ^{1}H NMR spectroscopies. From these results, the polymer was found to be formed by 1,6-addition through aromatic electrophilic substitution. Furthermore, since DiPMAn is considered to be an electron-donating monomer, DiPMAn may be copolymerized with electron-withdrawing monomers. In this chapter, the copolymerization of DiPMAn with MAnh is also described. DiPMAn reacted with MAnh without initiator to form polymer of molecular weight as high as 10,000. The result of the continuous variation method suggested that an alternating copolymerization took place. The structure of the copolymer was investigated by elemental analysis and IR and ^{1}H NMR spectroscopies. From these results, it was found that the copolymer was formed via a zwitterion mechanism.

Few papers have reported on the radical copolymerization of vinyl monomers and imines.[26] These results suggest that the imines function as retarders in radical polymerizations. 2,3-Diaza-1,3-butadiene and azastyrene derivatives, that is, azine compounds and *N*-methyleneaniline derivatives, respectively, have not been polymerized in the presence of radical initiators.[10,27,28] Thus, in **Chapter 8**, the radical polymerizability of DiPMAn is described. The elementary reactions of radical polymerization of vinyl and diene monomers have been investigated in detail by ESR spectroscopy, and the rate constants of the initiation[29] and the propagation[30] of vinyl or

diene monomers have been determined. The author estimated the rate constant of the reaction of diphenylphosphonyl radical with DiPMAn by using time-resolved ESR spectroscopy.[29]

References

(1) "The chemistry of the carbon-nitrogen double bond"; Patai, S., Ed.; John Wiley: London, 1970.

(2) Odian, G. "Principles of Polymerization", 3rd ed.; John Wiley: New York, 1991.

(3) (a) Khayar, S.; Guiman, G.; Pfister-Guillouzo, G.; Begtrup, M. *New J. Chem.*, **1989**, *13*, 551. (b) Giumanini, A. G.; Verardo, G.; Piana, M. *J. Prakt. Chem.*, **1988**, *330*, 161. (c) Cortolano, F. P.; Paster, S. D.; Ravichandran, R.; Steinberg, D. H. *Tetrahedron Lett.*, **1988**, *29*, 5875. (d) Lasne, M. C.; Ripoll, J. L.; Thuillier, A. *J. Chem. Res.*, **1982**, 214.

(4) Hall, H. K., Jr. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(5) (a) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159. (b) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(6) (a) Goodman, M.; Chen, S. *Macromolecules* **1970**, *3*, 398. (b) Goodman, M.; Chen, S. *Macromolecules* **1971**, *4*, 625. (c) Green, M. M.; Lifson, S.; Teramoto, A. *Chirality* **1991**, *3*, 285. (d) Green, M. M.; Andreola, C.; Munoz, B.; Reidy, M. P.; Zero, K. *J. Am. Chem. Soc.* **1988**, *110*, 4063. (e) Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 8850. (f) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452.

(7) (a) Patten, T. E.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 5065. (b) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436.

(8) Robinson, G. C. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3901.

(9) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520.

(10) (a) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504. (b) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931. (c) Kamachi, M.; Kajiwara, A.; Hashidzume, A. to be published.

(11) (a) Hofmann, A. W. *Chem. Ber.* **1870**, *3*, 761. (b) Snape, H. L. *J. Chem. Soc.* **1886**, *49*, 254. (c) Chadwick, D. H.; Allen, T. C. U.S. Patent 2,733,254, 1956.

(12) (a) Hall, H. K., Jr.; Ramezanian, M; Seava, F. D. *Tetrahedron Lett.* **1988**, *20*, 1235. (b) Ramezanian, M.; Padia, A. B.; Saeva, F. D.; Hall, H. K., Jr. *J. Org. Chem.* **1990**, *55*, 1768.

(13) (a) Kitayama, T.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 1451. (b) Kim, J. B.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1990**, *22*, 21.

(14) (a) Curtius, T.; Zinkeisen, E. *J. Prakt. Chem.* **1898**, *58*, 310. (b) Kost, A. N.; Grandberg, I. I. *Usp. Khim.* **1959**, *28*, 921. (c) Kolbah, D.; Loruncev, D. "Stickstoffverbindungen I"; Stroh, R., Ed.; George Thieme: Stuttgart, 1967; Band X/2, Teil 2, pp 89-122.

(15) Neureiter, N. P. *J. Am. Chem. Soc.* **1959**, *81*, 2910.

(16) (a) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295. (b) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(17) (a) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232. (b) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890. (c) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(18) (a) Miller, J. G.; Wagner, E. C. *J. Am. Chem. Soc.* **1932**, *54*, 3698. (b) Scheele, W.; Steike, L. *Kolloid-Z.* **1941**, *97*, 176.

(19) Bailey, W. E.; Hartz, R. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9*, 404.

(20) Distefano, G.; Giumanini, A. G.; Modelli, A.; Poggi, G. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1623.

(21) (a) Ha, H.-J.; Ahn, Y.-G. *Synth. Commun.* **1991**, *21*, 155. (b) Ha, H.-J.; Ahn, Y.-G. *Synth. Commun.* **1995**, *25*, 969. (c) Ha, H.-J.; Ahn, Y.-G.; Choi, J.-K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2631.

(22) Ikeda, K.; Achiwa, K.; Sekiya, M. *Tetrahedron Lett.* **1983**, *24*, 913.

(23) Overman, L. E.; Burk, R. M. *Tetrahedron Lett.* **1984**, *25*, 1635.

(24) Wakae, M.; Konishi, K. *Osaka Furitsu Kogyo-Shoreikan Hokoku* **1963**, *29*, 47.

(25) (a) Verardo, G.; Cauci, S.; Giumanini, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1787. (b) Giumanini, A. G.; Verardo, G.; Poiana, M. *J. Prakt. Chem.* **1988**, *330*, 161.

(26) (a) Ferruti, P.; Audisio, G.; Cottica, G.; Feré, A. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 451. (b) Barson, C. A.; Bevington, J. C., Hunt, B. J. *Eur. Polym. J.* **1995**, *31*, 249.

(27) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(28) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromol. Rapid Commun.* **1996**, *17*, 529.

(29) (a) Kajiwara, A.; Konishi, Y.; Morishima, M.; Schnabel, W.; Kuwata, K.; Kamachi, M. *Macromolecules* **1993**, *26*, 1656.

(30) For example: Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.

Part 1

Synthesis and Polymerization of 2,3-Diaza-1,3-butadiene Derivatives (Azine Compounds)

Chapter 2

Preparation and Chemical Reactions of Trifluoroacetaldehyde Azine (1,1,1,6,6,6-Hexafluoro-3,4-diaza-2,4-hexadiene)

Introduction

Polymerization of vinyl and carbonyl monomers are of course very familiar to polymer chemists. However, the polymerizations of imine monomers are conspicuous by their absence. Only a few papers have focused on the polymerizability of the C=N double bond.[1-7] Therefore, Kamachi *et al.*[8-15] investigated the polymerizability of azine compounds, and found that alkanal azines (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7) could be polymerized with Grignard reagents to form crystalline 1,4-polymers.[13,14] However, typical anionic initiators, such as *n*-butyllithium and naphthylsodium, gave only soluble oligomers of alkanal azines. The formation of oligomers is due to a chain-transfer reaction, in which protons on the α-carbons of the aldehyde are extracted by propagating anions.

In order to suppress the chain-transfer reaction we prepared trifluoroacetaldehyde azine (R=CF_3, TFAcAz), which has no protons on the α-carbons of the aldehyde, and investigated the polymerizability of TFAcAz. It has been found that TFAcAz can be polymerized in the frozen state (at *ca.* -20 °C) to form a crystalline 1,2-polymer with triethylamine, which does not react with the alkanal azines.[15] In the course of the study we found that a pale-yellow crystalline product was obtained without the formation of the 1,2-polymer when the polymerization was performed at 20 °C.

Although there are several papers concerning the syntheses of azine compounds containing fluorine atoms,[16-21] to our knowledge, no paper has been published on the preparation and chemical reactions of TFAcAz. A few papers have been published concerning the chemical reactivity of alkanal azines.[22, 23] It was found that the

chemical reactivity of TFAcAz was remarkably different from that of alkanal azines. In this chapter, the reactions of TFAcAz with bases and protic compounds will be described, and the chemical reactivity of TFAcAz based on the structures of the obtained products will be discussed.

Experimental Section

Materials. TFAcAz was prepared from trifluoroacetaldehyde hydrate[24] and hydrazine monohydrate, and was purified by successive distillations, as described in a paper.[15] Acetic acid and trifluoroacetic acid were dried with phosphorus pentaoxide and separated from the phosphorus pentaoxide by decantating immediately prior to use. Triethylamine (Et_3N) and tri-*n*-butylamine (n-Bu_3N) were dried with calcium hydride and distilled under reduced pressure. Tri-*n*-decylamine (n-Dec_3N) was dried with calcium hydride and separated from the calcium hydride by decantating immediately prior to use. Distilled water was used. Other reagents were used without further purification.

Reactivities of TFAcAz. A given amount of a reagent was added to TFAcAz (50 mg, 0.26 mmol) via a micro-syringe. The change in the reaction mixture was detected by means of gas chromatography.

Preparation of a Cyclic Dimer of TFAcAz. Et_3N (0.375 mL, 2.63 mmol) was added to TFAcAz (1.0 mL, 5.26 mmol) in an ampule at *ca.* 20 °C. After 24 h, a cyclic dimer of TFAcAz was isolated as pale-yellow crystals by using a gas chromatograph with a silicone (DC550, Gasukuro Kogyo Inc.) column: yield 142 mg, 14.2 %; mp 26.8-27.1 °C; IR (KBr) 1160 (CF), 1280 (CF), 1336 (C-F), 1633 (C=N) cm^{-1}; Raman 1680 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.04 (q, J = 8.1 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 53 (qq, J = 35.1, 3.1 Hz, CH_2N), 117 (q, J = 277.1 Hz, CF_3), 123 (q, J = 278.9 Hz, CF_3), 139 (q, J = 35.7 Hz, C=N); ^{19}F NMR

($CDCl_3$, 470.5 MHz) δ -65.5 (q, J = 1.8 Hz, CF_3), -72.2 (tq, J = 8.1, 1.8 Hz, CF_3); ^{14}N NMR ($CDCl_3$, 36.1 MHz) δ -81 (bs, C=N), -250 (bs, CH_2N). Anal. Calcd for $C_8H_4N_4F_{12}$: C, 25.01; H, 1.05; N, 14.59; F, 59.35. Found: C, 25.37; H, 1.32; N, 14.93. EI-MS [M^+] Calcd 384. Found 384.

X-ray Crystallographic Analysis of the Cyclic Dimer. Single crystals of the cyclic dimer were grown under reduced pressure (~ 10^{-1} mmHg) in sealed tubes.

Details of the crystal data, intensity collection, and refinement are given in Table 1. The intensity data were collected at *ca.* -12.5 °C on a Rigaku NL-1 diffractometer using Cu K_α radiation. Accurate cell constants for the cyclic dimer were determined using 25 general reflections (28.65 ° < θ < 30.12 °).

The intensities were measured by the ω (0 ° < 2θ < 80 °) and 2θ-ω (80 ° ≤ 2θ ≤ 120 °) scan techniques with background counts being made at the beginning and end of each scan for a total of half the scan time. The stability of the crystal was checked by monitoring the intensities of standard reflections every 100 measurements. Only minor variations were observed. The structure was solved by a direct method (MULTAN80[25]) and refined by least-squares methods in consideration of anomalous dispersion terms. All of the hydrogen atoms were located in difference Fourier syntheses, and were included in the refinement in an unconstrained isotropic form. The final refinement was carried out using full-matrix-least-squares techniques.

The atomic coordinates and temperature factors are listed in Table 2.[26]

Table 1. Crystal Data

molecular formula	$C_8F_{12}H_4N_4$
molecular weight	384.13
crystal system	tetragonal
space group	$P4_32_12$
a, Å	9.5598(8)
c, Å	14.532(1)
V, Å^3	1328.2(2)
Z	4
D_c, g cm^{-3}	1.921
μ (Cu K_α), cm^{-1}	22.2
crystal size, mm	0.3 x 0.3 x 0.2
scan method	ω, 2θ-ω
scan speed, deg min^{-1}	4.0
scan width, deg	1.8
2θ range, deg	0-120
standard reflections	-1 4 -7, 6 -1 2, 4 4 -4
standard variation, %	±2.3
number of measured reflections	2229
number of observation reflections	892
I≥3σ(I)	
final R, R_W	0.0415, 0.0448
largest shift /error in final cycle; Δ / σ	0.001

Table 2 Final Fractional Atomic Coordinates for the Cyclic Dimer of TFAcAz

atom	x	y	z	$B_{eq}{}^{a}$ / Å^2
F(1)	0.0493(4)	0.7579(4)	0.1882(2)	7.7
F(2)	0.2224(4)	0.6243(4)	0.1552(3)	8.5
F(3)	0.0454(4)	0.6394(4)	0.0663(2)	7.6
F(4)	0.2232(4)	0.9927(4)	- 0.2029(2)	8.2
F(5)	0.2269(4)	0.7925(4)	- 0.1376(2)	7.3
F(6)	0.3537(4)	0.9584(4)	- 0.0853(3)	8.5
N(1)	0.1016(4)	0.9230(4)	0.0291(3)	4.3
N(2)	0.0644(4)	1.0292(4)	0.0923(3)	4.6
C(1)	0.1127(5)	0.9744(5)	- 0.0606(3)	4.2
C(2)	0.2024(5)	0.8264(6)	0.0693(4)	4.9
C(3)	0.1281(6)	0.7115(6)	0.1190(4)	5.5
C(4)	0.2325(7)	0.9287(6)	- 0.1219(4)	6.2
H(1)	0.256(5)	0.870(5)	0.111(3)	2.2
H(2)	0.274(6)	0.783(5)	0.028(3)	3.7

^{a} $B_{eq} = (4/3)\sum_{i} B_{ii} a_i^2$

Preparation of an Adduct of TFAcAz with Methanol. Methanol (1.0 mL, 24.7 mmol) was added to TFAcAz (1.0 mL, 5.26 mmol) in an ampule at *ca.* 20 °C. After 24 h, an adduct of TFAcAz with methanol was isolated as colorless needles by using a gas chromatograph with a diethyleneglycol succinate (DEGS, Gasukuro Kogyo Inc.) column: mp 25.1-25.5 °C; IR (KBr) 1138 (C-F), 1275 (C-F), 1325 (C-F), 1630 (C=N) cm^{-1}; Raman 1135 (C-F), 1277 (C-F), 1620 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.50 (s, 3H, CH_3O), 4.92 (m, 1H, CHN), 6.40 (d, 1H, J = 7.5 Hz, NH), 7.00 (q, 1H, J = 4.2 Hz, CH=N); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 57.3 (s, CH_3O), 88.6 (q, J = 33.6 Hz, CHN), 120.4 (q, J = 269.8 Hz, CF_3), 122.1 (q, J = 282.0

Hz, CF_3), 126.5 (q, J = 39.7 Hz, CH=N); ^{19}F NMR ($CDCl_3$, 84.5 MHz) δ -80.7 (d, J = 4.9 Hz, CF_3), -64.8 (d, J = 4.3 Hz, CF_3). Anal. Calcd for $C_5F_6H_6N_2O$: C, 26.80; H, 2.70; N,12.50. Found: C, 26.56; H, 2.80; N, 12.94. EI-MS [M^+] Calcd 224. Found 224.

Preparation of an Adduct of TFAcAz with Water. Water (1.0 mL, 55.5 mmol) was added to TFAcAz (1.0 mL, 5.26 mmol) in an ampule at *ca.* 20 °C. After 24 h, colorless needles were deposited and separated from the solution by decantation. After recrystallization from diethyl ether-chloroform, an adduct of TFAcAz with H_2O was obtained as sublimable colorless needles: mp 98.0-99.0 °C (in a sealed tube); IR (KBr) 1140 (C-F), 1278 (CF), 1625 (C=N) cm^{-1}; Raman 1040 (CF), 1280 (CF), 1630 (C=N) cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ 5.22 (m, 1H, CHN), 7.21 (q, 1H, J = 5.0 Hz, CH=N), 7.40 (d, 1H, J = 5.8 Hz, NH), 9.20 (d, 1H, J = 8.3 Hz, OH); ^{13}C NMR (DMSO-d_6, 67.9 MHz) δ 80.1(q, J = 32.9 Hz, CHN), 121.4 (q, J = 278.3 Hz, CF_3), 123.2 (q, J = 283.2 Hz, CF_3), 123.7 (q, J = 36.6 Hz, CH=N); ^{19}F NMR (DMSO-d_6, 84.5 MHz) δ -80.0 (d, J = 5.6 Hz, CF_3), -64.8 (d, J = 4.6 Hz, CF_3). EI-MS [M^+] Calcd 210. Found 210.

Measurements. Infrared (IR) spectra were recorded on a JASCO FT/IR-3 spectrometer. Raman spectra were obtained on a JASCO R-800 spectrometer by using an argon-ion laser 5145 Å excitation line. A frequency calibration of the spectra was carried out with the natural emission of a neon lamp from 0 to 2000 cm^{-1}. ^1H NMR spectra were analyzed on a JEOL JNM-FX90Q spectrometer at 90 MHz under a neat condition. ^1H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270 spectrometer. ^{19}F NMR spectra were measured on a JEOL JNM-GX500 or JEOL JNM-90Q spectrometer as a $CDCl_3$ or DMSO-d_6 solution. A GPC analysis was performed in THF with a TOSOH CO-8011 system by using TSK columns. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron-impact (EI)

method. The mass number was calibrated by using cesium iodide (CsI). The absorption spectrum of TFAcAz was obtained on a Shimadzu UV-2100 spectrometer in cyclohexane at 20 °C.

Results and Discussion

Characterization of TFAcAz. TFAcAz was prepared from trifluoroacetaldehyde hydrate and hydrazine monohydrate, and purified by successive distillations as a pale-yellow liquid (λ_{max} = 209 ($\varepsilon = 4.1 \times 10^3$) and 226 nm ($\varepsilon = 1.4 \times 10^3$)).[15] TFAcAz freezes at a relatively high temperature (mp -4 to -6 °C). Although the molecular weight of TFAcAz (MW = 192) is larger than that of acetaldehyde azine (CH_3CH=N-N=$CHCH_3$, AcAz, MW = 84), TFAcAz is much more volatile (bp 54-56 °C) than AcAz (bp 98-100 °C), suggesting that the substitution with fluorine atoms reduces the intermolecular interactions.

Since there is no paper concerning the synthesis of TFAcAz, TFAcAz was characterized by means of elemental analysis and ^{1}H, ^{13}C, and ^{19}F NMR, IR, Raman, and EI-mass spectroscopies. The C, H, and N contents of TFAcAz (C, 24.53; H, 1.07; N, 14.39 %) were consistent with the calculated values (C, 25.01; H,1.05; N,14.59; F, 59.35 %). The EI-mass spectrum of TFAcAz showed a protonated molecular ion peak at *m/z* = 193. Only one signal was observed at 7.56 ppm, which splits into a quartet (J = 3.7 Hz) due to coupling with three fluorine nuclei of a trifluoromethyl group in the ^{1}H NMR spectrum of TFAcAz. In the ^{13}C NMR spectrum of TFAcAz (Figure 3, upper), two kinds of quartets are observed at 119 (J = 273.4 Hz) and 147 ppm (J = 39.1 Hz). The former is assignable to the carbon of the trifluoromethyl group; the latter is assignable to the carbon atom of the azine bond bound to the trifluoromethyl group.[27] In the ^{19}F NMR spectrum of TFAcAz, only one signal was observed which was due to the fluorine of trifluoromethyl group at -70.2 ppm,[27] which is split into a doublet (J = 3.7 Hz) due to coupling with one proton. Although the absorption band assignable to the stretching vibration of the

C=N double bond is not observed in the IR spectrum of TFAcAz, it is clearly observed at 1640 cm^{-1} in the Raman spectrum. Since the stretching vibration of the C=N double bond is IR-inactive and Raman-active, the TFAcAz molecule is considered to have exclusively an *s-trans* structure.[28]

Polymerizability of TFAcAz. Since TFAcAz is a new monomer, polymerizations of TFAcAz with various types of initiators have been carried out to study the polymerizability of TFAcAz. The results are shown in Table 3. No polymer was obtained by radical and cationic initiators, such as AIBN and $AlCl_3$. When a catalytic amount of *n*-BuLi, CH_3MgI, CH_3OK/18-crown-6, or DBU was added to TFAcAz under an argon atmosphere, only oligomers ($\overline{M}_w$ ~ 1200-1800) were obtained. However, when Et_3N was added to TFAcAz in a frozen state (at -20 °C), poly(TFAcAz) was obtained as a pale-yellow powder, whose structure was previously reported.[15] However, when catalytic amounts of amines, such as Et_3N, *n*-Bu_3N, and *n*-Dec_3N, were added to TFAcAz at room temperature (20 °C), a crystalline product was selectively formed. No reaction occurred with pyridine, which is a weaker base than Et_3N. When catalytic amounts of acids, such as acetic acid and trifluoroacetic acid, were added to TFAcAz, no change was detected by means of gas chromatography. No polymer was obtained by methanol or water. However, TFAcAz quantitatively reacted with a small excess of methanol or with water to form a colorless crystalline product, whose structure is discussed later.

Table 3. Reactions and Polymerizations of TFAcAz

reagent (mol %)	temp., °C	time, h	conv.,[a] %	product
				oligomers
n-BuLi (0.57)	-20	30	42 [b]	$\overline{M}_w \sim 1800$ [b]
CH_3MgI (0.57)	-20	30	23 [b]	$\overline{M}_w \sim 1300$ [b]
CH_3OK/18-crown-6 (1.0)	-20	30	49 [b]	$\overline{M}_w \sim 1800$ [b]
DBU (9.1)	-20	48	81 [b]	$\overline{M}_w \sim 1200$ [b]
Et_3N (2.4)	-20	72	59 [c]	an insoluble polymer
Et_3N (5)	20	18	60	a pale yellow crystal mp 26.8-27.1 °C
Et_3N (33)	20	6	88	
n-Bu_3N (5)	20	48	41	
n-Dec_3N (5)	20	168	25	
pyridine (9.1)	-20	72	0 [d]	-
CH_3COOH (5)	20	10	0	-
CF_3COOH (5)	20	10	0	-
				colorless crystals
H_2O (66)	20	200	~100	mp 98.0-99.0 °C
CH_3OH (66)	20	200	99.9	mp 25.1-25.5 °C

[a] By GC. [b] By GPC. [c] Acetone insoluble fraction. [d] By NMR.

Chemical Reactions of TFAcAz. (a) Reactions of TFAcAz with Et_3N. As shown above, TFAcAz was polymerized with Et_3N in the frozen state to form a crystalline 1,2-polymer. When the reaction of TFAcAz with Et_3N was carried out at room temperature (20 °C), no polymerization took place, and a crystalline compound was formed.

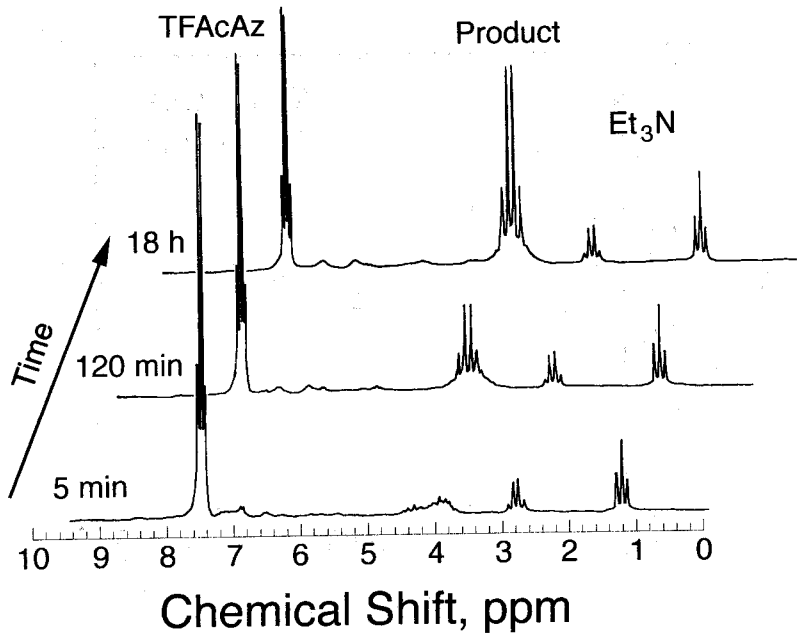


Figure 1. 90 MHz ^{1}H NMR spectra of TFAcAz-Et_3N (neat, molar ratio TFAcAz : Et_3N = 20 : 1).

When a catalytic amount of Et_3N was added to TFAcAz at 20 °C, the reaction mixture gradually changed from pale-yellow to red-orange. The reaction was followed by ^{1}H NMR spectroscopy. The results are shown in Figure 1. The spectra show that the signal of the product increases and that of TFAcAz decreases with an elapse of time, suggesting that TFAcAz selectively converts to the product. Furthermore, there is no change in the signals of Et_3N during the reaction, suggesting that Et_3N is merely a catalyst for the reaction. The reaction was also followed by gas chromatography. Figure 2 shows that most of the TFAcAz converts to the product.

The product was isolated as pale-yellow crystals by preparative gas chromatography; the structure of the crystalline product was studied in detail by means of elemental analysis and EI-mass, IR, Raman, and ^{1}H, ^{19}F, and ^{13}C NMR spectroscopies.

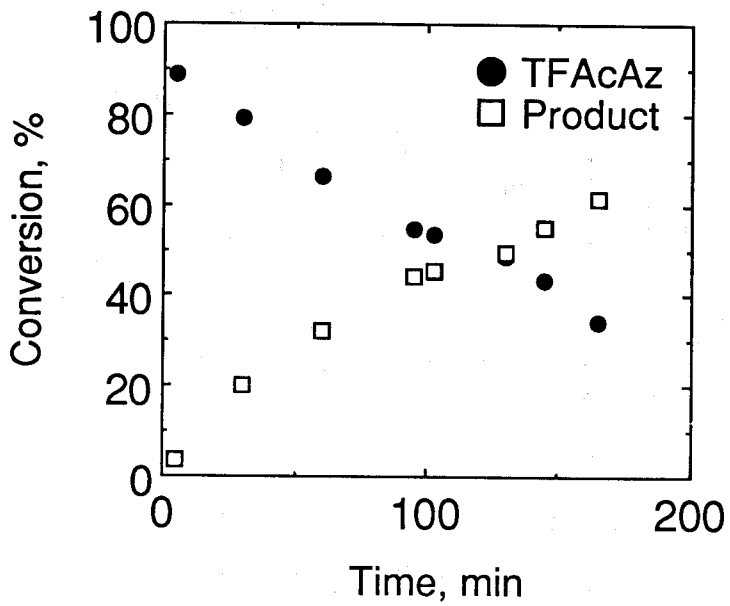


Figure 2. Time conversion of the reaction of TFAcAz with Et_3N (neat, molar ratio TFAcAz : Et_3N = 20 : 1).

The C, H, and N contents of the product shown in the Experimental Section are consistent with those of TFAcAz, indicating that the product is oligomers (dimer, trimer, and so on) of TFAcAz. The EI-mass spectrum of the product showed a peak at m/z = 384 as a molecular ion peak (Experimental Section). On the basis of these data, we can conclude that the crystalline product is a dimer of TFAcAz.

In the ^{1}H NMR spectrum of the product, only one quartet signal (J = 8.1 Hz) is observed at 4.04 ppm, whose coupling constant of the signal is larger than that of TFAcAz (J = 3.7 Hz). These results show that the carbon bound to the hydrogen in TFAcAz changes to sp^3-carbon in the product.[27]

In the ^{19}F NMR spectrum of the product, singlet and triplet signals are observed at -65.5 ppm and at -72.2 ppm, respectively. The triplet signal is due to coupling with two protons. A long-range coupling of the trifluoromethyl group is observed in each

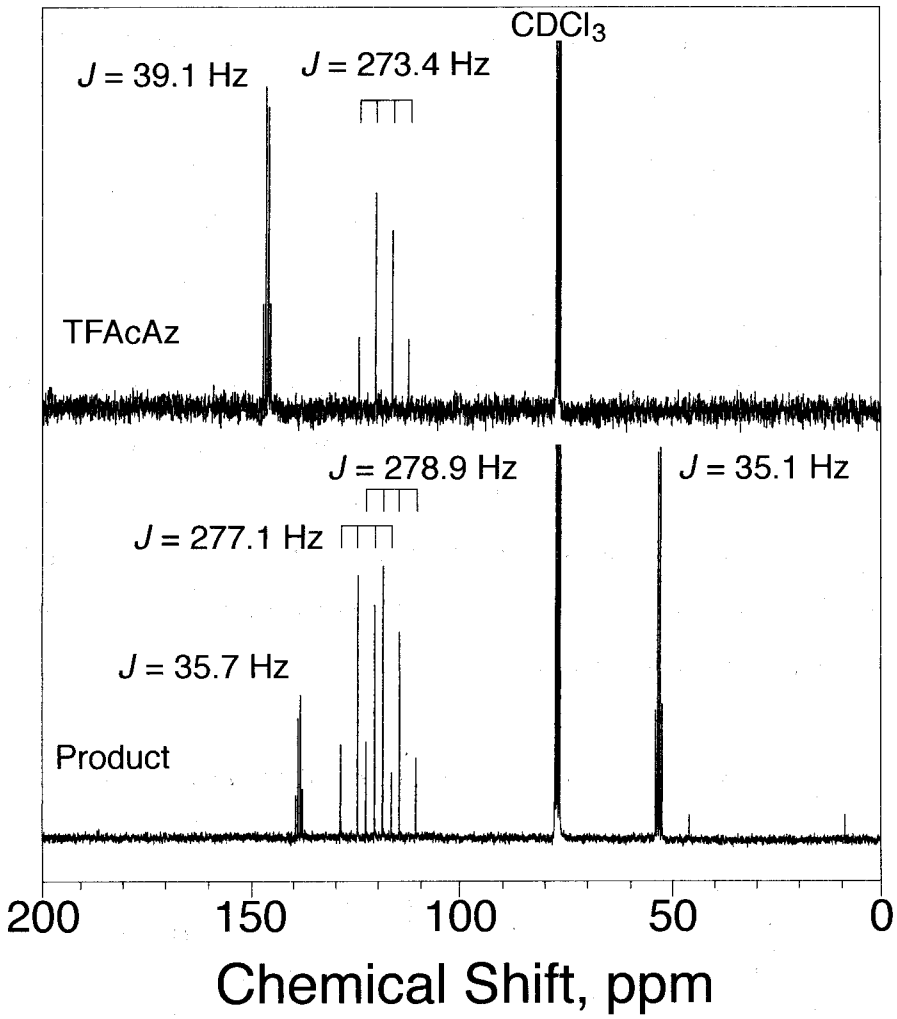


Figure 3. 67.9 MHz ^{13}C NMR spectra of TFAcAz and the product.

signal. These results show that the product has two kinds of trifluoromethyl groups; one binds to the carbon containing no hydrogen, and the other to a methylene group.

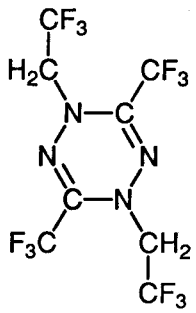
The ^{13}C NMR spectra of TFAcAz and the product are shown in Figure 3. In the spectrum of the product, four kinds of signals are observed. Two of them, at 117 and 123 ppm (J = 277.1 and 278.9 Hz, respectively), are ascribed to the carbons of the trifluoromethyl groups. The other two, at 53 and 139 ppm (J = 35.1 and 35.7 Hz, respectively), are due to the carbons bound to the trifluoromethyl groups. From the data shown above, it is concluded that the product has two kinds of trifluoromethyl

groups and two kinds of carbons bound to the trifluoromethyl group. Furthermore, it is concluded that the resonance bands observed at 53 and 139 ppm can be assigned to a single bond and a double bond, respectively.[29]

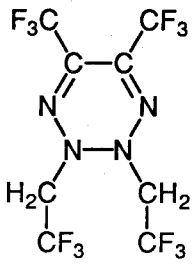
In the IR and Raman spectra of the product, the bands due to the stretching vibration of the C=N double bond are clearly observed at 1633 and 1680 cm^{-1}, respectively. These results show that the product has a C=N double bond. In the Raman spectra, the band due to the C=N double bond shifts to a higher wavenumber in the product. Therefore, the C=N double bond in the product is considered to be no longer conjugated, or to suffer stress.[30] Furthermore, the IR and Raman spectra show no band around 1550 cm^{-1}, indicating that the product has no N=N double bond.[30]

These spectroscopic data show that the product comprises two units, CF_3CH_2N- and CF_3C=N-. Since the product is a dimer, the three structures shown in Scheme 1 are considered to be the structure of the product.

Scheme 1. Proposed Structures of the Product



1



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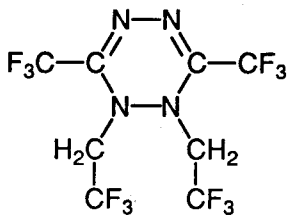

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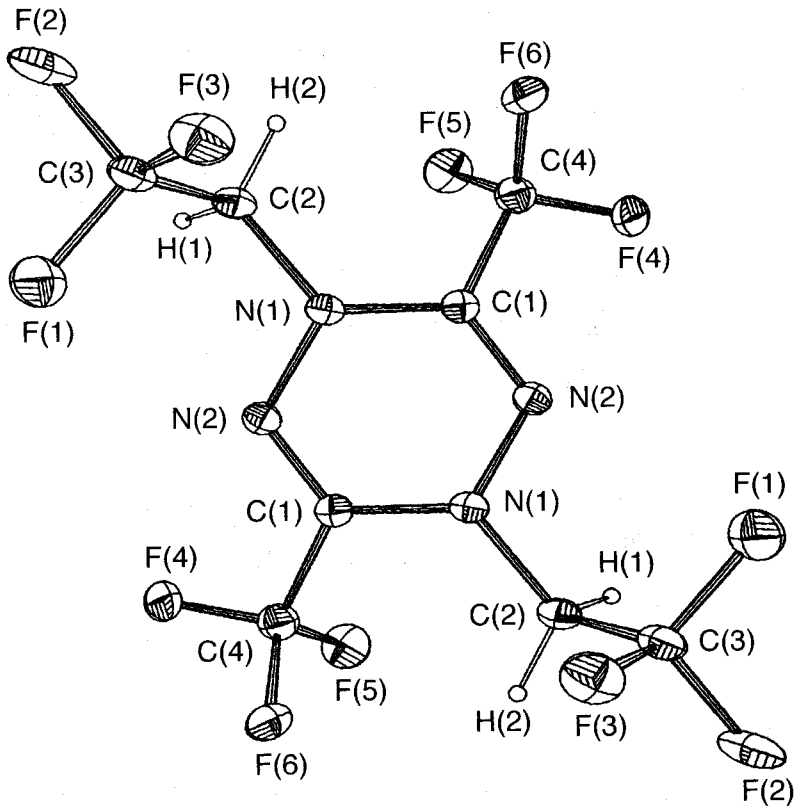
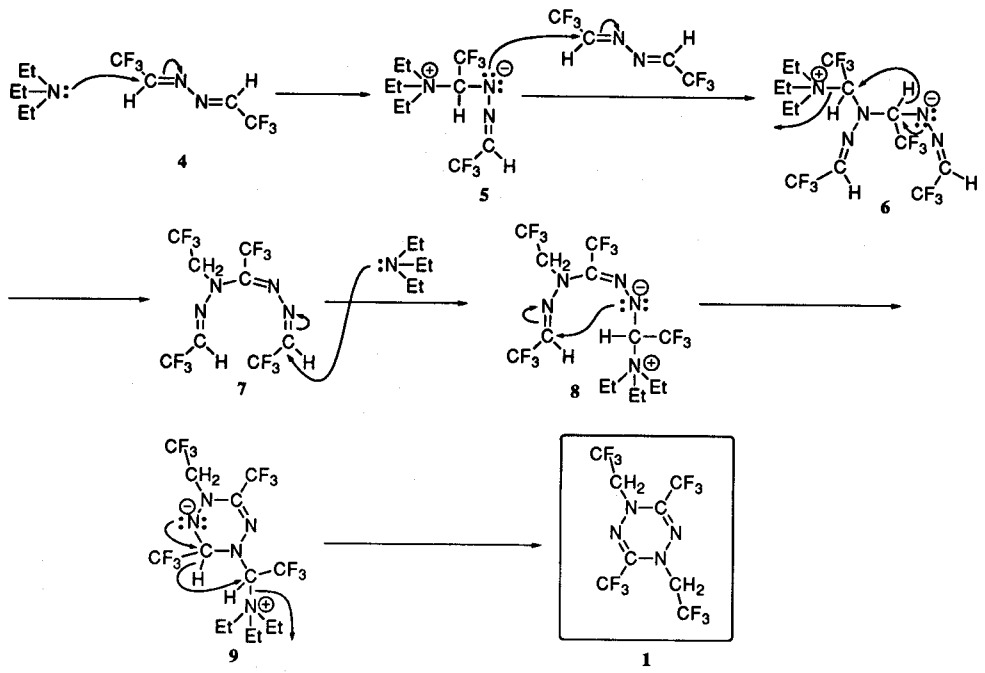


Figure 4. Molecular structure (ORTEP[31]) of the product.

In order to confirm the structure of the product, an X-ray crystallographic analysis was performed (Tables 1 and 2). The result is shown in Figure 4. It is consistent with the structure **1** (Scheme 1). The result shows that the reaction of TFAcAz with Et_3N at 20 °C gave the 1,4-dihydro-1,2,4,5-tetrazine derivatives. Various kinds of syntheses of 1,4-dihydro-1,2,4,5-tetrazine derivatives have been reported.[32, 33] However, to our knowledge, the formation of a 1,4-dihydro-1,2,4,5-tetrazine ring from azine compounds has not been previously reported.

Scheme 2. Proposed Mechanism for Formation of the Cyclic Dimer



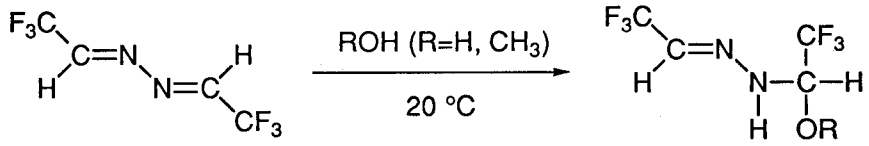
A tentatively proposed mechanism is shown in Scheme 2. Et_3N attacks the carbon of the C=N double bond of TFAcAz to form a zwitterion (step **4** to **5**), whose anion attacks another TFAcAz molecule to form a 1,2-dimer (step **5** to **6**). A conjugated double bond is reformed by the hydride shift to the carbon bound to the ammonium ion. Then Et_3N detaches (step **6** to **7**). Et_3N attacks the obtained conjugated C=N double bond to form a ring through an intramolecular 1,2-addition (step **7** to **8**). After the 1,3-hydride shift and elimination of the Et_3N, a cyclic dimer is formed (step **9** to **1**).

(b) Reactions of TFAcAz with Protic Compounds. The reactions of TFAcAz with protic compounds were also performed in order to investigate the chemical reactivity of TFAcAz.

When a small excess of methanol was added to TFAcAz, a certain product was quantitatively formed (Table 3). This product was isolated as colorless needles by

preparative gas chromatography. The structure of the product was investigated by means of ^{1}H, ^{13}C, and ^{19}F NMR, IR, Raman, and EI-mass spectroscopies and elemental analysis. The EI-mass spectrum of the product shows the peak at $m/z = 224$ as being a molecular ion peak, suggesting that the product is an adduct of TFAcAz (MW = 192) with methanol (MW = 32). An elemental analysis of the product also indicates that the product is an adduct of TFAcAz with methanol. The IR and Raman spectra of the product show signals due to the stretching vibration of the C=N double bond at 1630 and 1620 cm^{-1}, respectively. These results reveal that the product has a C=N double bond, suggesting that the product is formed through a 1,2-addition of methanol to TFAcAz. The ^{1}H, ^{13}C, and ^{19}F NMR spectra also support the idea that the product is formed through a 1,2-addition. We can thus conclude that the product is the 1,2-adduct shown in Scheme 3.

Scheme 3. Reactions of TFAcAz with Protic Compounds



Similarly, the formation of a 1,2-adduct with water was confirmed by ^{1}H, ^{13}C, and ^{19}F NMR, IR, Raman, and EI-mass spectroscopies (Scheme 3).

These results suggest that TFAcAz is easily attacked by nucleophiles, and that TFAcAz is more subject to a 1,2-addition than to a 1,4-addition. This is consistent with the formation of the 1,2-polymer and with the proposed mechanism for the formation of a cyclic dimer.

Conclusion

TFAcAz was prepared and its chemical reactivity was investigated. Consequently, we found that TFAcAz easily reacts with nucleophiles, such as Et_3N,

methanol, and water. The reactions of TFAcAz with Et_3N produced a cyclic dimer containing a 1,4-dihydro-1,2,4,5-tetrazine ring; that with methanol and water gave 1,2-adducts.

References and Notes

(1) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159.

(2) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(3) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436.

(4) Robinson, G. C. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3901.

(5) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520.

(6) Hall, H. K., Jr. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(7) Saegusa, T.; Kobayashi, S.; Furukawa, J. *Macromolecules* **1975**, *8*, 703 .

(8) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232.

(9) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(10) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(11) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(12) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(13) Harada, A.; H. Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(14) Harada, A.; Kajiwara, A; Fujii, H.; Kamachi, M. *Polym. J.* **1992**, *24*, 931.

(15) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(16) Middleton, W. J.; Krespan, C. G. *J. Org. Chem.* **1965**, *30*, 1398.

(17) Grayston, M. W.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 1278.

(18) Chambers, W. J.; Tullock, C. W.; Coffman, D. D. *J. Org. Chem.* **1962**, *84*, 2337.

(19) O'Brien, B. A.; DesMarteau, D. D. *J. Org. Chem.* **1984**, *49*, 1469.

(20) Burger, K.; Schickaneder, H.; Thenn, W. *Tetrahedron Lett.* **1975**, *16*, 1125.

(21) Bell, D.; Eltoum, A. O. A.; O'Reilly, N. J.; Tipping, A. E. *J. Fluorine Chem.* **1993**, *64*, 151.

(22) Curtius, T.; Zinkeisen, E. *J. Prakt. Chem.* **1898**, *58*, 310.

(23) Kost, A. N.; Grandberg, I. I. *Usp. Khim.* **1959**, *28*, 921.

(24) Braid, M.; Iserson, H.; Lawlor, F. E. *J. Am. Chem. Soc.* **1954**, *76*, 4027.

(25) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; J. P. Declercp, J. P.; Woolfson, M. M. "MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univ. of York, England and Louvain, Belgium (1980).

(26) The F_O-F_C table, the coordinate of atoms, the anisotropic thermal parameters for non-hydrogen atoms, and the parameters for atoms are deposited as Document No. 68031 at the Office of the Editor of Bull. Chem. Soc. Jpn.

(27) Emsley, J. W.; Feeney, J.; L. H. Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon: Oxford, 1966; Vol. 2, Chapter 11, pp 871-968.

(28) Brame, E. G., Jr.; Grasselli, J. G. "Infrared and Raman Spectroscopy"; Marcel: New York, 1977; pp 480-481.

(29) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic: New York, 1972; pp 55-101.

(30) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; John Willey: New York, 1958; pp 267-273.

(31) Johnson, C. K. "ORTEP II, Report ORNL-5138," Oak Ridge National Laboratory, Tennessee (1976).

(32) Neunhoeffer, H.; Wiley, P. F. "The Chemistry of Heterocyclic Compounds"; John Willey: New York, 1978; vol. 33, pp 1120-1128.

(33) Ivanova, V.; Buzykin, B. I.; Sysoeva, L. P.; Kitaev, Yu. P. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 2499.

Chapter 3

Polymerization of Trifluoroacetaldehyde Azine (1,1,1,6,6,6-Hexafluoro-3,4-diaza-2,4-hexadiene)

Introduction

Although a number of compounds with C=C or C=O double bonds have been polymerized to high molecular weight polymers by radical or ionic initiators, there are no papers on the polymerization of compounds with C=N double bonds, to our knowledge, except for carbodiimides,[1] isocyanates,[2,3] imines,[4] 1-azabutadienes,[4] and azine compounds.[5-12] Formaldehyde azine (CH_2=N-N=CH_2), which is the simplest azine, was prepared in 1959,[5] but there had been no systematic studies on the polymerizations of azine compounds before the studies by Kamachi *et al.*[6-10] The polymerizabilities of azine compounds have been systematically investigated in order to understand the polymerizabilities of the C=N double bond and to obtain new polymers.[6-10] Recently, the formation of crystalline *trans*-1,4-polymer by anionic polymerization of alkanal azine compounds (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7) with Grignard reagents was reported.[11-13]

In the extension of the research concerning the polymerizability of the C=N double bond, attention was also paid to trifluoroacetaldehyde azine (R=CF_3, TFAcAz), because TFAcAz does not have any hydrogen atoms on its α-carbon, which may cause chain transfer. The polymerizability of TFAcAz was investigated by using various initiators at various temperatures, and TFAcAz was found to polymerize to give a new type of crystalline polymer with trialkylamine at -20 °C. In this chapter, the polymerizability of TFAcAz and the structure of the obtained polymer will be described.

Experimental Section

Preparation of Trifluoroacetaldehyde Azine (TFAcAz). A solution of trifluoroacetaldehyde hydrate[14] (114.3 g, 0.761 mol) in diethyl ether (100 mL) was placed in a 500 mL flask fitted with a dropping funnel, a magnetic stirrer, and a condenser. A solution of hydrazine monohydrate (19.2 mL, 0.381 mol) in water (40 mL) was added slowly with continuous stirring for 30 min. Stirring was continued under reflux for 2 h. An organic layer was separated from an aqueous layer, and the aqueous layer was extracted with diethyl ether (50 mL) four times. A combined organic layer was washed with saturated aqueous sodium chloride (50 mL) and dried with anhydrous sodium sulfate. After successive distillations over calcium hydride, TFAcAz was obtained as a pale yellow liquid (*Warning!* TFAcAz has a pungent smell and irritates the mucous membrane): yield 20.5 g, 28.0 %; mp -6 to -4 °C; bp 54-56 °C; IR (KBr) 1160 (CF), 1280 (CF), 1328 (CF) cm^{-1}; Raman 975 (NN), 1640 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.56 (q, J = 3.74 Hz); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 119 (q, J = 273.4 Hz), 147 (q, J = 39.1 Hz); ^{19}F NMR ($CDCl_3$, 470.5 MHz) δ -71 (d, J = 3.76 Hz). Anal. Calcd for $C_4F_6H_2N_2$: C, 25.01; H,1.05; N,14.59; F, 59.35. Found: C, 24.53; H, 1.07; N, 14.39; EI-MS [MH^+] Calcd 193. Found 193.

Initiators. Commercially available *n*-butyllithium (*n*-BuLi) (1.5 M *n*-hexane solution) and methylmagnesium iodide (CH_3MgI) (2.0 M diethyl ether solution) were transferred to ampules, respectively, by means of syringes under an argon atmosphere. The concentration was determined by double titration. Potassium methoxide/18-crown-6 complex (CH_3OK/18-crown-6) was prepared according to the method by Kurcok *et al.*[15] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was dried with calcium hydride and stored under an argon atmosphere. Triethylamine (Et_3N), tri-*n*-butylamine (*n*-Bu_3N) and pyridine were distilled over calcium hydride under reduced pressure and stored under an argon atmosphere.

Polymerizations of TFAcAz with Trialkylamines. A typical polymerization of TFAcAz with triethylamine is described below.

TFAcAz (0.5 mL, 2.6 mmol) in an ampule was cooled with an ice-salt-water bath to -20 °C. Triethylamine (0.010 mL, 0.065 mmol) was added to the TFAcAz under an argon atmosphere and the ampule was sealed. After *ca.* 30 min, the reaction mixture solidified. After 72 h, the ampule was opened. The solidified products were washed with acetone and dried. Poly(TFAcAz) was obtained as a pale yellow powder. The polymer was insoluble in toluene, *p*-xylene, benzene, chloroform, dichloromethane, DMF, DMSO, 1,4-dioxane, *N*-methylpyrrolidone, quinoline, hexafluoro-2-propanol, ethyl acetate, methanol, ethanol, acetone, *n*-hexane, 1,1,2-trichloro-1,2,2-trifluoroethane, THF, trifluoroacetic acid, diethyl ether, and TFAcAz: yield 58.6 %; mp 250-270 °C (dec.); IR (KBr) 1140 (CF), 1270 (CF), 1638 (C=N) cm^{-1}; Raman 1045 (CF), 1265 (CF), 1648 (C=N) cm^{-1}; solid-state ^{13}C NMR (100.5 MHz) δ 65.9, 120.8. Anal. Calcd for $(C_4F_6H_2N_2)_n$: C, 25.01; H,1.05; N,14.59; F, 59.35. Found: C, 24.99; H, 1.11; N, 14.60.

Polymerizations of TFAcAz with *n*-BuLi, CH_3MgI, CH_3OK/18-crown-6, DBU, or Pyridine. A given amount of an initiator was added to TFAcAz (1 mL, 5.2 mmol) in an ampule under an argon atmosphere at -20 °C and the ampule was sealed. After 30, 48, or 72 h, the ampule was opened. The resulting products were investigated by GPC and ^1H NMR spectroscopy.

Oligomerization of TFAcAz. TFAcAz (1 mL, 5.3 mmol) in an ampule was cooled with an ice-salt-water bath to -20 °C. Et_3N (0.3 mL, 2.2 mmol) was added to TFAcAz under an argon atmosphere. After 4.5 h, the polymerization was terminated with methanol (3 mL). A solution was separated from the obtained polymer by centrifugation. After evaporation of volatile fractions, adducts of monomer and of dimer with methanol were obtained as a red-orange viscous oil. Their structures were investigated by ^1H NMR and EI-mass spectroscopies: Adduct of monomer with

methanol: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.50 (s), 4.89 (m), 7.04 (q, J = 4.7 Hz), 7.45 (bs); EI-MS [M^+] Calcd 224. Found 224. Adduct of dimer with methanol: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.42 (s), 3.65-3.80 (m), 5.06 (q, J = 5.3 Hz), 5.94 (bs), 6.38 (q, J = 4.2 Hz); EI-MS [M^+] Calcd. 416. Found 416.

Thermal Depolymerization of Poly(TFAcAz). Poly(TFAcAz) (15 mg) in an ampule was heated at *ca.* 200 °C under vacuum (~ 10^{-2} mmHg) for 10 h. TFAcAz was obtained as a volatile product: yield 9 mg, 60 %; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.56 (q, J = 3.74 Hz); EI-MS [M^+] Calcd 192. Found 192.

Measurements. Infrared spectra were recorded on a JASCO FT/IR-3 spectrometer. Raman spectra were obtained on a JASCO R-800 spectrometer by using an argon-ion laser 5145 Å excitation line. Frequency calibration of the spectra was carried out with the natural emission of a neon lamp from 0 to 2000 cm^{-1}. ^{1}H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270 spectrometer. ^{19}F NMR spectra were measured on a JEOL JNM-GX500 spectrometer as a $CDCl_3$ solution. GPC analysis was performed in THF with a TOSOH CO-8011 system by using TSK columns. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron impact (EI) method. Mass number was calibrated by using cesium iodide (CsI). Powder X-ray diffraction patterns were taken by using nickel-filtered Cu K_α radiation with a Rigaku RAD-ROC diffractometer. Thermogravimetric analysis was carried out under a slow stream of nitrogen (20 mL/min) by using a Rigaku PTC-10 program temperature controller at a heating rate of *ca.* 10 °C/min.

Results and Discussion

Synthesis and Identification of TFAcAz. TFAcAz was synthesized from trifluoroacetaldehyde hydrate and hydrazine monohydrate according to the procedure of Curtius *et al.*[16] Successive distillations over calcium hydride were required for purification of TFAcAz, because TFAcAz has a low boiling point (54-56 °C) and easily reacts with moisture. TFAcAz was identified by ^{1}H, ^{13}C, ^{19}F NMR, IR, Raman, and EI-mass spectroscopies and elemental analysis (Experimental Section).

Seeking Initiators for Polymer Formation. TFAcAz, similarly to alkanal azines, could not be polymerized with 2,2'-azobis(isobutyronitrile) (AIBN) or with aluminum chloride.[11, 12]

Anionic polymerizabilities were investigated with six kinds of initiators. The results on bulk polymerizations at -20 °C are shown in Table 1. Oligomers ($\overline{M}_w$ = 1800) were formed with *n*-BuLi, a typical anionic initiator. When the polymerization was performed with CH_3MgI, that gave polymers in the case of alkanal azine compounds,[11, 12] only soluble oligomers ($\overline{M}_w$ = 1300) were obtained.

Table 1. Bulk Polymerizations of TFAcAz[a]

initiator (mol%)	time, h	conv., %	polymer yield, %	$\overline{M}_w$ [b]
n-BuLi (0.57)	30	42 [b]	0	1800
CH_3MgI (0.57)	30	23 [b]	0	1300
CH_3OK/18-crown-6 (1.0)	30	49 [b]	0	1800
DBU (9.1)	48	81 [b]	0	1200
Et_3N (2.4)	72		59 [d]	- [e]
pyridine (9.1)	72	0 [c]	0	

[a] At -20 °C. [b] By GPC. [c] By ^{1}H NMR. [d] Acetone-insoluble fraction. [e] Insoluble in THF.

CH_3OK/18-crown-6 also gave only soluble oligomers ($\overline{M}_w$ = 1800) and did not give polymers. Furthermore, organic bases were used as initiators to investigate the polymerizability with initiators that have weaker nucleophilicities than the above three initiators. When DBU, one of the strongest organic bases, was used, oily oligomers ($\overline{M}_w$ = 1200) were generated. However, a solid polymer was obtained in the frozen state (below -10 °C) by the polymerization with Et_3N. Moreover, no reaction occurred with pyridine, which is a weaker base than Et_3N.[17] Thus, Et_3N was found to be an appropriate initiator for the polymerization of TFAcAz.

Polymerizations of TFAcAz with Trialkylamines. To obtain optimum conditions for the polymerization of TFAcAz, the polymerizations with trialkylamines were performed under various conditions, and the results are shown in Table 2. The polymerization system gradually changed from pale yellow to red-brown upon addition of each of the amines. After *ca.* 30 min, the system solidified. After 24 or 72 h, the ampule was opened and the reaction mixture was washed with acetone to remove remaining monomer, oligomer, and the added amine. And then polymer was obtained as a pale yellow powder.

Table 2. Bulk Polymerization of TFAcAz[a]

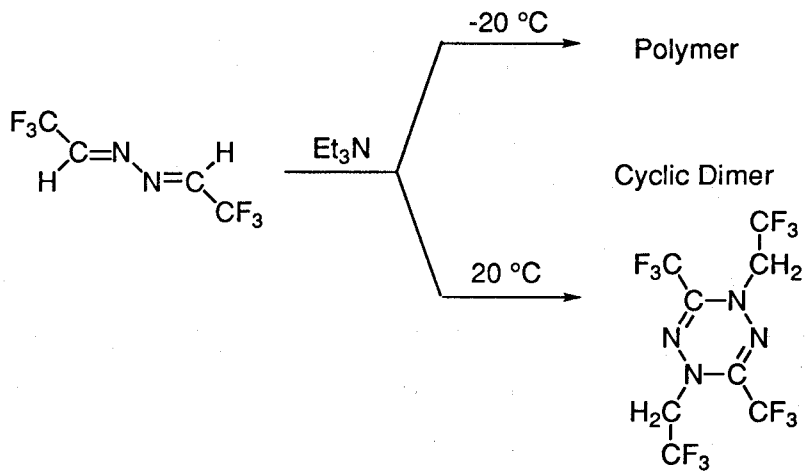
TFAcAz, mL(mmol)	catalyst (mol%)	time, h	yield,[d] %
1.0 (5.2) [b]	Et_3N (2.0)	24	31.0
0.50 (2.6) [c]	Et_3N (2.4)	72	58.6
0.50 (2.6) [c]	Et_3N (9.1)	24	39.3
0.50 (2.6) [c]	Et_3N (9.1)	72	48.6
0.50 (2.6) [c]	Et_3N (23.1)	72	28.2
0.50 (2.6) [c]	*n*-Bu_3N (1.7)	72	19.9
0.50 (2.6) [c]	*n*-Bu_3N (9.1)	72	30.6

[a] At -20 °C. [b] In air. [c] Under an argon atmosphere. [d] Acetone insoluble fraction.

Table 2 shows that the polymerization rate is not high as compared to those of usual radical or ionic polymerizations. The result is mainly due to the formation of a considerable amount of soluble oligomeric species.[18] Triethylamine gave the polymer in a higher yield than tri-*n*-butylamine, as shown in Table 2. The obtained polymer was insoluble in most solvents (Experimental Section). Since no suitable solvent has been found, the molecular weight of the polymer could not be determined. However, low molecular weight polymer was found in solution of the reaction mixture with molecular weight about one thousand. Therefore, the molecular weight of the insoluble polymer should be higher than one thousand.

When the reactions of TFAcAz with trialkylamines were performed at +20 °C, a cyclic dimer of TFAcAz was obtained as a pale yellow crystal (mp 26.8-27.1 °C) (Scheme 1).[19] At -20 °C, the polymerization preferentially took place in the frozen state, indicating that the cyclization reaction may be suppressed in the frozen state. However, at -78 °C, polymerization did not occur. The optimum temperature for the polymerization in the frozen state was surveyed to find it to be about -20 °C.

Scheme 1. Reactions of TFAcAz with Et_3N



Structure of Poly(TFAcAz). The C, H, and N contents in the polymer were consistent with those in TFAcAz (Experimental Section), indicating that the polymer is formed by addition polymerization.

The IR and Raman spectra of the monomer and the polymer are shown in Figures 1 and 2. The absorption band assignable to the stretching vibration of the C=N double bond cannot be observed in the IR spectrum of the monomer whereas it is clearly observed at 1640 cm^{-1} in the Raman spectrum. These results suggest that the TFAcAz molecule has exclusively *s-trans* structure, so that the stretching vibration of the C=N double bond is IR-inactive and Raman-active.

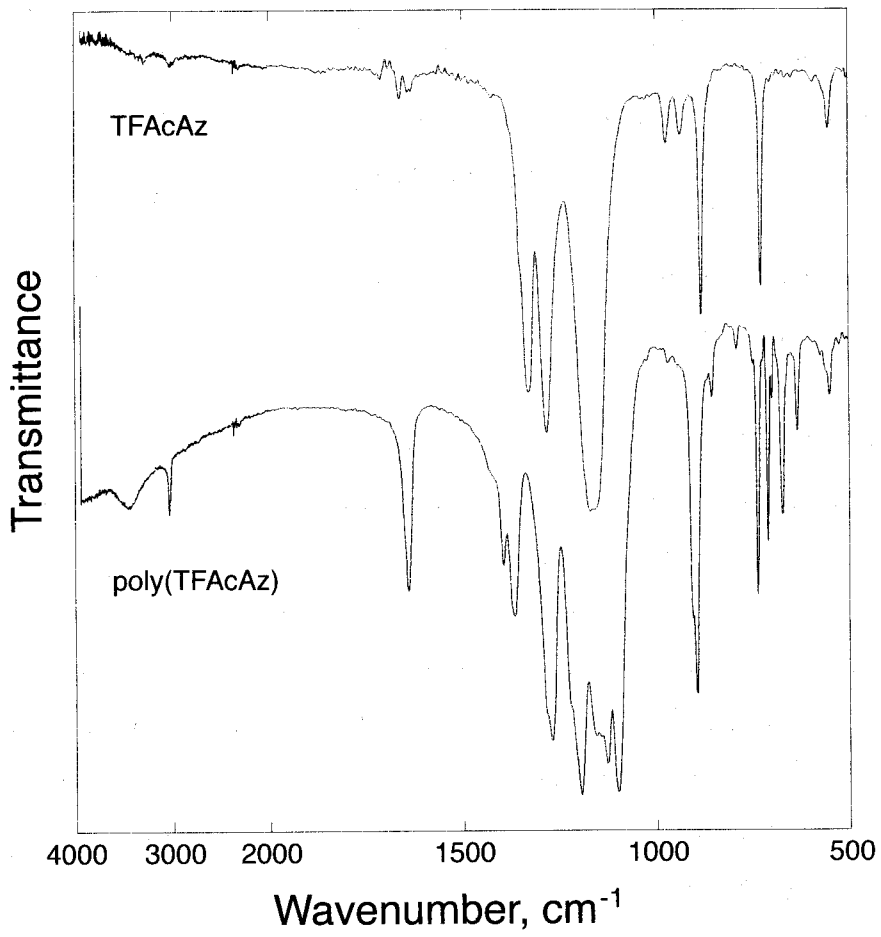


Figure 1. IR spectra of TFAcAz and poly(TFAcAz) (KBr).

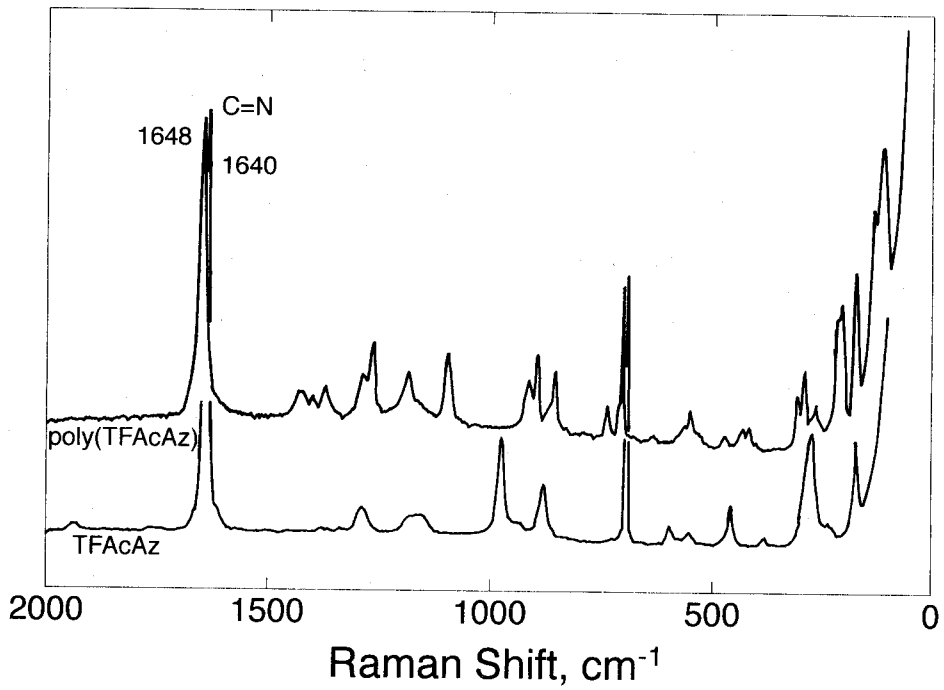


Figure 2. Raman spectra of TFAcAz and poly(TFAcAz) (5145 Å argon-ion laser excitation).

On the other hand, in the IR and Raman spectra of the polymer, the signals of the C=N double bonds were observed at 1640 and 1648 cm^{-1}, respectively. These results show that the polymer has a C=N double bond. In the Raman spectra, the peak due to the C=N double bond shifted to higher wavenumber in the polymer, suggesting that the C=N double bonds in the polymer are no longer conjugated. Furthermore, no stretching vibration mode due to the N=N double bond, which was found at *ca.* 1550 cm^{-1} in the Raman spectra of poly(alkanal azine)s,[11, 12] could be observed in poly(TFAcAz). Therefore, it can be concluded that the polymer is composed of exclusively 1,2-units.

Since the polymer is insoluble in organic solvents, the ^{13}C NMR spectrum of poly(TFAcAz) was measured in the solid state. Two resonance bands are observed as shown in Figure 3. On the basis of reference data[20] and relative intensities, the signal at a higher field is assignable to the methine carbon in the main chain of the obtained polymer and that at a lower field is assignable to the methine carbon in the pendant group and to the carbons of trifluoromethyl groups. In the case of poly(TFAcAz), no peak could be found in the region due to a methine carbon binding to an N=N group at *ca.* 80 ppm.[11, 12] These results also support that the polymer is composed of 1,2-units.

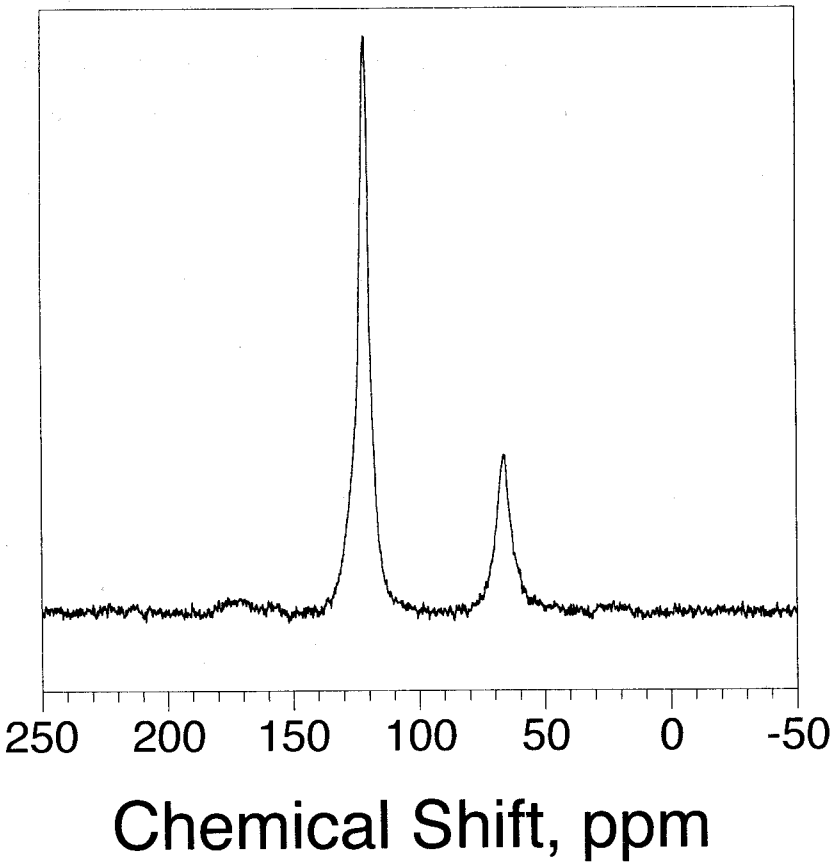
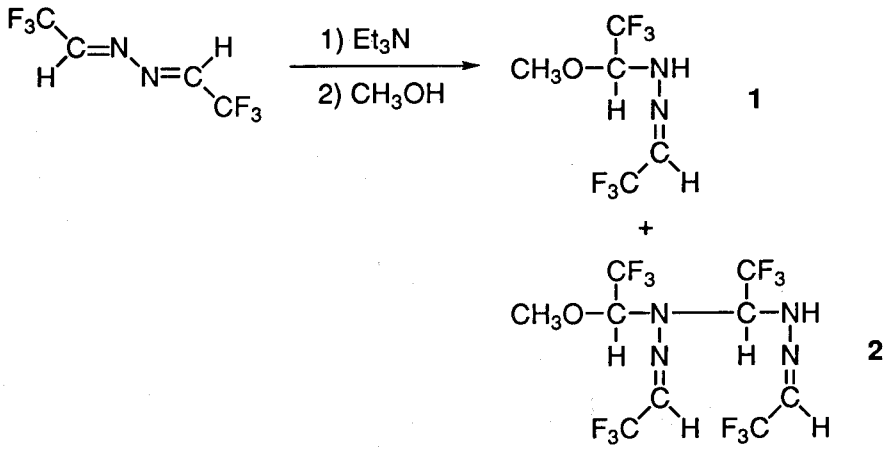


Figure 3. 100.5 MHz solid-state ^{13}C NMR spectrum of poly(TFAcAz) (powder).

Since the polymer is insoluble in organic solvents, soluble oligomers were prepared by the termination of polymerization in an early stage with methanol to confirm the structure of the polymer. After evaporation of volatile fractions, the red-orange viscous oil was obtained. The structures of the products were investigated by means of EI-mass and ^{1}H NMR spectroscopies. The mass spectrum shows that there are peaks at m/Z = 224 and 416 and is reasonably assigned to **1** and **2** on the basis of their fragmentation (Scheme 2). In the ^{1}H NMR spectrum, there were two peaks assignable to N-H at 5.94 and 7.45 ppm, which bound to $CHCF_3$ in addition to the signals due to OCH_3, $CHCF_3$, and CH=N. These spectra show that **1** and **2** were obtained. These results show the termination of polymerization of TFAcAz with methanol gave a head-to-tail 1,2-dimer, suggesting that polymerization proceeds through head-to-tail 1,2-addition so that the obtained polymer is composed of head-to-tail 1,2-units.

Scheme 2. Oligomerization of TFAcAz



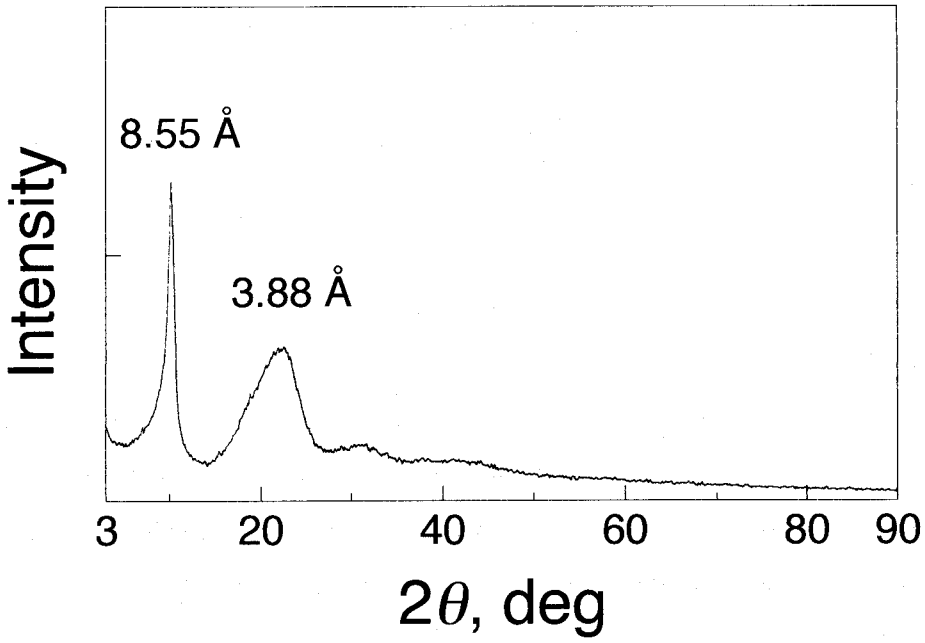


Figure 4. Powder X-ray diffraction pattern of poly(TFAcAz).

The powder X-ray diffraction of poly(TFAcAz) is shown in Figure 4. Clear diffraction patterns were observed at 2θ = 22.9 ° and 10.3 °, indicating that the polymer is crystalline. These 2θ angles correspond to distances of 3.88 and 8.55 Å, respectively. Similar X-ray diffraction patterns have been observed in poly(alkanal azine)s.[11, 12] On the basis of the substituent effect on the distances, the longer distance was reasonably assigned to the interchain regular structure and the shorter distance to the fiber period of the main chain. If the polymer takes a planar zigzag structure, the estimated distance (3.88 Å) corresponds to two C-N units. Since the polymer is suggested to be composed of head-to-tail 1,2-units, the estimation that the fiber period is composed of two C-N units suggests that the polymer has a syndiotactic regular structure. Poly(TFAcAz) is not soluble in organic solvents, suggesting that the polymer is cross-linked through pendant C=N double bonds. However, the formation of crystalline polymer suggests that the insolubility may be ascribed to the interchain regular structure rather than the cross-linking. Furthermore,

no swelling of the obtained polymer was observed in any solvents. The result also suggests that cross-linking does not occur during the polymerization.

Thermal properties of poly (TFAcAz). The thermal behavior of poly(TFAcAz) was investigated by thermogravimetric analysis (TGA). The result is shown in Figure 5. A gradual weight loss started near 150 °C, with full decomposition at *ca.* 280 °C. This result shows that poly(TFAcAz) is a thermally degradable polymer.

To obtain information on the pyrolysis of poly(TFAcAz), the products obtained by pyrolysis were collected and their structures were analyzed by ^{1}H NMR and EI-mass spectroscopies. These spectra showed that *ca.* 60 % of the collected products was the monomer, indicating that depolymerization of poly(TFAcAz) occurred at *ca.* 200 °C.

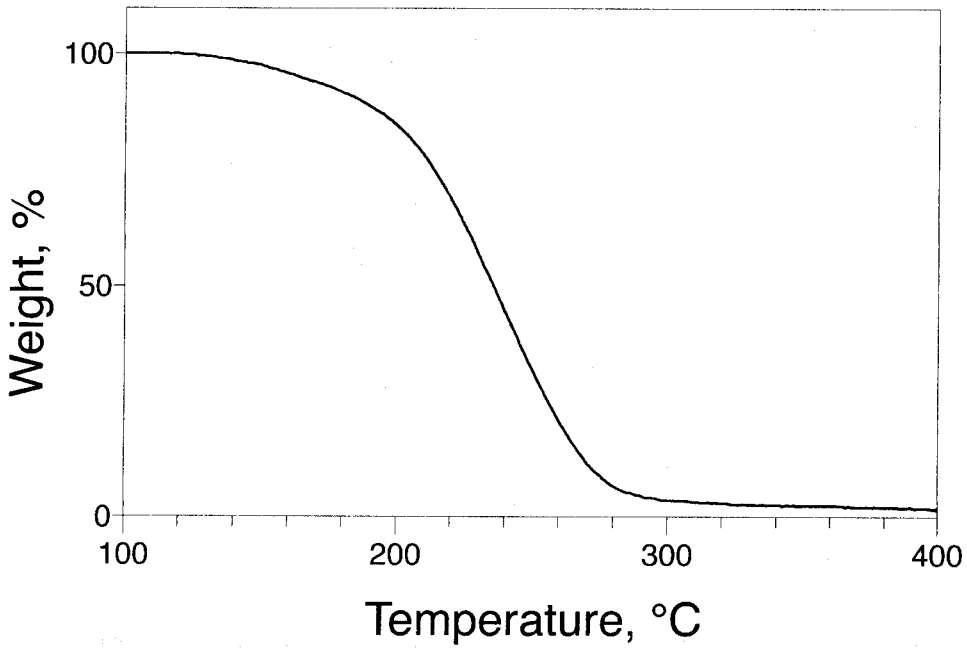


Figure 5. Thermogravimetric analysis (TGA) curve of poly(TFAcAz) in a nitrogen atmosphere. Sample, 1.88 mg; heating rate, 10 °C/min.

Conclusions

TFAcAz was synthesized and isolated as a new monomer and its polymerizability was studied. Only oligomers were formed by polymerization with *n*-BuLi, CH_3MgI, CH_3OK/18-crown-6, or DBU. However, poly(TFAcAz) was obtained by bulk polymerization either with triethylamine or with tri-*n*-butylamine at -20 °C. The obtained polymer was found to be crystalline, composed of 1,2-units, and depolymerized at *ca.* 200 °C. The TFAcAz was found to have a considerably different polymerizability from those of alkanal azine compounds.

References and Notes

(1) Robinson, G. C. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3901.

(2) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159.

(3) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(4) Hall, H. K., Jr. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(5) Neureiter, T. P. *J. Am. Chem. Soc.* **1959**, *81*, 2910.

(6) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232.

(7) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(8) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(9) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(10) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(11) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(12) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931.

(13) Kamachi, M.; Kajiwara, A.; Hashidzume, A., to be published.

(14) Braid, M.; Iserson, H.; Lawlor, F. E. *J. Am. Chem. Soc.* **1954**, *76*, 4024.

(15) Kurcok, P.; Kowalczuk, M.; Hennek, K.; Jedlínski, Z. *Macromolecules* **1992**, *25*, 2017.

(16) Curtius, T.; Zinkeisen, E. *J. Prakt. Chem.* **1898**, *58*, 310.

(17) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(18) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M., to be published.

(19) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M.; Kusunoki, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2025.

(20) In the ^{13}C NMR spectrum of the cyclic dimer of TFAcAz, the signals of carbons of the trifluoromethyl groups were observed at 117 and 123 ppm, that of C-N at 53 ppm, and that of C=N at 139 ppm.[19]

Chapter 4

Preparation, Chemical Reactivity, and Polymerizability of *n*-Butyl Glyoxylate Azine (1,4-Carbobutoxy-2,3-diaza-1,3-butadiene)

Introduction

Many papers have been published concerning the polymerization of compounds with a C=C or C=O double bond. However, only a few papers have focused on the polymerizability of the C=N double bond.[1-7] Therefore, Kamachi *et al.*[8-16] investigated the polymerizability of azine compounds, and found that alkanal azines (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7) could be polymerized with Grignard reagents to form crystalline 1,4-polymers.[13-15] In order to suppress the chain-transfer reaction observed in the polymerization of alkanal azines, we prepared trifluoroacetaldehyde azine (R=CF_3, TFAcAz), which has no hydrogen on the α-carbon of the C=N double bond, and investigated its polymerizability. As described in previous chapters, a 1,2-polymer has been prepared from TFAcAz.[16]

As an extension of this work, attention was paid to the azine compounds containing ester groups, which are electron accepting substituents. These azines containing ester groups have no hydrogen atom on the α-carbon of the C=N double bond, which causes the chain-transfer reaction. The aldehyde azine compounds containing ester groups have not been previously reported. In this chapter the preparation, chemical reactivity, and polymerizability of *n*-butyl glyoxylate azine (R=*n*-C_4H_9OCO, BgAz) will be described

Experimental Section

Materials and Initiators. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was dried with calcium hydride and decanted immediately before use. Triethylamine (Et_3N) and pyridine were distilled over calcium hydride under reduced pressure, and stored under an argon atmosphere. Methanol, ethanol, 2-propanol, and *t*-butanol were distilled over calcium hydride under reduced pressure, and stored under an argon atmosphere. Tetrahydrofuran (THF) was purified by distillation over sodium-benzophenone ketyl under an argon atmosphere. Commercially available *t*-butyllithium (*t*-BuLi) (1.7 M *n*-pentane solution) and *n*-butyllithium (*n*-BuLi) (1.6 M *n*-hexane solution) were transferred to ampules, respectively, by using a syringe under an argon atmosphere. The concentration was determined by double titration.[17] Other reagents were used without further purification.

Preparation of *n*-Butyl Glyoxylate Azine (BgAz). BgAz was prepared from *n*-butyl glyoxylate[18] and hydrazine monohydrate according to the procedure of Curtius *et al.*[19] Hydrazine monohydrate (1.4 mL, 28.8 mmol) was added to a solution of *n*-butyl glyoxylate (10 g, 77 mmol) in toluene (100 mL) at 25 °C with stirring. After stirring for 15 min, toluene was evaporated. Then a pale yellow residue was obtained. Crude BgAz was obtained by distillations under high vacuum (< 10^{-5} mmHg). BgAz was isolated by recrystallization in THF-hexane at -78 °C: yield 1.34 g, 6.8 %; mp -12 to -10 °C; IR (NaCl) 1745 (C=O), 1725 (C=O), 1620 (C=N) cm^{-1}; Raman 1726 (C=O), 1598 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.93 (t, 6H, J = 7.59 Hz), 1.1-1.3 (m, 4H), 1.6-1.8 (m, 8H), 4.29 (t, 4H, J = 6.60 Hz), 7.44 (s, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 13.6, 19.0, 30.4, 66.2, 146.3, 161.9. Anal. Calcd for $C_{12}H_{20}N_2O_4$: C, 56.24; H, 7.87; N, 10.93. Found: C, 56.24; H, 7.94; N, 10.78. EI-MS [MH^+] Calcd 257. Found 257.

Reaction and Polymerization of BgAz. A reagent or an initiator was added to BgAz under an argon atmosphere at 20 °C. After 0.25, 24, 48, 72, or 120 h, GPC and NMR analyses of the reaction mixtures were carried out.

Preparation of the Adduct of BgAz with Methanol. Methanol (2 mL, 45 mmol) was added to BgAz (500 mg, 2.0 mmol). The reaction mixture gradually changed from pale yellow to colorless. After evaporation of the unreacted methanol, a viscous oil was obtained: yield 92.0 %; IR (NaCl) 3250 (NH), 1740 (C=O), 1710 (C=O), 1570 (C=N) cm^{-1}; ^1H NMR (C_6D_6, 270 MHz) δ 0.75 (t, 3H, J = 7.3 Hz), 0.77 (t, 3H, J = 7.3 Hz), 1.1-1.3 (m, 4H), 1.3-1.5 (m, 4H), 3.24 (s, 3H), 3.98 (td, 1H, J = 5.8, 1.7 Hz), 4.12 (td, 1H, J = 6.6, 0.7 Hz), 5.18 (d, 1H, J = 7.9 Hz), 6.96 (s, 1H), 7.69 (d, 1H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 13.6, 13.7, 19.1, 19.3, 30.6, 31.0, 55.4, 64.5, 65.5, 88.1, 128.6, 164.2, 167.8. EI-MS [M^+] Calcd 288. Found 288.

Reaction of BgAz with Alcohols. An alcohol was added to a solution of BgAz in benzene-d_6. The reaction was followed by ^1H NMR spectroscopy. The yields were estimated from the ratio of the integrals of the absorption bands due to the products and the solvent.

Measurements. GPC analyses were performed in THF with a TOSOH CCP & 8010 system by using TSK columns at 40 °C. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. The molecular weights were calibrated by polystyrene standards (TOSOH TSK POLYSTYRENE standard). Infrared (IR) spectra were recorded on a JASCO FT/IR-3 spectrometer. ^1H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270 spectrometer using $CDCl_3$ or benzene-d_6 as a solvent at 30 °C. Mass spectrum was recorded on a JEOL JMS SX-102 mass spectrometer by electron impact (EI) method. Mass number was calibrated by using cesium iodide (CsI).

Results and Discussion

Preparation and Characterization of BgAz. BgAz was prepared from *n*-butyl glyoxylate and hydrazine monohydrate, and purified by successive distillations under high vacuum (bp ~ 80 °C (~ 10^{-5} mmHg)) and by subsequent recrystallization (mp -12 to -10 °C). The yield of BgAz was quite low (6.8 %), since *n*-butyl glyoxylate was predominantly polymerized by itself to form oligomer.

BgAz was characterized by elemental analysis and EI-mass, ^{1}H and ^{13}C NMR, IR, and Raman spectroscopies.

The C, H, and N contents of BgAz (C, 56.24; H, 7.94; N, 10.78 %) agree with the calculated values (C, 56.24; H, 7.87; N, 10.93 %). The EI-mass spectrum of BgAz showed a protonated molecular ion peak at m/z = 257.

In the ^{1}H NMR spectrum of BgAz, the absorption bands due to the methyl proton and three methylene protons of the *n*-butyl group were observed at 0.93, 1.3-1.5, 1.6-1.8, and 4.29 ppm, respectively. Furthermore, the absorption band assignable to the proton of the CH=N was observed at 7.44 ppm.[20] In the spectrum of ^{13}C NMR spectrum of BgAz, the absorption bands due to the methyl carbon and three methylene carbons of the *n*-butyl group were observed at 13.6, 19.0, 30.4, and 66.2 ppm, respectively.[20] Furthermore, the absorption bands assignable to the carbon of the C=N and C=O double bonds were observed at 146.3 and 161.9 ppm, respectively.[20]

In the IR spectrum of BgAz (Figure 1, upper), the absorption bands assignable to the stretching vibration of the carbonyl of the ester group were observed at *ca.* 1725 and 1745 cm^{-1}. The absorption band due to the stretching vibration of the C=N double bond is also observed at *ca.* 1620 cm^{-1}.[21] In the Raman spectrum of BgAz, the absorption band due to the stretching vibration of the C=N double bond was observed at *ca.* 1598 cm^{-1}.[21]

From these results, it is concluded that BgAz was prepared.

Chemical Reactivity of BgAz. Since BgAz is a newly prepared azine, its chemical reactivity was also investigated. The results of the reactions of BgAz with some reagents are listed in Table 1.

(a) Reaction of BgAz with Alcohols. When an excess of methanol was added to BgAz, a certain product was quantitatively formed, as shown in Table 1. The structure of the product was investigated by EI-mass, ^{1}H and ^{13}C NMR, and IR spectroscopies.

The EI-mass spectrum of the product showed a peak at m/z = 288 as being a molecular ion peak, suggesting that the product was an adduct of BgAz (MW = 256) with methanol (MW = 32).

Table 1. Reactions of BgAz with Some Reagents[a]

reagent (mol%)	temp., °C	time, h	conv.,[b] %	result
CH_3OH (96)	25	120	~ 100	colorless oil MW = 288[c]
DBU (33)	20	48	~100	oligomers $\overline{M}_w$ ~ 710[b]
Et_3N (33)	20	48	~100	$\overline{M}_w$ ~ 570[b]
pyridine (33)	20	48	73.2	$\overline{M}_w$ ~ 1400[b]
acetic acid (33)	20	48	34.8	$\overline{M}_w$ ~ 690[b]
TFA (50)	20	48	92.6	$\overline{M}_w$ ~ 2500[b]

[a] Under an argon atmosphere. [b] By GPC. [c] By EI-mass.

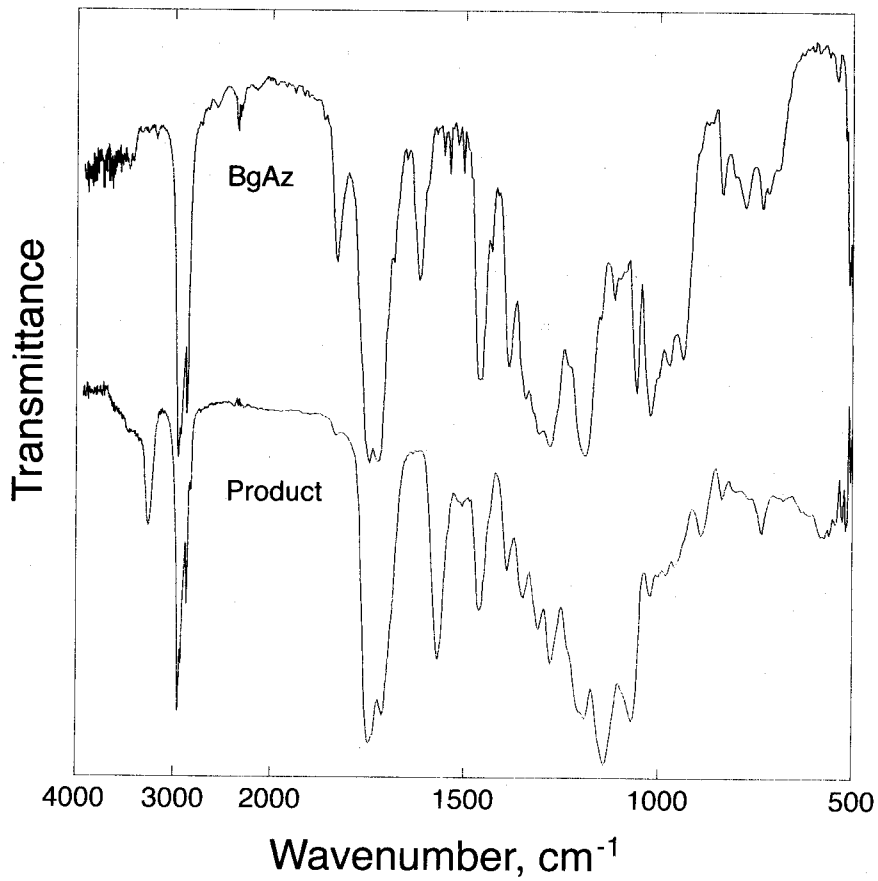


Figure 1. The IR spectra of BgAz (upper) and the product (lower) (NaCl).

The IR spectra of BgAz and the product are shown in Figure 1. In the IR spectrum of the product, the absorption band due to the stretching vibration of the C=N double bond is observed at 1570 cm^{-1}.[21] This result reveals that the product has a C=N double bond, suggesting that the adduct was formed by 1,2-addition of methanol to BgAz. The ^{1}H and ^{13}C NMR spectra also supported the proposition that the adduct was formed through a 1,2-addition (Experimental Section). From these results, it can be concluded that the product has the structure shown in Scheme 1.

Furthermore, the reactions of BgAz with the other alcohols were carried out. The results are shown in Table 2. In each case, the 1,2-adduct was obtained (Scheme 1).

These results suggest that BgAz is readily attacked by nucleophiles, and that BgAz is more subject to a 1,4-addition than to a 1,2-addition, being similar to TFAcAz.

Scheme 1. Reaction of BgAz with Alcohols

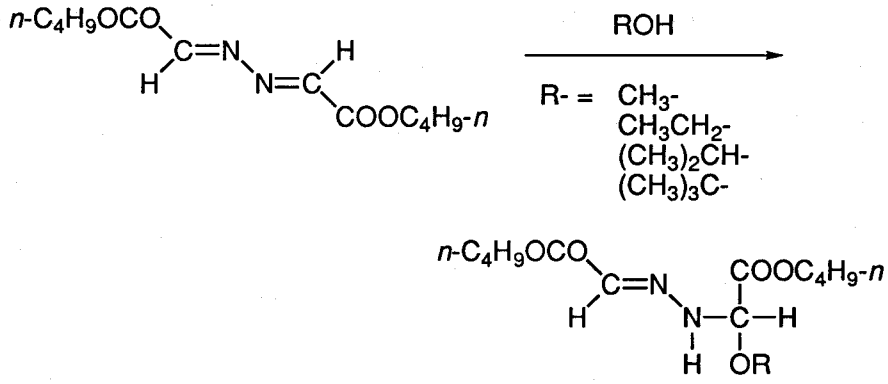


Table 2. Reaction of BgAz with Alcohols[a]

alcohol	yield,[b] %
methanol	~ 100
ethanol	93.1
2-propanol	79.9
t-butanol	75.0

[a] BgAz: 37 mg (1.5 mmol); benzene-d_6: 0.5 mL; alcohol: 1.1 mmol. At 20 °C for 238 h. [b] Based on alcohol.

(b) Reaction of BgAz with Organic Bases and Acids. As shown in Table 1, products with molecular weights higher than that of BgAz were obtained by the reactions of BgAz with organic bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (Et_3N), and pyridine. These results suggest that BgAz is electrophilic, being similar to TFAcAz. The structure of the oligomer obtained by the reaction of BgAz with organic bases, which are anionic initiators, will be discussed later.

As shown in Table 1, products with molecular weights higher than that of BgAz were obtained by the reactions of BgAz with acids, such as acetic acid and trifluoroacetic acid (TFA). When the reaction of BgAz with sodium trifuloroacetate was carried out, the conversion of BgAz with sodium trifluloroacetate was much lower than that with TFA. The result suggests that proton concerns the reaction. Therefore, the product may depend on the pK_a of the acid used. These results suggest that BgAz is more nucleophilic than TFAcAz, which did not react with these acids. The structure of the oligomer obtained by the reaction of BgAz with TFA, which is a cationic initiator, will be discussed later.

Polymerizability of BgAz. Since BgAz is a new monomer, the polymerizability of BgAz was investigated by using some types of initiators. The results of the bulk polymerizations are shown in Table 3.

When an anionic initiator, such as *t*-BuLi, DBU, Et_3N, or pyridine, was added to BgAz under an argon atmosphere, only oligomers ($\overline{M}_w$ ~ 1100-1600) were obtained. These results suggest that BgAz is easily polymerized with anionic initiators to form oligomer. However, the molecular weight of the oligomer hardly increased upon decreasing the amount of initiator, suggesting that chain-transfer reaction takes place in these anionic polymerizations.

Table 3 Bulk Polymerizations of BgAz with Some Initiators[a]

initiator (mol%)	temp., °C	time, h	conv.,[b] %	$\overline{M}_w$[b]
t-BuLi (18)	20	0.25	24.5	1600
DBU (5)	20	48	~100	1400
DBU (33)	20	48	~100	710
Et_3N (5)	20	48	89.1	1100
Et_3N (33)	20	48	~100	570
pyridine (5)	20	120	88.9	1400
pyridine (33)	20	48	73.2	1500
TFA (10)	20	48	97.2	2900
TFA (50)	20	48	92.6	2500

[a] Under an argon atmosphere. [b] By GPC.

As shown in Table 3, when TFA, a cationic initiator, was added to BgAz under an argon atmosphere, oligomer ($\overline{M}_w$ ~ 2500-2900) was obtained in a high yield (> 90 %). These results show that BgAz is easily polymerized with TFA to form oligomer. However, the molecular weight of the oligomer hardly increased upon decreasing the amount of TFA, suggesting that chain-transfer reaction takes place in the cationic polymerization of BgAz.

In attempt to obtain high molecular weight polymer, polymerizations were performed in THF. The results of the solution polymerization of BgAz are listed in Table 4. The results show the molecular weights of the oligomers obtained by the solution polymerizations are lower than those obtained by the bulk polymerizations. These results suggest that the chain-transfer reaction takes place more predominantly in the solution polymerization than in the bulk polymerization.

The preparation of high molecular weight polymer of BgAz remains to be waiting for a future study.

Table 4. Solution Polymerizations of BgAz with Some Initiators[a]

initiator (mol%)	temp., °C	time, h	conv.,[b] %	$\overline{M}_w$[b]
n-BuLi (10)	-20	24	83.0	1400
DBU (5)	20	72	73.7	760
Et_3N (5)	20	72	88.3	720
pyridine (5)	20	72	43.1	410
TFA (5)	20	72	87.7	660

[a] In THF (1.0 M) under an argon atmosphere. [b] By GPC.

The Structure of the Oligomer. The EI-mass spectrum of the oligomer obtained by the polymerization of BgAz with Et_3N showed a peak due to a tetramer of BgAz at m/z = 1024. Furthermore, the peak due to a trimer of BgAz was observed at m/z = 770 in the EI-mass spectrum of the oligomer obtained by the polymerization of BgAz with TFA in THF. These results suggest that the oligomers were formed by addition polymerization of BgAz.

The IR spectra of BgAz and the oligomers obtained by Et_3N and TFA are shown in Figure 2. In the spectra of the oligomers, the absorption bands due to the stretching vibration of he C=N and N=N double bonds are observed at *ca.* 1550 cm^{-1}.[21] The result suggests that the oligomers were formed through both 1,2- and 1,4-additions.

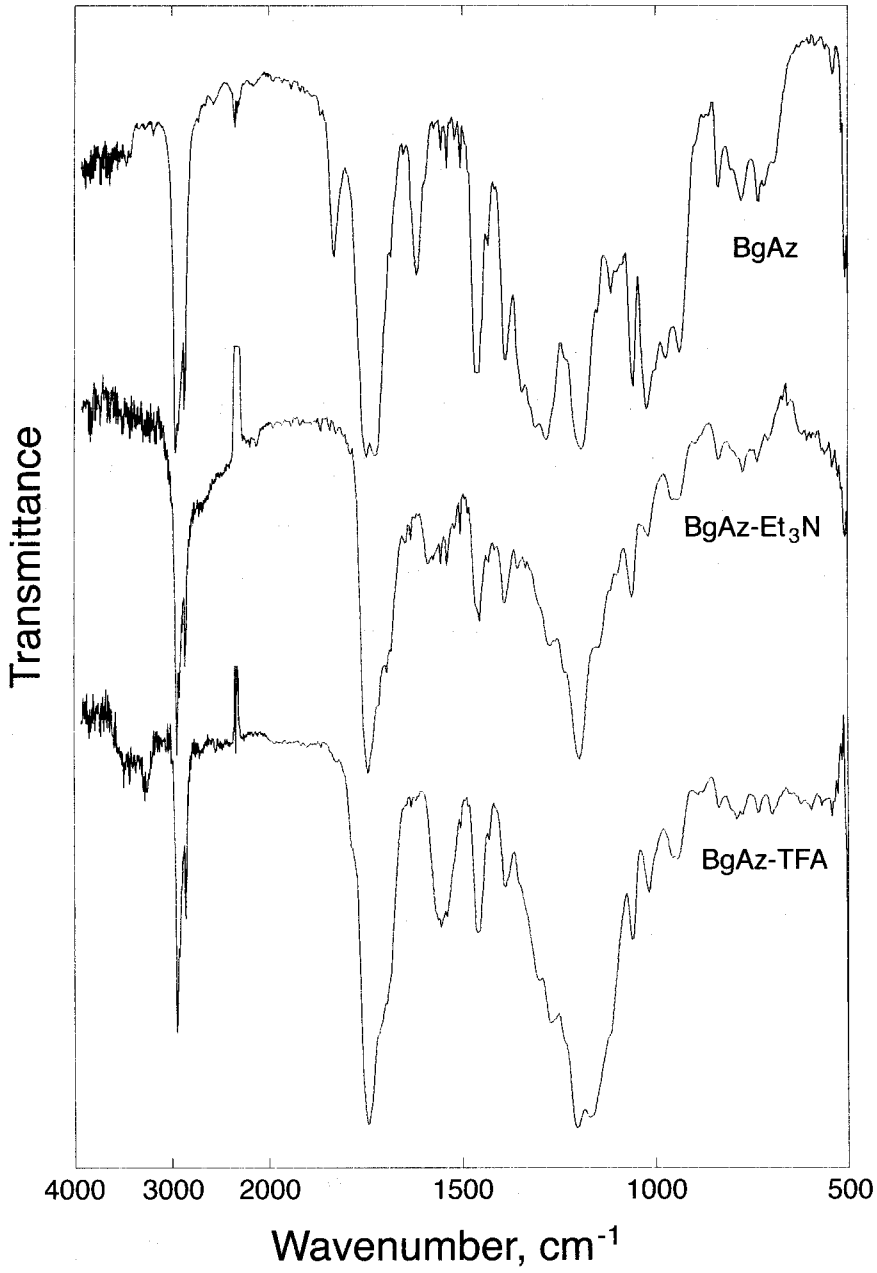


Figure 2. The IR spectra of BgAz and the oligomers obtained by the polymerization of BgAz with Et_3N and TFA (NaCl).

In 270 MHz ^{1}H NMR spectra of the oligomers obtained by Et_3N and TFA, absorption bands due to the protons of the CH=N and the CH-N were observed around 6.4-7.2 and 4.5-5.6 ppm, respectively.[20] From the ratios of the areas of the absorption bands, the contents of 1,2-unit were estimated to be 60 and 55 % for the oligomers obtained by Et_3N and TFA, respectiveley. These results support the proposition that the oligomers were formed through both 1,2- and 1,4-additions.

Conclusion

BgAz, a new monomer, was prepared, and its chemical reactivity and polymerizability were investigated. BgAz reacts with primary, secondary, and tertiary alcohols to form 1,2-adducts. BgAz was polymerized by anionic initiators, such as *t*-BuLi, *n*-BuLi, DBU, Et_3N, and pyridine, to give oligomers. Furthermore, oligomer was obtained by the polymerization of BgAz with TFA. These results suggest that BgAz has anionic and cationic polymerizabilities. The structures of the oligomers were investigated by IR and ^{1}H NMR spectroscopies. It was found that the oligomers were formed through both 1,2- and 1,4-addition.

References

(1) Robinson, G. C. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3901.

(2) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520.

(3) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159.

(4) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(5) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436.

(6) Hall, H. K., Jr. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(7) Neureiter, N. P. *J. Am. Chem. Soc.* **1959**, *81*, 2910.

(8) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(9) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(10) Kamachi, M.; Murahashi, S *Makromol. Chem.* **1968**, *119*, 232.

(11) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(12) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(13) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(14) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931.

(15) Kamachi, M.; Kajiwara, A.; Hashidzume, A., to be published.

(16) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(17) Gulman, H.; Houbein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515

(18) Wolf, F. J.; Weijland, J. *Org. Synth. Coll. Vol.* **1963**, *4*, 124.

(19) Curtius, T.; Zinkeisen, E. *J. Prakt. Chem.* **1898**, *58*, 310.

(20) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon: Oxford, 1966; Vol. 2.

(21) Socrates, G. "Infrared Characteristic Group Frequencies"; John Wiley: Chichester, 1994.

(22) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Chapter 5

Spontaneous Copolymerization of Acetaldehyde Azine and Maleic Anhydride

Introduction

As described in previous chapters, Kamachi *et al.*[1-9] investigated the polymerizability of azine compounds, because there are few papers concerning the polymerization of compounds with the C=N double bond.[10-16] Consequently, they synthesized *trans*-1,4-polymers from alkanal azine compounds (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7)[5-8] and a 1,2-polymer from trifluoroacetaldehyde azine (R=CF_3).[9]

In the course of the study on the polymerization of azine compounds, Kamachi[17] found that acetaldehyde azine (R=CH_3, AcAz) reacted with maleic anhydride (MAnh) without any initiators to form polymeric product. Curtius *et al.*[18] reported that alkanal azine compounds having hydrogen atoms on the α-carbon of the C=N double bond reacts with carboxylic acids, such as formic acid, to form pyrazoline rings. To our knowledge, however, there is no paper concerning the reaction of alkanal azines with acid anhydrides for understanding the polymer formation. Therefore, we were motivated to perform detailed studies of copolymerization of AcAz and MAnh. In this chapter, the copolymerization of AcAz with MAnh and the structure of the copolymer will be described.

Experimental Section

Materials. Acetaldehyde azine (AcAz) was prepared from acetaldehyde and hydrazine monohydrate according to the procedure of Curtius *et al.*[18] Maleic anhydride (MAnh) and succinic anhydride (SAnh) were recrystallized from

chloroform and dried *in vacuo*. Tetrahydrofuran (THF) was distilled over benzophenone-ketyl and stored under an argon atmosphere. Other reagents were used as received without further purification.

Copolymerization of AcAz and MAnh. A typical copolymerization of AcAz with MAnh is described below.

AcAz (168 mg, 2.0 mmol) was added to MAnh (196 mg, 2.0 mmol) in a sample tube. The reaction mixture gradually changed from pale yellow to red-brown. After 24 h, the reaction mixture was washed with THF and dried *in vacuo* to give a pale yellow powder: yield 206 mg, 56.6 %; mp 218-223 °C; IR (KBr) 3450 (OH), 3250 (NH), 1720 (carboxylic acid C=O), 1630 (amide C=O, C=N) cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ 0.7-1.4, 1.5-2.3, 2.6-5.0, 6.5-7.2; Anal. Calcd for $(C_8H_{10}N_2O_3)_n$: C, 52.74; H, 5.53; N,15.38. Found: C, 53.22; H, 5.87; N, 14.56.

Preparation of the Adduct of AcAz with MAnh. AcAz (0.96 mL, 10 mmol) was added to a solution of MAnh (980 mg, 10 mmol) in THF (10 mL) in a flask under an argon atmosphere. The solution was stirred at *ca.* 20 °C for 36 h. The reaction solution was separated from the precipitate formed by centrifugation. After evaporation of the THF, an orange viscous oil was obtained. The adduct was extracted from the orange oil with toluene (30 mL). *n*-Hexane (300 mL) was added to the solution in toluene to obtain the adduct of AcAz and MAnh. The adduct was recrystallized in toluene-hexane: yield 99 mg, 5.5 %; mp 107.5-108.1 °C; IR (KBr) 1705 (carboxylic acid C=O), 1623 (amide C=O, C=N), 1550 (C=C) cm^{-1}; ^1H NMR (DMSO-d_6, 270 MHz) δ 1.22 (d, 3H, J = 6.4 Hz), 2.52 (ddd, 1H, J = 12.5, 3.1, 1.8 Hz), 3.12 (ddd, 1H, J = 15.5, 6.2, 1.6 Hz), 4.38 (m, 1H), 6.15 (d, 1H, J = 12.1 Hz), 6.78 (d, 1H, J = 12.1Hz), 7.15 (t, 1H, J = 1.6 Hz), 12.81 (s, 1H); ^{13}C NMR (DMSO-d_6, 67.9 MHz) δ 19.0, 41.2, 50.1, 128.0, 131.9, 149.3 162.6, 166.4. Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N,15.38. Found: C, 52.80; H, 5.43; N, 15.33. EI-MS [M^+] Calcd 182. Found 182.

Reactions of the Adduct of AcAz with MAnh. A reagent was added to the solution of the adduct of AcAz with MAnh in THF. After 72 h, ^{1}H NMR spectra and gel permeation chromatography (GPC) of the reaction mixture were measured.

Preparation of the Adduct of AcAz with SAnh. AcAz (0.96 mL, 10 mmol) was added to a solution of SAnh (900 mg, 10 mmol) in THF (10 mL) in a flask under an argon atmosphere. The solution was stirred at *ca.* 20 °C for 36 h. After evaporation of the THF, a pale yellow viscous oil was obtained; IR (NaCl) 1730 (carboxylic acid C=O), 1640 (amide C=O), 1600 (C=N) cm^{-1}; ^{1}H NMR (DMSO-d_6, 270 MHz) δ 1.23 (d, 3H, J = 6.6 Hz), 2.53 (t, 2H, J = 6.9 Hz), 2.54 (ddd, 1H, J = 19.3, 5.2, 2.1 Hz), 2.81 (t, 1H, J = 6.9 Hz), 2.82 (t, 1H, J = 6.9 Hz), 3.16 (ddd, 1H, J = 18.5, 11.0, 1.7 Hz), 4.37 (m, 1H), 7.16 (t, 1H, J = 1.7 Hz), 12.09 (s, 1H).

Measurements. Infrared (IR) spectra were recorded on a JASCO FT/IR-3 spectrometer. Raman spectra were obtained on a JASCO R-800 spectrometer by using an argon-ion laser 5145 Å excitation line. ^{1}H, ^{13}C, 2D H-H COSY, and 2D C-H COSY NMR spectra were measured in DMSO-d_6 on a JEOL JNM-EX270 spectrometer. GPC analysis was performed in THF by a TOSOH CO-8011 system by using TSK columns. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. Molecular weights of the oligomers were calibrated by polystyrene standards (TOSOH TSK standard POLYSTYRENE). Viscosity measurements were carried out in methanol at 35 °C by using an Ubbelohde viscometer. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron impact (EI) method. Mass was calibrated by using cesium iodide (CsI).

Results and Discussion

Copolymerization of AcAz and MAnh. The results of the copolymerization of AcAz and MAnh under neat condition are listed in Table 1. When AcAz was added to MAnh, an exothermic reaction took place to form a resin. The resin was crushed with a micro spatula into powder. The powder was washed with THF to finally give pale yellow powder as a THF-insoluble fraction. The powder was soluble in polar solvents, such as methanol, ethanol, dimethyl sulfoxide (DMSO), and water; and insoluble in THF, acetone, chloroform, diethyl ether, and *n*-hexane. The molecular weight of the product was *ca.* 2000, suggesting that polymerization took place. The elemental analysis of the polymer showed that the polymer was composed of both the AcAz and MAnh units (Experimental Section). From these results, it can be concluded that the polymer was formed by the copolymerization of AcAz and MAnh.

Table 1. Reaction of AcAz with MAnh[a]

AcAz, mmol	MAnh, mmol	yield, mg (%[b])	η_{sp}/C, cm^3g^{-1} [c]	$\overline{M}_v$ [d]
1.2	2.8	25 (6.7)	3.2	2200
2.0	2.0	206 (56.6)	-[e]	-[e]
2.4	1.6	157 (43.8)	2.8	1800
3.2	0.8	65 (18.7)	2.4	1500

[a] At 20 °C; Reaction time: 24 h. [b] Based on the total comonomer. [c] In methanol solution at 35 °C. [d] *K* and *a* values of poly(vinylpyrrolidone) in methanol were used.[19] [e] This polymer was not completely soluble in methanol.

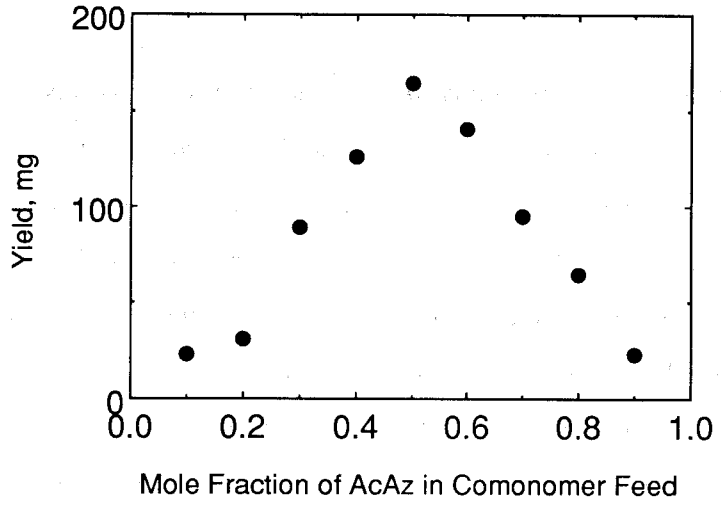


Figure 1. Continuous variation plots for the copolymerization of AcAz with MAnh at 20 °C for 24 h.

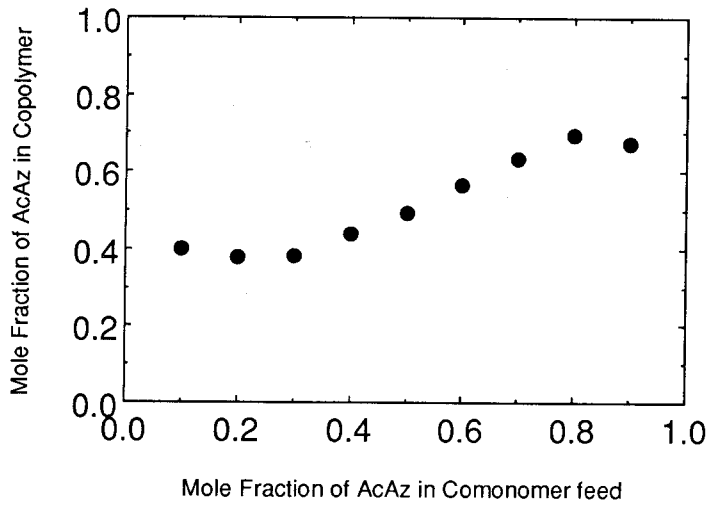


Figure 2. Dependence of the mole fraction of AcAz in the obtained copolymer on the mole fraction of AcAz in the comonomer feed.

In order to obtain information about the type of the copolymerization, a continuous variation method was carried out. The result is shown in Figure 1. A maximum in the yield of the copolymer is observed at the mole fraction of AcAz of

0.5. The dependence of the mole fraction of AcAz in copolymer on comonomer feed is shown in Figure 2. Figure 2 shows that the mole fractions of AcAz in the copolymers range from 0.38 to 0.69. These results suggest that the copolymer was formed mainly by alternating copolymerization.

Isolation and Characterization of the Adduct of AcAz with MAnh. A colorless crystalline product was isolated from a THF-soluble fraction obtained by washing the resin with THF. The chemical structure of the crystalline product was investigated by elemental analysis and EI-mass, IR, and ^{1}H, ^{13}C, 2D H-H COSY, and 2D C-H COSY NMR spectroscopies.

The C, H, and N contents of the crystalline product (C, 52.80; H, 5.43; N, 15.33 %) agree with those estimatied as the one-to-one adduct of AcAz with MAnh (C, 52.74; H, 5.53; N, 15.38 %).

The EI-mass spectrum of the crystalline product showed a signal at m/z = 182 as a molecular ion peak. The result also supports that the product is the one-to-one adduct of AcAz (MW = 84) with MAnh (MW = 98).

The IR spectrum of the crystalline product is shown in Figure 3. The absorption bands due to the stretching vibrations of the C=O double bonds of the carboxylic acid and amide are observed at 1705 and 1623 cm^{-1}, respectively.[20] Furthermore, the C=N and C=C double bonds are observed at 1623 and 1550 cm^{-1}, respectively.[20]

The 270 MHz ^{1}H NMR of the product is shown in Figure 4. The AB type of absorption bands observed at 6.15 and 6.78 ppm are assignable to the protons of the CH=CH.[21] The result suggests that the C=C double bond of MAnh was not consumed during the formation of the crystalline product and that ring opening took place on MAnh. In addition, the absorption bands assignable to the protons of the CH=N and of the carboxylic acid are observed at 7.15 and 12.81 ppm, respectively.[21] The results suggest that the product contains a C=N double bond and a carboxylic acid.

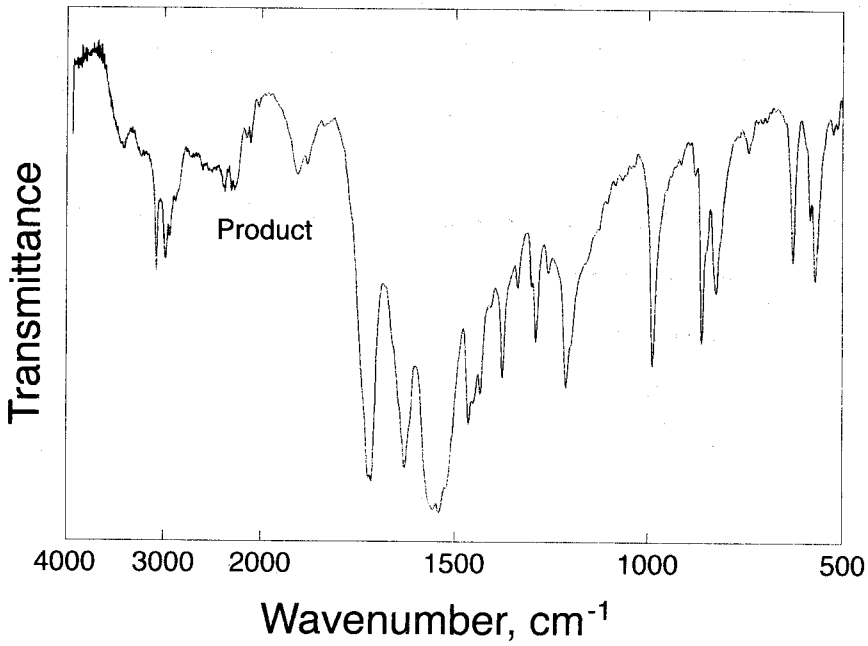


Figure 3. IR spectrum of the adduct of AcAz with MAnh.

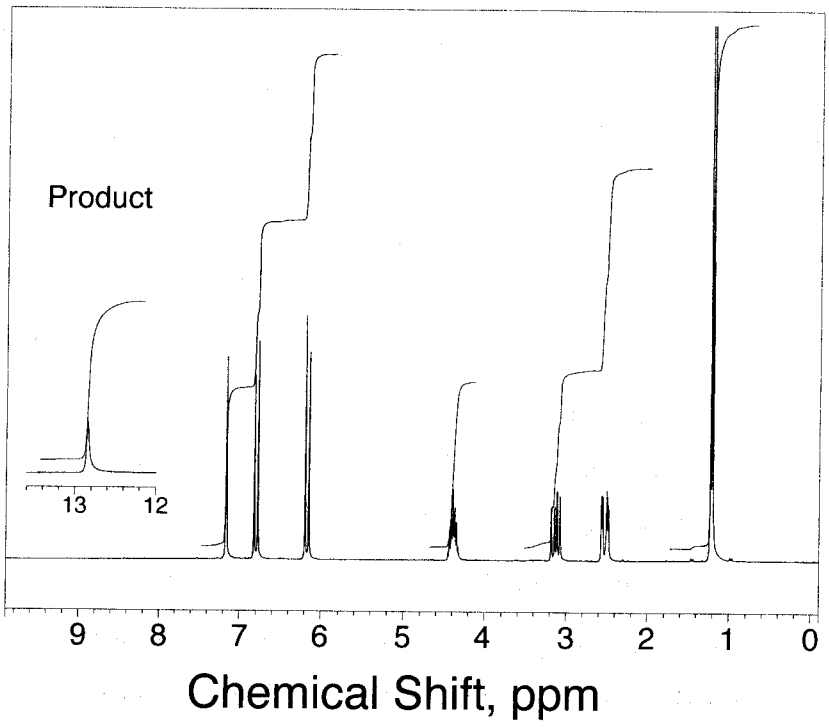


Figure 4. 270 MHz ^{1}H NMR spectrum of the adduct of AcAz with MAnh.

The 2D H-H COSY NMR spectrum of the product is shown in Figure 5. The absorption band observed at 4.38 ppm correlates with those at 1.22, 2.52, and 3.12 ppm. The absorption band at 7.15 ppm correlates with those at 2.52 and 3.12 ppm.

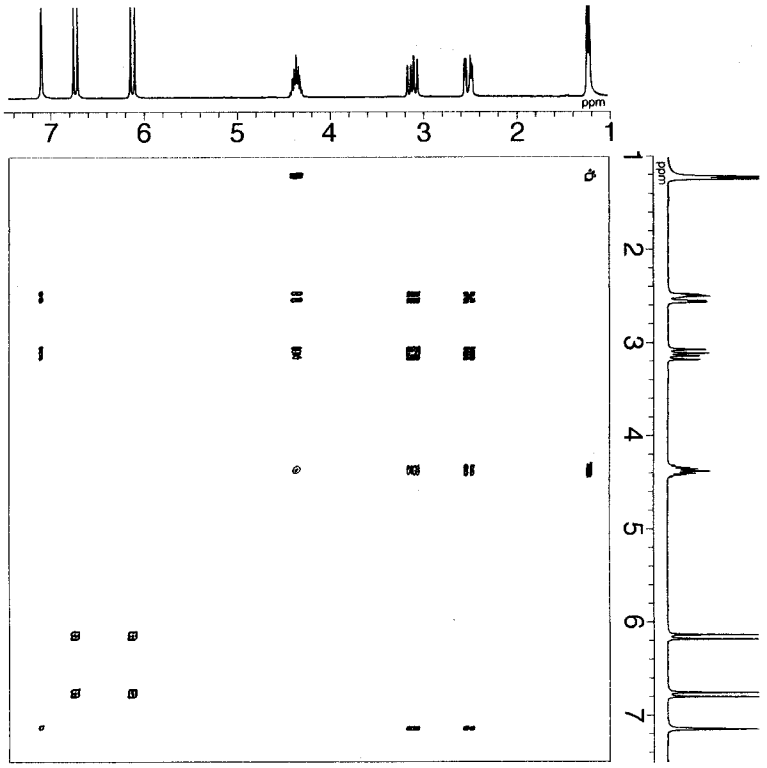


Figure 5. The 2D H-H COSY NMR spectrum of the adduct of AcAz with MAnh.

The 2D C-H COSY NMR spectrum of the product is shown in Figure 6. All correlation peaks are clearly observed.

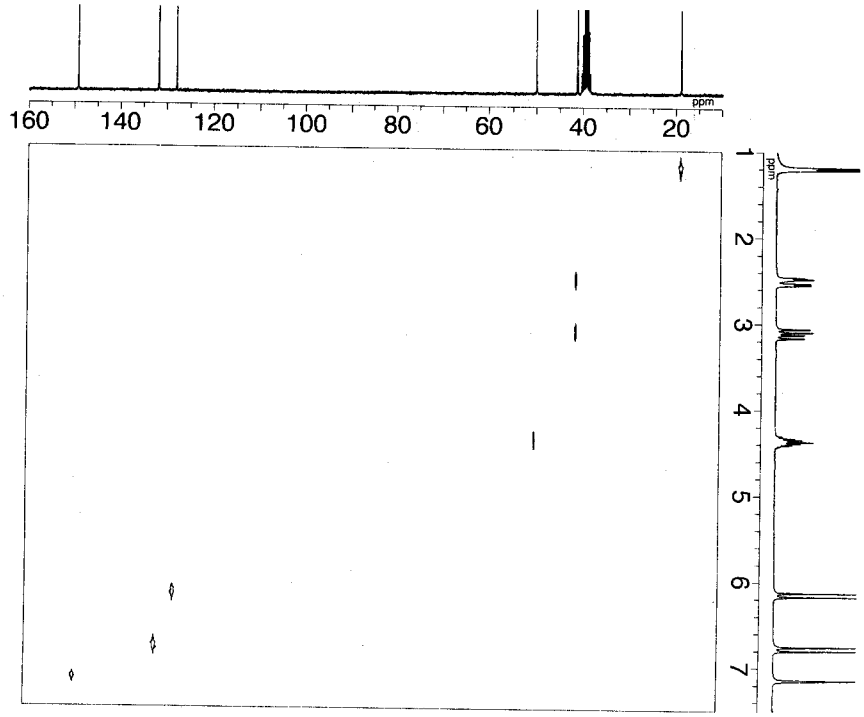
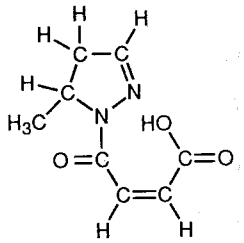


Figure 6. The 2D C-H COSY NMR spectrum of the adduct of AcAz with MAnh.

From these results, the product is the adduct of AcAz with MAnh, which has the structure (**1**) in Scheme 1.

Scheme 1. The Structures of the Adducts of AcAz with MAnh



1

Role of the Adduct in the Copolymerization of AcAz with MAnh. In order to investigate the role of the adduct obtained in the copolymerization of AcAz with MAnh, the reactivity of the adduct was studied. The results are listed in Table 2.

The adduct itself was stable at 30 °C. It was also stable against triethylamine, acetic acid, and methanol at 30 °C. Furthermore, the adduct did not react with maleic anhydride. However, the adduct reacted with AcAz to form polymer; although the adduct did not react with trifluoroacetaldehyde azine and benzaldehyde azine, which contain stronger electron-accepting groups than AcAz. In addition, oligomerization occurred upon the addition of propionaldehyde azine to the adduct.

The IR and 270 MHz ^{1}H NMR spectra of the polymer given by the reaction of the adduct with AcAz were similar to those of the copolymer obtained from the mixturte of AcAz with MAnh. These results suggest that the adduct is a precursor of the copolymerization between AcAz with MAnh.

Table 2 Reactions of the Adduct of AcAz with MAnh[a]

adduct, mg (mmol)	reagent	mg (mmol)	THF, mL	time, h	result
55 (0.3)	-	-	0.3	72	no reaction
18 (0.1)	Et_3N [b]	10 (0.1)	0.2	72	no reaction
18 (0.1)	Et_3N [b]	20 (0.2)	0.2	72	no reaction
18 (0.1)	CH_3COOH	6 (0.1)	0.2	72	no reaction
18 (0.1)	CH_3COOH	12 (0.2)	0.2	72	no reaction
18 (0.1)	CH_3OH	3 (0.1)	0.2	72	no reaction
18 (0.1)	CH_3OH	6 (0.2)	0.2	72	no reaction
55 (0.3)	MAnh	29 (0.3)	0.3	72	no reaction
55 (0.3)	AcAz	25 (0.3)	0.3	72	polymerization (yield 5 mg, 9 %) [c]
55 (0.3)	AcAz	2.5 (0.03)	0.6	72	polymerization (yield 2 mg, 4 %) [c]
18 (0.1)	AcAz	84 (1.0)	1.0	72	polymerization (trace) [c]
18 (0.1)	PrAz [d]	11 (0.1)	0.2	72	oligomerization
18 (0.1)	TFAcAz [e]	19 (0.1)	0.2	72	no reaction
18 (0.1)	BzAz [f]	21 (0.1)	0.2	72	no reaction

[a] Under an argon atmosphere at 30 °C. [b] Triethylamine. [c] THF insoluble fraction. [d] Propionaldehyde azine. [e] Trifluoroacetaldehyde azine. [f] Benzaldehyde azine.

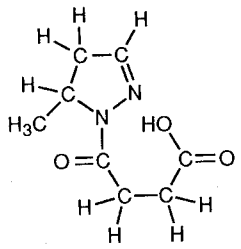
In order to obtain information on the copolymerization of AcAz and MAnh, the reaction of AcAz with SAnh was tried. THF-soluble resin was not obtained, but crystalline product was formed. The structure of the product was investigated by IR and ^1H NMR spectroscopies.

The IR spectrum of the product is shown in Figure 7 (bottom). In the spectrum, the absorption bands due to the stretching vibration of the carboxylic acid C=O, amide C=O, and C=N double bonds are observed at 1730, 1640, and 1600 cm^{-1}, respectively.[20] Naturally, there are no absorption bands due to the stretching vibration of the C=C double bond at *ca.* 1580 cm^{-1}.

The ^1H NMR spectrum of the product is shown in Figure 8 (bottom). In the spectrum, the signals due to the 5-methylpyrazoline ring were observed at 1.23, 2.54, 3.16, 4.37, and 7.16 ppm. Furthermore, the absorption bands assignable to the CH_2CH_2 were observed at 2.53, 2.81, and 2.82 ppm.[21] In addition, the absorption band due to the COOH was observed around 12.09 ppm.[21]

From these results, it is concluded that the product was the one-to-one adduct of AcAz with SAnh of the structure (**2**) shown in Scheme 2, indicating that double bond is necessary for the formation of resin of azine with acid anhydride.

Scheme 2. The Structures of the Adducts of AcAz with SAnh



2

Structure of the Copolymer of AcAz with MAnh. The structure of the copolymer was investigated by the comparison of the IR and the ^1H NMR spectra of the copolymer with those of the adducts of AcAz with MAnh and SAnh, whose structures have been made clear.

The IR spectra of the adducts of AcAz with MAnh and the copolymer are shown in Figure 7 (top and middle, respectively). In the spectrum of the adduct, the absorption bands due to the stretching vibration of the C=O double bond of the

carboxylic acid and amide are observed at 1705 and 1623 cm^{-1}, respectively.[20] Furthermore, in the spectrum of the adduct, the absorption bands due to the stretching vibration of the C=N and C=C double bonds are observed at 1623, and 1550 cm^{-1}, respectively.[20] The absorption band due to the stretching vibration of the C=C double bond disappeared in the spectrum of the copolymer. The result suggests that the C=C double bond of the adduct was consumed during copolymerization. In addition, the absorption bands due to the stretching vibrations of the O-H and N-H bonds are observed at 3450 and 3250 cm^{-1}, respectively.[20]

The 270 MHz ^1H NMR spectra of the copolymer and the adduct are shown in Figure 8. In the spectrum of the adduct, the AB type of the absorption bands due to the protons of the CH=CH are observed at 6.15 and 6.78 ppm,[21] while the signals assignable to the protons of the CH=CH almost disappeared in the spectrum of the copolymer. These results suggest that the polymerization proceeds mainly through the C=C double bond. In addition, the decrease in the signal intensity of the proton of the CH=N suggests that intramolecular salt is partially formed between the carboxylic acid and the C=N double bond. This proposition is supported by the fact that the copolymer was soluble in polar solvents.

From these results, it is deduced that the copolymer is mainly composed of the structure (**6**) shown in Scheme 3. Furthermore, the fact that the spectrum of the one-to-one adduct of AcAz with SAnh (**2**) resembles that of the copolymer supports the proposition that the copolymer is mainly composed of the structure (**6**).

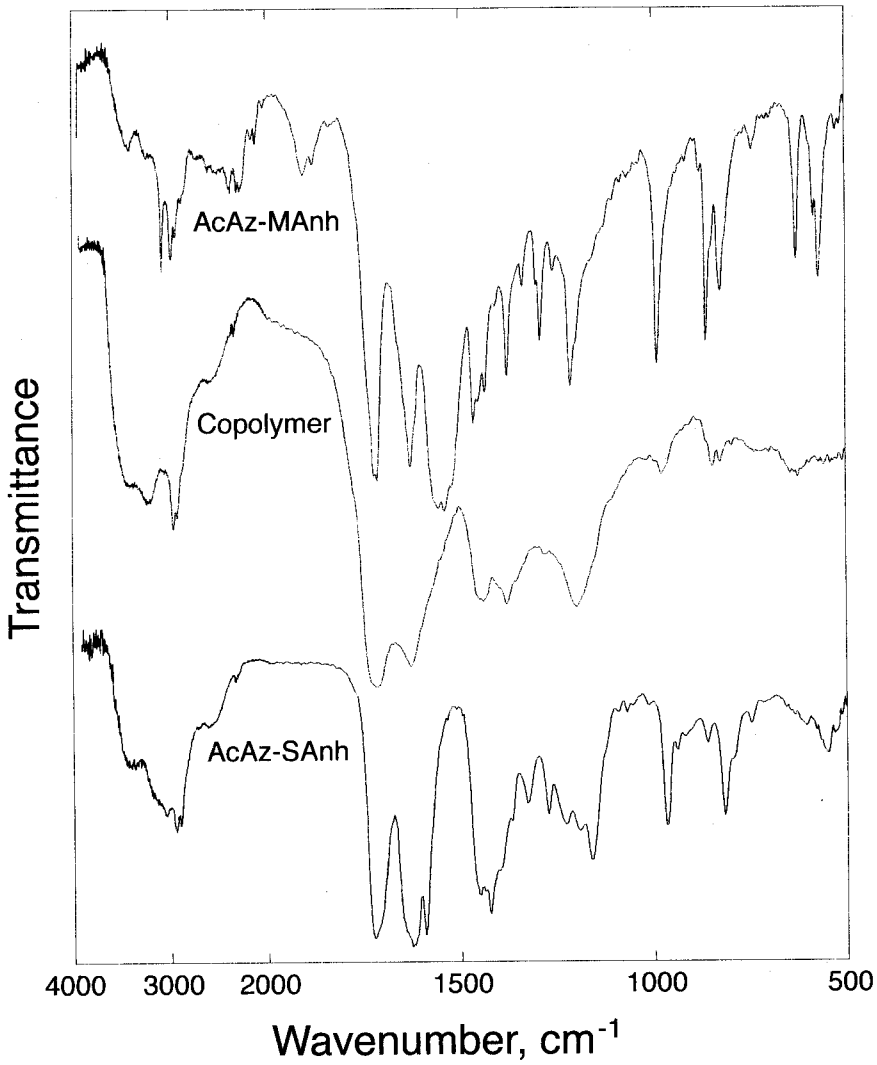


Figure 7. The IR spectra of the adduct of AcAz with MAnh (top), the copolymer of AcAz with MAnh (middle), and the adduct of AcAz with SAnh (bottom).

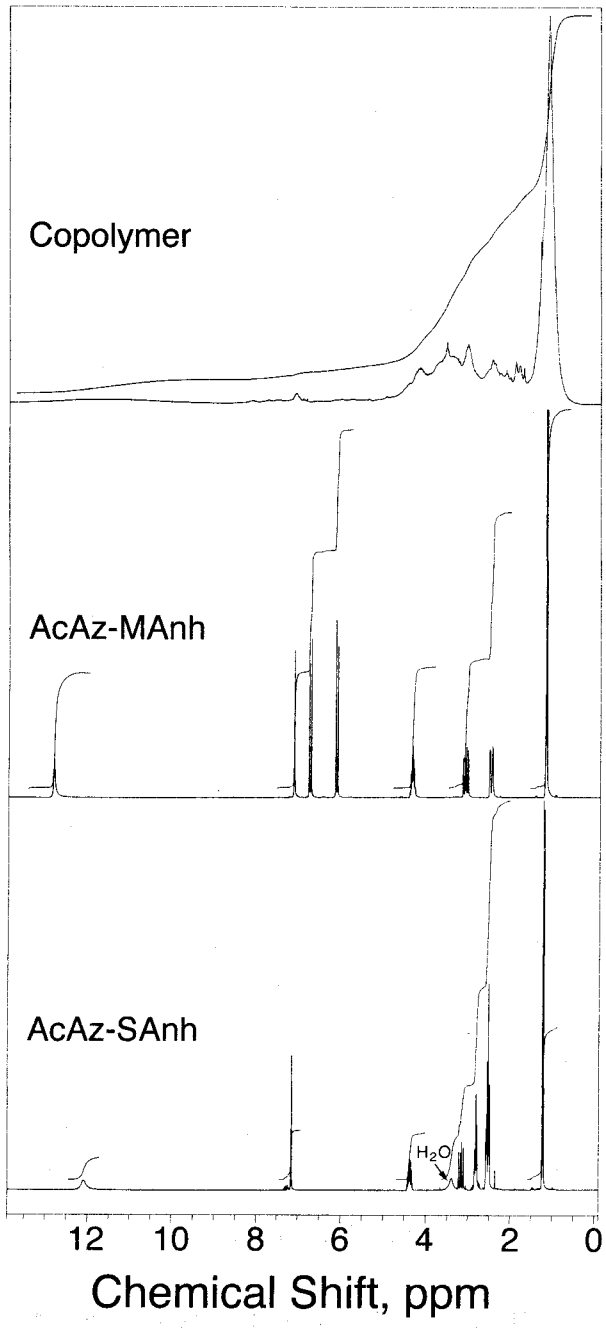
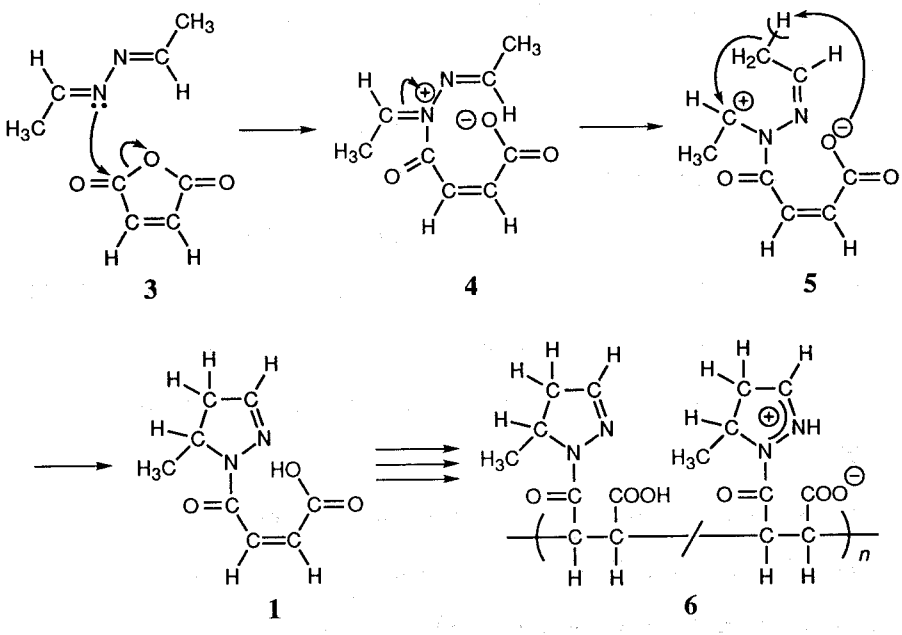


Figure 8. 270 MHz ^{1}H NMR spectra of the copolymer (top), the adduct of AcAz with MAnh (middle), and the adduct of AcAz with SAnh (bottom) (DMSO-d_6).

Tentative Mechanism for the Copolymerization of AcAz and MAnh. A mechanism for the copolymerization of AcAz and MAnh proposed on the basis of results mentioned above is shown in Scheme 3. The lone pair of the nitrogen of AcAz attacks the carbonyl of MAnh to form a zwitterion (step **3** to **5**). When ring closure takes place with the shift of the proton from the α-carbon of the C=N double bond to the carboxylate, the adduct is formed (step **5** to **1**). Following this, the copolymer was formed by the addition of the adduct of AcAz with MAnh through the C=C double bond (step **1** to **6**). This proposition is supported by the fact that no polymer obtained by the reaction of AcAz with SAnh.

The initiation of the polymerization of the adduct of AcAz with MAnh has remained as a subject of future studies.

Scheme 3. Tentative Mechanism for the Copolymerization of AcAz with MAnh



Conclusion

Copolymer was obtained from a mixture of AcAz and MAnh. The copolymerization was investigated by a continuous variation method, which showed that the copolymer was formed in a maximum yield at a mole fraction of AcAz of 0.5. The one-to-one adduct of AcAz with MAnh, which contained a pyrazoline ring, was isolated from a THF-soluble fraction obtained by the copolymerization. The adduct was polymerized by AcAz, and the adduct was found to be the precursor of the copolymerization. Consequently, the copolymer was considered to be formed by the addition polymerization of the adduct mainly through the C=C double bond.

References

(1) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(2) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(3) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232.

(4) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(5) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(6) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(7) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931.

(8) Kamachi, M.; Kajiwara, A.; Hashidzume, A., to be published.

(9) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(10) Robinson, G. C. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3901.

(11) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520.

(12) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159.

(13) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(14) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436.

(15) Hall, H. K., Jr., *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(16) Neureiter, N. P. *J. Am. Chem. Soc.* **1959**, *81*, 2910.

(17) Kamachi, M., unpublished results.

(18) Curtius, T.; Zinkeisen, E. *J. Prakt. Chem.* **1898**, *58*, 310.

(19) Frank, H.; Levy, G. *J. Polym. Sci.* **1953**, *10*, 371.

(20) Socrates, G. "Infrared Characteristic Group Frequencies"; John Wiley: Chichester, 1994.

(21) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon: Oxford, 1966; Vol. 2.

Part 2

Preparation and Polymerization of Azastyrene (N-Methyleneaniline) Derivatives

Chapter 6

Preparation, Chemical Reactions, and Polymerization of Azastyrene, *N*-Methyleneaniline

Introduction

Although many papers have been reported on the formation of high molecular weight polymers of compounds containing C=C or C=O double bonds by radical or ionic initiators, there are no papers concerning the addition polymerization of compounds with the C=N double bonds, to our knowledge, except for carbodiimides,[1, 2] isocyanates,[3-5] imines,[6] 1-azabutadienes,[6] and azine compounds.[7-16] 2,3-Diaza-1,3-butadiene, formaldehyde azine (CH_2=N-N=CH_2, FAz), which is the simplest azine, was prepared by Neureiter[7] in 1959. Although Neureiter reported that FAz spontaneously polymerized above its melting point, he did not mention the type of the polymerization and the structural units of the polymer. Kamachi *et al.*[8] succeeded in the storage of FAz without polymerization as a dilute THF solution. Therefore, they investigated the polymerizability of FAz, and found that FAz was easily polymerized by various types of initiators to form polymer containing 1,2- and 1,4-units.[9] Furthermore, the polymerizabilities of other azine compounds have systematically been investigated in order to understand the polymerizabilities of the C=N double bond and to obtain new polymers.[10-12] Consequently, *trans*-1,4-polymers have been synthesized from alkanal azine compounds (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7).[13-15] As described in Chapters 2 and 3, a 1,2-polymer has been also prepared from trifluoroacetaldehyde azine (R=CF_3).[16]

In the extension of this research concerning the polymerization of the C=N double bond, attention has been also paid to *N*-methyleneaniline (CH_2=NC_6H_5, MeAn). Since MeAn is a styrene-analogue containing a C=N double bond, the chemical reaction and the polymerization of this compound have long been attracted

much attention.[17] Although MeAn is known to be stable in the gas phase,[18] it has been reported that MeAn is so unstable as to be immediately converted to a cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine, in its condensed phase.[19] Therefore, only a few reactions of MeAn have been reported so far.[20-22] In these cases, reactions which produced MeAn as a transient product were used. MeAn may have been thought to be an intermediate of the reactions, because there were no data which supported the existence of MeAn. Thus, we think that there are no papers concerning the chemical reactivity and polymerizability of MeAn. We found that MeAn was stable in THF below -40 °C, and investigated its chemical reactivity and polymerizability. In this chapter, the author will describe the preparation, stability, reactivity, and polymerizability of MeAn and the structures of the obtained products.

Experimental Section

Materials and Initiators. Tetrahydrofuran (THF) and tetrahydrofuran-d_8 (THF-d_8) were dried with sodium, and distilled under high vacuum immediately before use. Diisopropylamine and ethyl isobutyrate were distilled over calcium hydride under reduced pressure and stored under an argon atmosphere. Commercially available *n*-butyllithium (*n*-BuLi) (1.6 M *n*-hexane solution) and *n*-butylmagnesium chloride (*n*-BuMgCl) (2.0 M THF solution) were transferred to ampules, respectively, via syringes under an argon atmosphere. The concentration was determined by double titration.[23] Commercially available titanium tetrachloride (1.0 M dichloromethane solution) and tin tetrachloride (1.0 M *n*-pentane solution) were used. Other reagents were used as received without further purification.

Preparation of Hexahydro-1,3,5-triphenyl-1,3,5-triazine. An aqueous solution of formaldehyde (37 %, 35 mL, 0.43 mol) was added to a solution of aniline (28.0 g, 0.30 mol) in benzene (60 mL) with stirring. After completion of the addition, stirring was continued. After 2 h, colorless microcrystals were separated from the

solution by filtration and washed with benzene (3 x 10 mL). Hexahydro-1,3,5-triphenyl-1,3,5-triazine was recrystallized in benzene and dried *in vacuo*: yield 18.0 g, 57 %; mp 147.5-148.2 °C; IR (KBr) 1600 (aromatic C=C), 1500 (aromatic C=C), 1160 (C-N), 755 (aromatic CH), 690 (aromatic CH) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.91 (s, 6H), 6.90 (t, 3H, J = 8.02 Hz), 7.03 (d, 6H, J = 8.02 Hz), 7.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 68.7, 117.9, 121.0, 129.3, 148.6; Anal. Calcd for $C_{21}H_{21}N_3$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.87; H, 6.66; N, 13.23; EI-MS [M^+] Calcd 315. Found 315.

Preparation of a Solution of MeAn in THF-d_8 for NMR Measurements. Figure 1 (a) shows the apparatus used for the preparation of a solution of MeAn in THF-d_8. Hexahydro-1,3,5-triphenyl-1,3,5-triazine (200 mg, 0.66 mmol), which was dried at 100 °C under high vacuum for 4 h, was placed in ampule **A**. The apparatus was connected to a high vacuum line. The hexahydro-1,3,5-triphenyl-1,3,5-triazine was gradually pyrolyzed under high vacuum at 300 °C with a Shimadzu SARF-30K electric furnace to prepare MeAn. The formed MeAn was collected in NMR tube **B** with liquid nitrogen. After breaking break-seal **C**, THF-d_8 (0.50 mL) was distilled into the NMR tube under high vacuum. Then, NMR tube **B** was sealed under high vacuum. After the solution was warmed up to -78 °C to be made homogeneous, the solution was kept at the temperature of liquid nitrogen until NMR measurements: yield 17 mg, 3.5 %; ^1H NMR (THF-d_8, 270 MHz) δ 7.05 (m, 2H), 7.18 (tt, 1H, J = 1.94, 7.34 Hz), 7. 30 (m, 2H), 7.31 (d, 1H, J = 16.91 Hz), 7.57 (d, 1H, J = 16.91 Hz); ^{13}C NMR (THF-d_8, 67.9 MHz) δ 121.3, 127.0, 129.9, 153.9, 154.9.

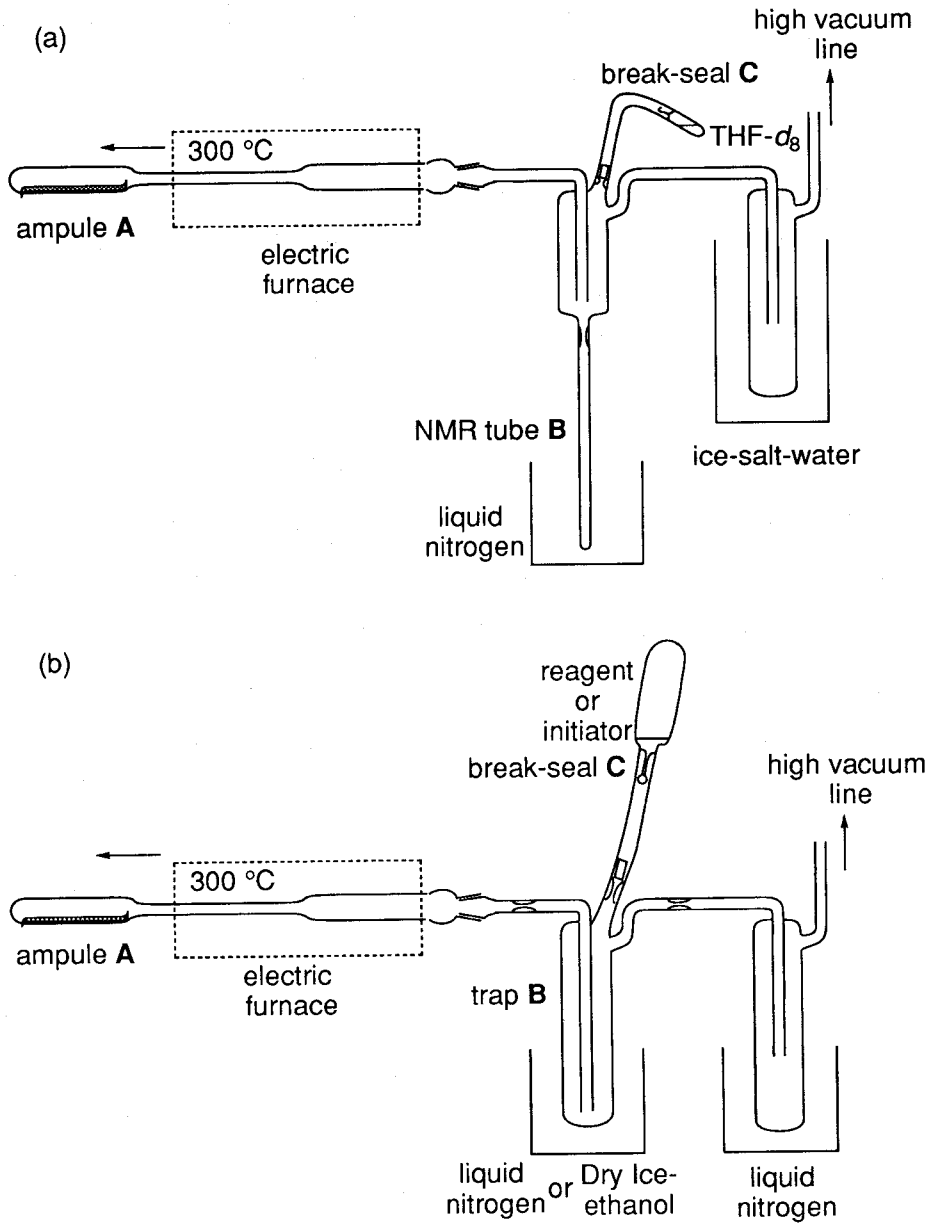


Figure 1. Apparatus for (a) the preparation of a solution of MeAn in THF-d_8 for NMR measurements and (b) the reaction and polymerization of MeAn.

Observation of the Equilibrium between MeAn with the Cyclic Trimer in DMSO-d_6. A solution of hexahydro-1,3,5-triphenyl-1,3,5-triazine (1.3 mg, 4.1

*m*mol) in DMSO-d_6 (0.50 mL) was placed in an NMR tube. The NMR measurements of the sample were carried out at 30, 50, 70, 100, 120, and 150 °C.

Reaction of MeAn with *n*-BuLi. The apparatus shown in Figure 1 (b) was used for the reaction of MeAn with *n*-BuLi. Hexahydro-1,3,5-triphenyl-1,3,5-triazine (500 mg, 1.6 mmol), which was dried at 100 °C under high vacuum for 4 h, was placed in ampule **A**. THF (10 mL) was distilled into trap **B** under high vacuum. The hexahydro-1,3,5-triphenyl-1,3,5-triazine was gradually pyrolyzed under high vacuum at 300 °C with a Shimadzu SARF-30K electric furnace to prepare MeAn. The formed MeAn was introduced into trap **B** at -78 °C. After a solution of *n*-BuLi in *n*-hexane (1.6 M, 3.0 mL, 4.8 mmol) was added into trap **B** by breaking break-seal **C**, trap **A** was sealed under high vacuum. After the reaction mixture was maintained at -78 °C for 4 h, it was gradually warmed to 25 °C. When the trap was opened, methanol (10 mL) was poured to the reaction mixture in order to terminate the reaction. After evaporation of the solvents, a pale yellow oil was obtained. The pale yellow oil was dissolved in diethyl ether. The solution in diethyl ether was washed with saturated aqueous sodium chloride (10 mL) and dried with anhydrous sodium sulfate. After evaporation of the diethyl ether, a pale yellow oil was obtained: IR (KBr) 3400 (NH), 1505 (aromatic C=C), 1600 (aromatic C=C) 750 (aromatic CH), 695 (aromatic CH) cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.96 (t, 3H, J = 6.93 Hz), 1.40 (m, 2H), 1.65 (m, 4H), 3.12 (t, 2H, J = 5.41 Hz), 3.61 (s, 2H), 6.63 (t, 2H, J = 7.59 Hz), 6.71 (t, 1H, J = 7.59 Hz), 7.20 (t, 2H, J = 7.76 Hz); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 14.0, 22.5, 29.2, 29.3, 43.9, 112.7, 117.0, 129.1, 148.5.

Reaction of MeAn with Ethyl Isobutyrate in the Presence of Lithium Diisopropyl Amide (LDA). The apparatus shown in Figure 1 (b) was used for the reaction of MeAn with ethyl isobutyrate in the presence of LDA. A solution of *n*-BuLi in *n*-hexane (1.6 M, 1.9 mL, 3.0 mmol), diisopropylamine (0.42 mL, 3.0 mmol), and THF (10 mL) were placed in trap **B** to prepare LDA. Ethyl isobutyrate (0.35 g,

3.0 mmol) was added to the LDA at -78 °C under high vacuum. Hexahydro-1,3,5-triphenyl-1,3,5-triazine (500 mg, 1.6 mmol) was gradually pyrolyzed under high vacuum at 300 °C with a Shimadzu SARF-30K electric furnace to prepare MeAn. The formed MeAn was introduced to the reaction mixture in trap **B** at -78 °C. Then trap **B** was sealed under high vacuum. After the reaction mixture was maintained at -40 °C for 4 h, it was warmed to 25 °C. Trap **B** was opened, and the reaction mixture was poured into a saturated aqueous solution of sodium chloride (5 mL) to terminate the reaction. The product was extracted with ethyl acetate (3 x 15 mL). The combined solution in ethyl acetate was washed with water (5 mL) and dried with anhydrous sodium sulfate. After evaporation of the ethyl acetate, the product was purified by column chromatography by using THF-hexane (1:20) as an eluent: yield 20 mg, 3.8 %; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.41 (s, 6H), 3.41 (s, 2H), 7.29 (m, 5H); EI-MS [M^+] Calcd. 175. Found 175.

Polymerization of MeAn with 1,1'-Azobis(1-cyclohexane nitrile) in DMSO. Hexahydro-1,3,5-triphenyl-1,3,5-triazine (65 mg, 0.21 mmol), 1,1'-azobis(1-cyclohexane nitrile) (15 mg, 0.067 mmol), and DMSO (5 mL) were placed in an ampule. The ampule was connected to a high-vacuum system, outgassed by three freeze-pump-thaw cycles with an oil rotary pump and by three freeze-pump-thaw cycles with an oil diffusion pump, and then sealed under high vacuum. The ampule was maintained at 100 °C. After 24 h, the ampule was opened and gel permeation chromatography (GPC) and NMR analyses were performed for the polymerization system.

Polymerization of MeAn in THF. A typical polymerization of MeAn in THF is described below.

The apparatus shown in Figure 1 (b) was used for the polymerization of MeAn. A solution of *n*-BuLi in *n*-hexane (1.6 M, 0.05 mL, 0.8 mmol) was placed in trap **B** by breaking break-seal **C**, and then the solvent was evaporated under high vacuum.

Hexahydro-1,3,5-triphenyl-1,3,5-triazine (500 mg, 1.6 mmol) placed in ampule **A** was gradually pyrolyzed under high vacuum at 300 °C with a Shimadzu SARF-30K electric furnace to prepare MeAn. The formed MeAn was condensed in trap **B** with liquid nitrogen. After THF (1 mL) was distilled into trap **B** under high vacuum, trap **B** was sealed under high vacuum. The reaction mixture was warmed to -78 °C in order to be made homogeneous, and then the sealed trap was maintained at 25 °C for 24 h. After the trap was opened, the solidified polymerization system was washed with THF (2 x 20 mL) and toluene (2 x 20 mL), and dried *in vacuo* to obtain polymer as a colorless powder. The polymer was insoluble in THF, toluene, diethyl ether, *N*-methylpyrrolidone, chroloform, methanol, ethanol, *n*-hexane, 1,4-dioxane, benzene, dimethylsulfoxide, and *N*,*N*-dimethylformamide: the soluble fraction was also dried *in vacuo* after evaporation of the solvents. Insoluble fraction: yield 278 mg, 86.9 %; IR (KBr) 1595 (aromatic C=C), 1490 (aromatic C=C), 1160 (C-N), 750 (aromatic CH), 690 (aromatic CH) cm^{-1}. Anal. Calcd for $(C_7H_7N)_n$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.69; H, 6.67; N, 13.27. Soluble fraction: yield 42 mg, 13.1 %; IR (KBr) 1600 (aromatic C=C), 1490 (aromatic C=C), 1140 (C-N), 750 (aromatic CH), 690 (aromatic CH) cm^{-1}. FAB-MS Found 610.5, 701.6.

Measurements. ^1H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270 spectrometer using THF-d_8, DMSO-d_6, toluene-d_8 or $CDCl_3$ as a solvent. GPC analyses were performed in THF with a TOSOH CCP & 8010 system by using TSK columns at 40 °C. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. The molecular weights were calibrated by polystyrene standards (TOSOH TSK POLYSTYRENE standard). Infrared (IR) spectra were recorded on a JASCO FT/IR-3 spectrometer. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron impact (EI) or the fast atom bombardment (FAB) method. Mass number was calibrated by using cesium iodide (CsI). In the FAB-mass measurements, 2-nitrobenzyl alcohol was used as a matrix.

Results and Discussion

Preparation and Characterization of MeAn. Kamachi *et al.*[8,9] found that formaldehyde azine, which had been considered to be unstable in its liquid phase, was stable in THF under water-free conditions. According to the procedure of Kamachi *et al.*,[8,9] we focused on the storage of MeAn as solution. In order to confirm the existence of MeAn in solution, NMR measurements were carried out by using THF-d_8 as a solvent. Hexahydro-1,3,5-triphenyl-1,3,5-triazine, the cyclic trimer of MeAn, was pyrolyzed to form MeAn, which was collected in an NMR tube with liquid nitrogen. After THF-d_8 dried with sodium was distilled into the NMR tube, the NMR tube was sealed under high vacuum.

The 270 MHz ^{1}H NMR spectrum of MeAn is shown in Figure 2. In the spectrum, the AB type of absorption bands assignable to the methylene protons of the CH_2=N are observed at 7.31 and 7.57 ppm.[24] The ratio of the integrals of the signals is consistent with the structure of MeAn. Furthermore, the additional peak observed at 4.90 ppm is assignable to the methylene protons of the cyclic trimer of MeAn by the comparison with the spectrum of an authentic sample. The result shows that MeAn exists in THF-d_8 at -80 °C.

The ^{13}C NMR spectrum of MeAn is shown in Figure 3. The absorption bands due to the *meta*-, *para*-, *ortho*-, *ipso*-, and methylene-carbons are observed at 121.3, 127.0, 129.9, 153.9, and 154.9 ppm, respectively.[24] The result also shows that MeAn exists in THF at -80 °C.

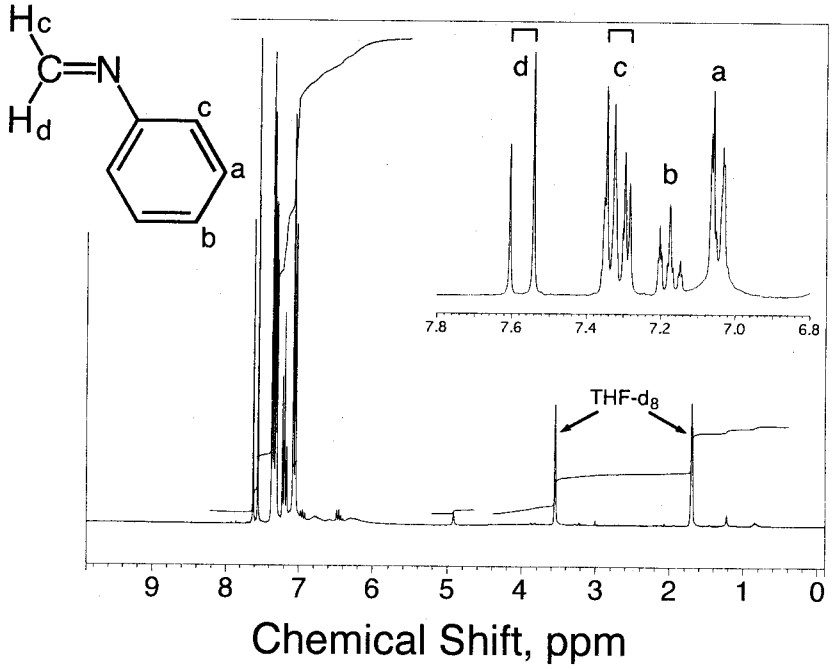


Figure 2. 270 MHz ^{1}H NMR spectrum of MeAn (THF-d_8).

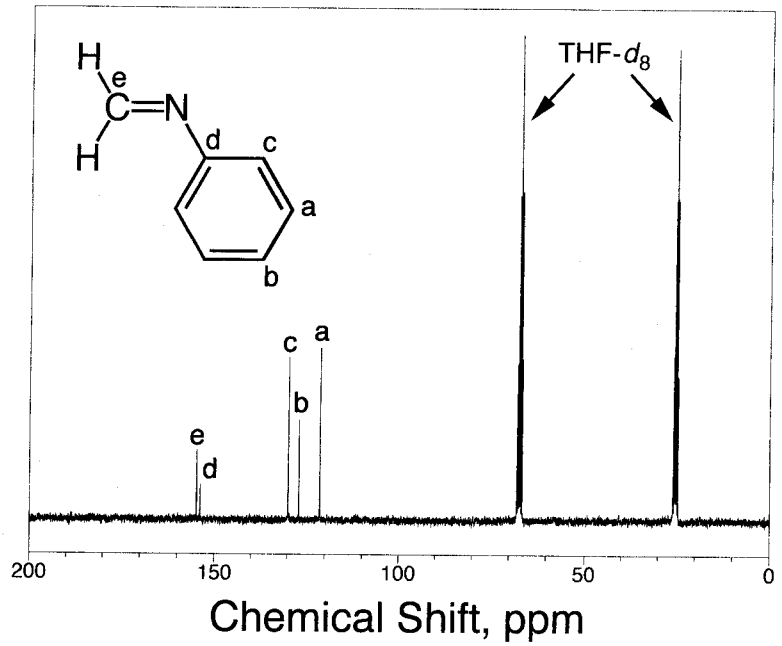


Figure 3. 67.8 MHz ^{13}C NMR spectrum of MeAn (THF-d_8).

Stability of MeAn in Solution. In order to investigate the stability of MeAn in THF, ^{1}H NMR spectra of MeAn were measured by using THF-d_8 as a solvent at -80, -40, -20, 0, and 30 °C. Figure 4 shows the plots of the concentration of MeAn, estimated from the ratio of the integrals of the signals of the methylene of MeAn and the solvent in ^{1}H NMR spectra, versus time. The solid line represents the temperatures at which the NMR spectra were measured. Figure 4 shows that the concentration of MeAn does not decrease at lower temperature up to -40 °C. The result suggests that MeAn is stable in THF-d_8 up to -40 °C. In non-ideal cases (Figure 4 (a)), the signals due to MeAn nearly disappeared above -40 °C, and the ^{1}H NMR spectra showed the formation of the cyclic trimer. In ideal cases (Figure 4 (b)), however, MeAn existed in THF even at 30 °C, although the concentration of MeAn was relative low (~ 100 mM).

Furthermore, in the ideal cases, MeAn did not completely disappear upon opening the NMR tube and upon the addition of ethanol. However, MeAn was immediately converted to the cyclic trimer upon the addition of acetic acid. These results suggest that a small amount of acid formed by pyrolysis causes the cyclic trimerization of MeAn which has long been reported.

In order to confirm this proposition, the NMR measurements were carried out by using THF-d_8 as a solvent in the presence of triethylamine (Figure 4 (c)). Although the cyclic trimerization of MeAn took place at -20 °C, MeAn existed in the concentration of *ca.* 100 mM in THF-d_8 even at 30 °C. Furthermore, MeAn was unstable in THF-d_8 even at -78 °C in the presence of acetic acid. These results support the proposition that a small amount of the acid formed by pyrolysis causes the cyclic trimerization.

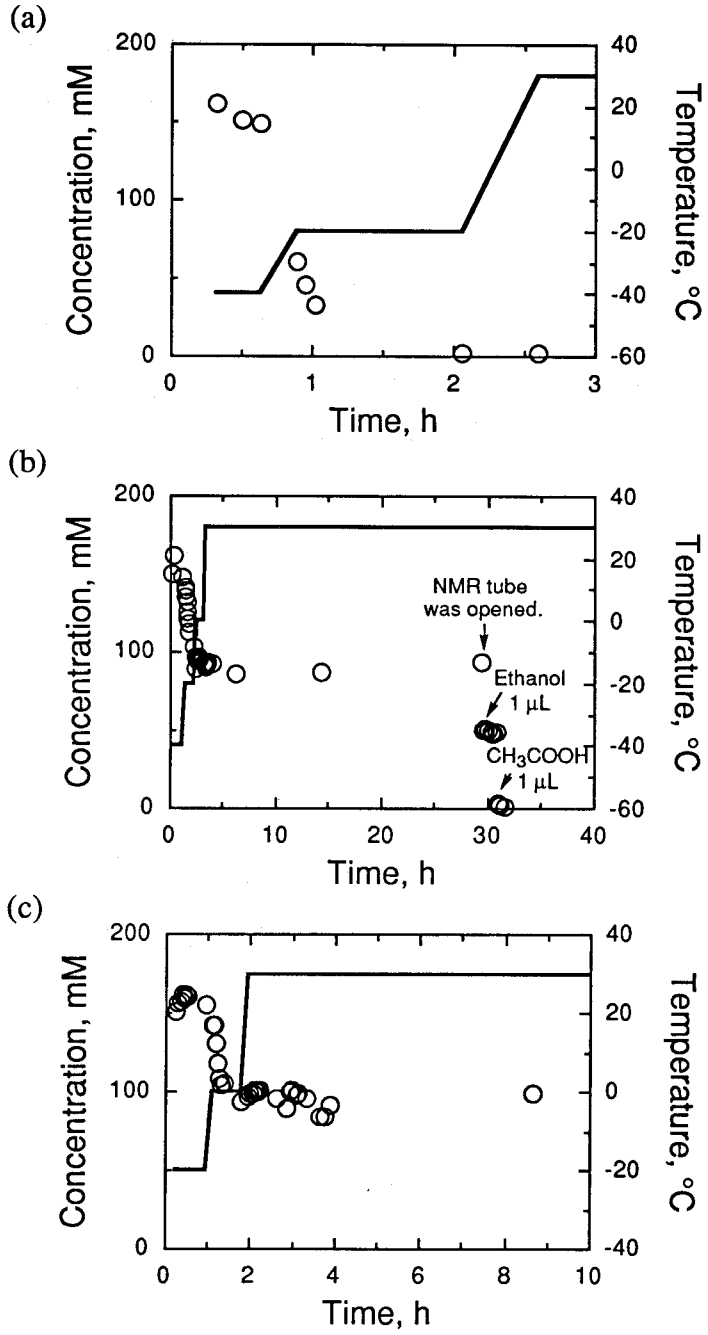
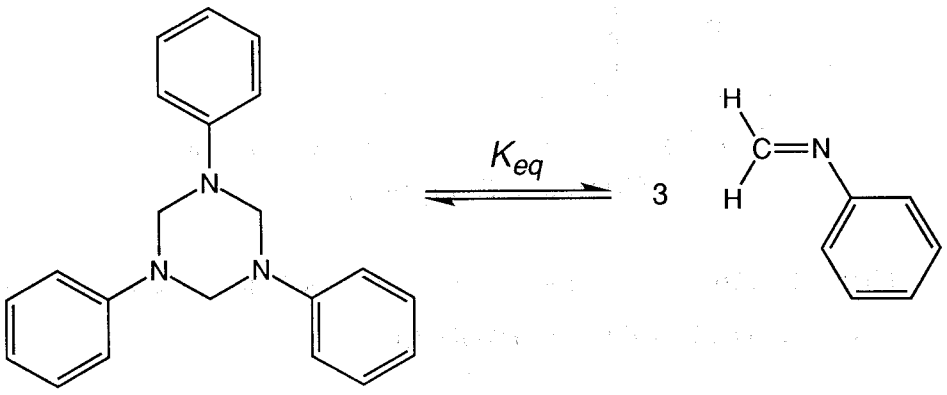


Figure 4. The plots of the concentration of MeAn in THF-d_8 versus time. (a) Non-ideal case. (b) Ideal case. (c) In the presence of triethylamine. (Solid lines represent the temperatures on measurement.)

In addition, ^{1}H NMR measurements were carried out by using toluene-d_8 as a solvent in order to investigate the stability of MeAn in toluene. In this case, the concentration of MeAn could not be determined because strong absorption bands due to the solvent were observed around 7.0 ppm. In the spectrum obtained at -80 °C, however, the absorption bands due to the methylene protons of the cyclic trimer were hardly observed around 5.0 ppm, suggesting that MeAn exists in toluene-d_8 at -80 °C.

Observation of Equilibrium between MeAn and the Cyclic Trimer of MeAn in DMSO-d_6. Figure 5 shows 270 MHz ^{1}H NMR spectra of the cyclic trimer obtained in DMSO-d_6 at 30, 120, and 150 °C. In the spectrum obtained at 30 °C, the absorption bands due to the methylene and phenyl protons are observed at 4.90 and 6.9-7.3 ppm, respectively.[24] This spectrum is ascribed to the cyclic trimer of MeAn. In the spectra at 120 and 150 °C, the absorption bands due to the proton of the methylene of the C=N double bond are observed at 7.57 ppm.[24] The result shows that MeAn exists in DMSO-d_6 at 120 and 150 °C. The intensity of the peak at 7.57 ppm decreased with decreasing the temperature of the measurements. These results show that there is an equilibrium between the monomer and the cyclic trimer of MeAn in DMSO-d_6 (Scheme 1). In addition, the absorption band due to the proton of the methylene of the C=N double bond was not observed in toluene-d_8 at 100 °C, suggesting that a polar solvent is required for the equilibrium.

Scheme 1. Equilibrium between the Monomer and the Cyclic Trimer of MeAn



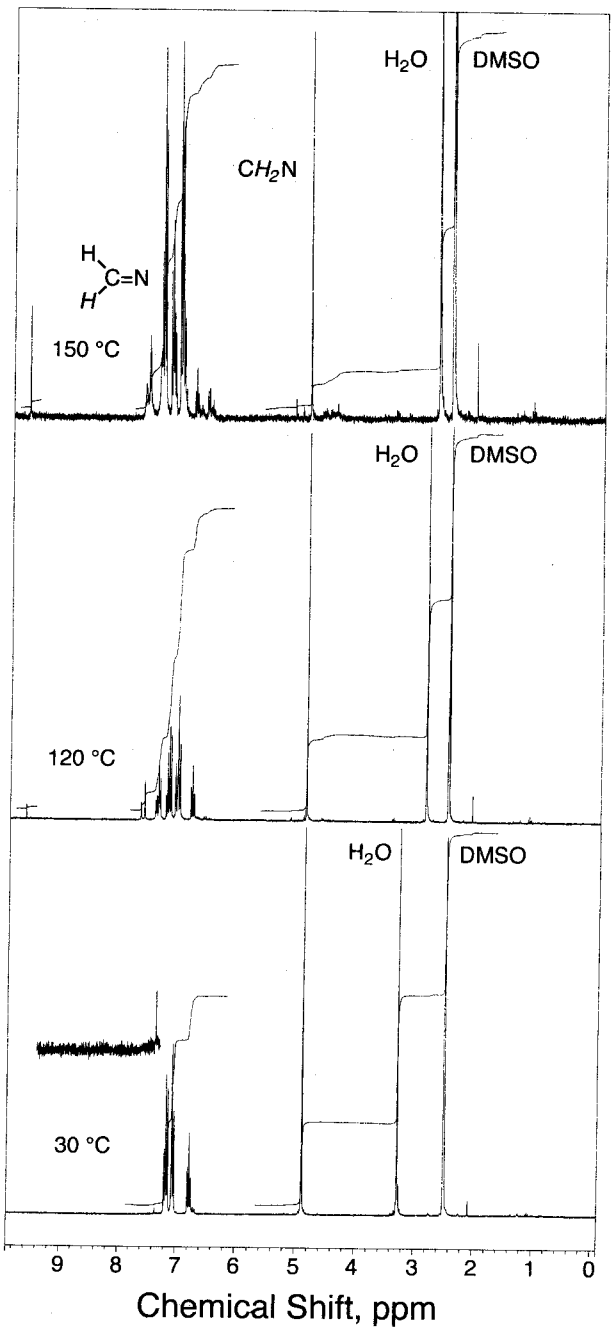


Figure 5. 270 MHz ^{1}H NMR spectra of the cyclic trimer of MeAn observed at 30, 120, and 150 °C (DMSO-d_6).

In these cases, the equilibrium constant (K_{eq}) is obtained as

$$K_{eq} = \frac{[M]^3}{[CT]}$$

where [M] and [CT] are the concentrations of the monomer and the cyclic trimer, respectively. The epuilibrium constants obtained at 100, 120, and 150 °C are listed in Table 1.

The plots of the natural logarithm of the equilibrium constant (ln K_{eq}) versus the reciprocal of the temperature ($1/T$) yielded a linear relationship as shown in Figure 6. Thus, lnK_{eq} follows

$$\ln K_{eq} = -\frac{E_{eq}}{RT} + C$$

where E_{eq} is the enthalpy of the equilibrium, T is the temperature in Kelvin, R is the gas constant, and C is a constant. From the slope of the line shown in Figure 6, the E_{eq} value was estimated to be +35 kcal/mol.

Table 1. Equilibrium Constants (K_{eq}'s) between the Monomer and the Cyclic Trimer of MeAn

temperature, °C	K_{eq}, M^2
100[a]	6.3×10^{-6}
120[a]	8.4×10^{-5}
150	1.7×10^{-3}
120[b]	6.4×10^{-5}
100[b]	6.4×10^{-6}

[a] Temperature increased. [b] Temperature decreased.

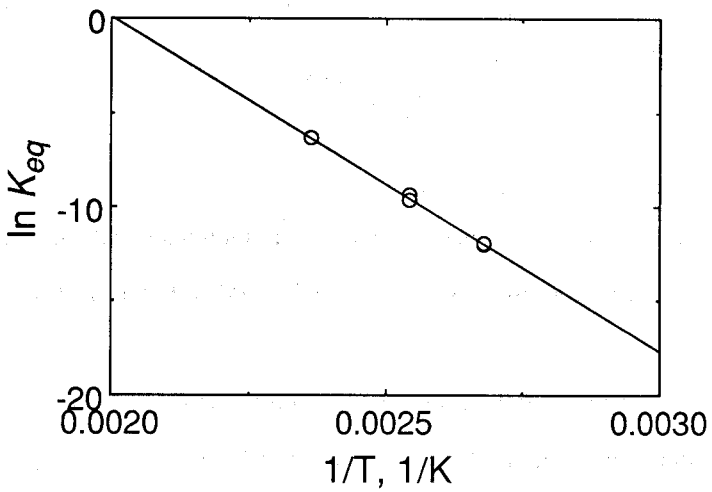


Figure 6. Plots of ln K_{eq} versus $1/T$.

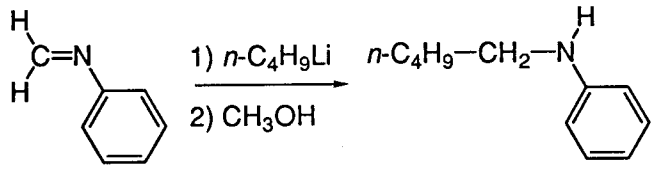
Reactions of MeAn. Since MeAn was confirmed to be stable in THF below -40 °C, the reactivity of MeAn was investigated.

(a) Reaction of MeAn with *n*-BuLi. The reaction of MeAn with *n*-BuLi was performed under high vacuum at -78 °C. After terminating the reaction with methanol and removing the formed lithium salts with water, a pale yellow oil was obtained.

The structure of the oily product was investigated by ^{1}H and ^{13}C NMR and IR spectroscopies. In the ^{1}H NMR spectrum of the product, the absorption bands due to the protons of the *n*-pentyl group were observed at 0.96, 1.40, 1.65, and 3.12 ppm. In addition, the relatively broad absorption band due to the proton of the N-H is observed around 3.61 ppm.[24] The results suggest that the obtained product is *N*-pentylaniline. In the ^{13}C NMR spectrum of the product, the absorption bands due to the five kinds of carbons of the *n*-pentyl group were observed at 14.0, 22.5, 29.2, 29.3, and 43.9 ppm.[24] Furthermore, the absorption bands due to the four kinds of the carbons of the phenyl group were observed at 112.7, 117.0, 129.1, and 148.5 ppm.[24] The ^{13}C NMR spectrum supports the proposition that the product is *N*-pentylaniline. The IR spectrum of the product showed the absorption band due to the stretching

vibration of the N-H bond at *ca.* 3400 cm^{-1}.[25] These results led us to conclude that *n*-BuLi attacks the carbon of the C=N double bond of MeAn.

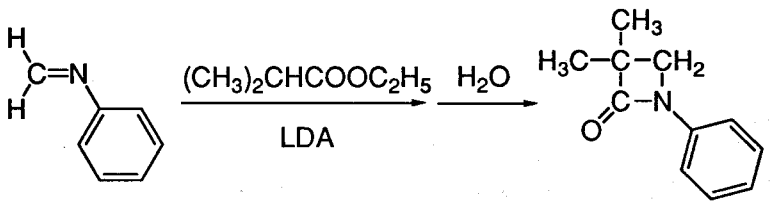
Scheme 2. Reaction of MeAn with *n*-BuLi



(b) Reaction of MeAn with Ethyl Isobutyrate in the Presence of LDA. In 1995, Shimizu *et al.*[26] reported the formation of β-lactams from *N*-benzylideneaniline or its derivatives with some isobutyrates in the presence of LDA. Therefore, we prompted to prepare β-lactam from MeAn and ethyl isobutyrate in the presence of LDA.

The product was isolated by column chromatography by using THF-hexane (1:20) as an eluent. The structure of the product was investigated by ^{1}H NMR and EI-mass spectroscopies. In the ^{1}H NMR spectrum of the product, the absorption bands assignable to the methyl, methylene, and phenyl protons are observed at 1.41, 3.41, and 7.29 ppm, respectively.[24] The integrals of the bands due to the methyl, methylene, and phenyl protons are 6H, 2H, and 5H, respectively. The EI-mass spectrum of the product showed a signal at m/z = 175 as a molecular ion peak. From these results, it can be concluded that the product is a β-lactam, 3,3-dimethyl-1-phenyl-2-azetidinone (Scheme 3).

Scheme 3. Reaction of MeAn with Ethyl Isobutyrate in the Presence of LDA



Polymerizability of MeAn. It was shown that MeAn existed in DMSO-d_6 at high temperatures (100-150 °C). Thus, the polymerization of MeAn was attempted with a radical initiator in DMSO at 100 °C. After a solution of the cyclic trimer in DMSO containing 1,1'-azobis(1-cyclohexane nitrile) was maintained at 100 °C for 24 h, the cyclic trimer was quantitatively recovered. The result suggests that MeAn could not be polymerized under this condition.

It was suggested that MeAn exists in toluene-d_8 at -80 °C, as described earlier. Therefore, the polymerizations of MeAn were attempted in toluene. When the polymerization was carried out in toluene by using titanium tetrachloride or tin tetrachloride as a initiator, oligomers were obtained. However, the structures of the oligomers were unclear, because the polymerization system was complicated. Judging from the polymerization of 2,6-diisopropyl-*N*-methyleneaniline,[27] aromatic electrophilic substitution may take place at the phenyl group of MeAn.

The storage of MeAn in THF without cyclic trimerization was successful. Thus, the polymerizations of MeAn were carried out in THF with several kinds of initiators. When *n*-BuMgCl was used as a initiator, the cyclic trimer was obtained in a high yield (~ 80 %). The results of the polymerization of MeAn in THF by the other initiators are listed in Table 2. In each case, THF-insoluble fraction was obtained in a high yield. Since the cyclic trimer was soluble in THF, the THF-insoluble fraction might be polymer of MeAn.

Table 2. Polymerization of MeAn[a]

MeAn, mg (mmol)	initiator	mol%	THF, mL (M)	polymer yield,[b] %
213 (2.0)	-[c]	-	1.0 (2.0)	81.2
237 (2.3)	CH_3COOH	3.9	1.0 (2.3)	89.0
320 (3.0)	*n*-BuLi	2.6	1.0 (3.0)	86.9

[a] At 20 °C under high vacuum for 24 h. [b] THF-insoluble fraction.

[c] Without initiator.

However, the molecular weight has not been determined, since the THF-insoluble fraction was insoluble in most organic solvents (Experimental Section). Since the THF-soluble fraction was found to contain heptamer by FAB-mass spectroscopy, the THF-insoluble fraction should be polymers with molecular weights higher than heptamer. These results suggest that MeAn is polymerized by cationic or anionic initiators. Furthermore, the polymer was obtained in the absence of initiator. This polymerization is considered to be due to a small amount of acid formed by pyrolysis of the cyclic trimer during the monomer formation.

The melting points of the polymers were measured. The polymer obtained by *n*-BuLi was gradually decomposed from *ca.* 150 °C, and the melting point of the polymer was not observed. On the other hand, the polymers obtained by the acids melted at 142-145 °C. These results suggest that the molecular weight of the polymer obtained by *n*-BuLi is much higher than those of the polymers obtained by the acids.

In addition, when the polymerizations of MeAn were carried out in dilute solutions (0.16-0.29 M), the yield of the polymer is much lower (~ 30 %) than those shown in Table 2. The results suggest that a high concentration of MeAn (2.0-3.0 M) is required for a high yield of the polymer.

Structure of the Polymer. The C, H, and N contents of the polymer agreed with those of MeAn (Experimental Section). This result shows that the polymer was formed by addition polymerization.

The IR spectra of the cyclic trimer and the polymer produced by *n*-BuLi are shown in Figure 7. In the IR spectrum of the polymer, the absorption bands due to the out-of-plane deformation of the mono-substituted benzene are observed at 750 and 690 cm^{-1}.[25] The result suggests that substitution did not take place during the polymerization. In the spectrum of the cyclic trimer, the absorption bands due to the stretching vibration of the C-N bond are observed at 1160 cm^{-1}, while the corresponding absorption band is observed at lower wave numbers (1140 cm^{-1}) in the spectrum of the polymer.[25] The result shows that the strain of the C-N bonds of the

polymer is lower than that of the cyclic trimer,[28] which suggests that the polymer is linear as shown in Scheme 4. In addition, the IR spectrum of the polymer produced by acetic acids was almost the same as that of the polymer obtained by *n*-BuLi, suggesting that this polymer is also linear.

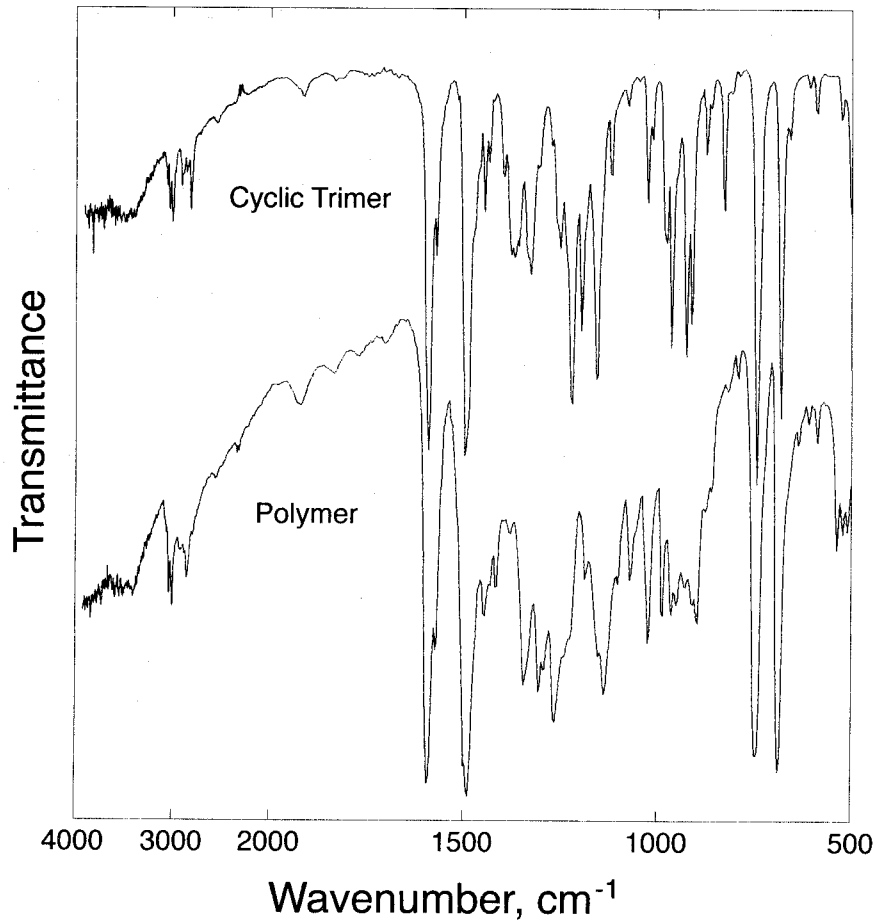
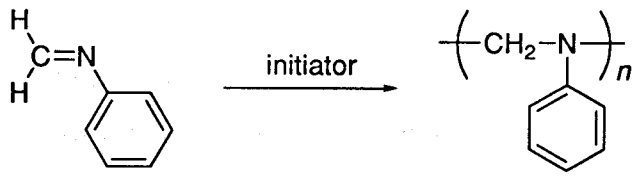


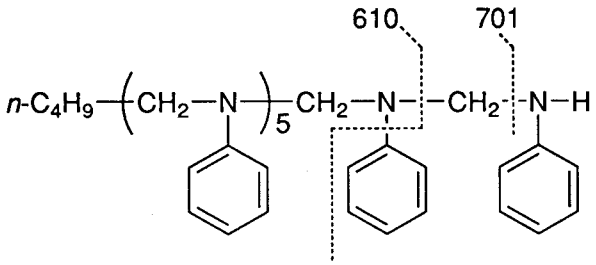
Figure 7. IR spectra of the cyclic trimer and the polymer (KBr).

Scheme 4. Polymerization of MeAn



Since the polymer is insoluble in organic solvents (Experimental Section), soluble oligomers were isolated from the polymerization system by using *n*-BuLi as an initiator in order to obtain further information on the structure of the polymer. The structure of the soluble oligomer was investigated by IR and FAB-mass spectroscopies. The IR spectrum of the soluble oligomer was similar to those of the polymers, suggesting that the oligomer is also linear as shown in Scheme 4. In the FAB-mass spectrum of the soluble oligomer, the peaks observed at m/z = 610.5 and 701.6 were assignable to the fragment ion peaks of the hexamer and the heptamer with an *n*-butyl group at the chain end (Scheme 5). These results show that the soluble oligomer was formed by addition polymerization initiated by *n*-BuLi. Furthermore, the results suggest that the insoluble polymer should have a higher molecular weight than the heptamer (MW = 792) in this polymerization.

Scheme 5. Structure of the Soluble Oligomer



Conclusion

MeAn was prepared by the pyrolysis of the cyclic trimer of MeAn, hexahydro-1,3,5-triphenyl-1,3,5-triazine. MeAn was found to be completely stable in THF below -40 °C. Furthermore, MeAn was also found to be stable in dilute solution in THF even at 30 °C under acid-free conditions. It was suggested that a small amount of the acid formed by pyrolysis caused the cyclic trimerization of MeAn. In addition, the equilibrium between MeAn and the cyclic trimer of MeAn was observed in DMSO-d_6.

A few direct reactions of MeAn were carried out. *N*-Pentylanililne was obtained by the reaction of MeAn with *n*-BuLi. Furthermore, 3,3-dimethyl-1-phenyl-2-azetidinone was formed by the reaction of MeAn with ethyl isobutyrate in the presence of LDA.

The polymerizability of MeAn was also investigated. Polymer was obtained by the polymerization of MeAn with acetic acid or *n*-BuLi in THF. The polymer was insoluble in many organic solvents. The structure of the polymer was investigated by IR spectroscopy. The result suggests that the polymer is linear. Soluble linear oligomer was isolated from the polymerization system by using *n*-BuLi as an initiator. The structure of the soluble oligomer was investigated by IR and FAB-mass spectroscopies. These results show that the soluble oligomer is formed by the addition polymerization of MeAn by *n*-BuLi. Since the soluble oligomer was considered to contain heptamer (MW = 792), the insoluble polymer should have a higher molecular weight than heptamer.

References

(1) Robinson, G. C. *J. Polym. Sci., Polym. Chem. Ed.* **1964**, *2*, 3901.

(2) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520.

(3) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159.

(4) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(5) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436.

(6) Hall, H. K., Jr. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(7) Neureiter, N. P. *J. Am. Chem. Soc.* **1959**, *81*, 2910.

(8) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(9) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(10) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232.

(11) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(12) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(13) Harada, A.; Fujii, F.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(14) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931.

(15) Kamachi, M.; Kajiwara, A.; Hashidzume, A. to be published.

(16) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(17) For example: Bailey, W. J.; Hartz, R. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9*, 404.

(18) Distefano, G.; Giumanini, A. G.; Modelli, A.; Poggi, G. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1623.

(19) For example: (a) Miller, J. G.; Wagner, E. C. *J. Am. Chem. Soc.* **1932**, *54*, 3698; (b) Scheele, W.; Steike, L. *Kolloid-Z.* **1941**, *97*, 176.

(20) (a) Ha, H.-J.; Ahn, Y.-G. *Synth. Commun.* **1991**, *21*, 155. (b) Ha, H.-J.; Ahn, Y.-G. *Synth. Commun.* **1995**, *25*, 969. (c) Ha, H.-J.; Ahn, Y.-G.; Choi, J.-K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2631.

(21) Ikeda, K.; Achiwa, K.; Sekiya, M. *Tetrahedron Lett.* **1983**, *24*, 913.

(22) Overman, L. E.; Burk, R. M. *Tetrahedron Lett.* **1984**, *25*, 1635.

(23) Gulman, H.; Houbein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.

(24) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon: Oxford, 1966; Vol. 2.

(25) Socrates, G. "Infrared Characteristic Group Frequencies"; John Wiley: Chichester, 1994.

(26) Shimizu, M.; Teramoto, Y.; Fujisawa, T. *Tetrahedron Lett.* **1995**, *36*, 729.

(27) Hashidzume, A; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromol. Rapid Commun.* **1996**, *17*, 529.

(28) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; John Wiley: New York, 1958.

Chapter 7

Homo- and Co-polymerization of an Azastyrene Derivative, 2,6-Diisopropyl-*N*-methyleneaniline

Introduction

Although many literatures have focused on the polymer formation from compounds containing C=C or C=O double bonds, there are few papers on the polymerization through the C=N double bonds.[1-7] Thus, Kamachi *et al.*[8-16] have first investigated the polymerizability of azine compounds, and synthesized *trans*-1,4-polymers from alkanal azine compounds (RCH=N-N=CHR, R=CH_3, C_2H_5, *n*-C_3H_7)[13-15] and a 1,2-polymer from trifluoroacetaldehyde azine (R=CF_3).[16]

Recently, in the extension of this research, we have also focused on *N*-methyleneaniline (CH_2=NC_6H_5). Since *N*-methyleneaniline is a styrene-analogue containing a C=N double bond, the polymerization of this compound has long been attracted interests of polymer chemists.[17] Although *N*-methyleneaniline is known to be stable in the gas phase,[18] it has been reported that *N*-methyleneaniline is so unstable as to be immediately converted to a cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine, in the liquid phase.[19]

In 1985, Verardo *et al.*[20,21] reported a stable monomeric azastyrene derivative, 2,6-diisopropyl-*N*-methyleneaniline (DiPMAn), whose isopropyl groups retarded the cyclic trimerization. To our knowledge, however, no paper reported the polymerizability of this azastyrene derivative. Therefore, the polymerizability of DiPMAn was investigated, and it was found that poly(DiPMAn) was obtained by cationic initiators, such as trifluoroacetic acid (TFA), $TiCl_4$-TFA, and $SnCl_4$-TFA.

Furthermore, since DiPMAn should be an electron-donating monomer,[18] spontaneous alternating copolymerization is reasonably considered to take place upon the addition of an electron-withdrawing monomer to DiPMAn. Therefore, the

copolymerizability of DiPMAn with maleic anhydride (MAnh) was investigated, and copolymer was prepared.

In this chapter, the homo- and co-polymerizability of DiPMAn and the structures of the obtained homo- and co-polymers will be described.

Experimental Section

Materials. DiPMAn was prepared from 2,6-diisopropylaniline and paraformaldehyde according to the method of Verardo *et al.*[20] DiPMAn was purified by successive distillations under reduced pressure over calcium hydride and stored under an argon atmosphere. The purity of DiPMAn was checked by gas chromatography (GC) and ^{1}H NMR spectroscopy.

Chloroform, dichloromethane, and 1,2-dichloroethane were distilled under reduced pressure over calcium hydride and stored under an argon atmosphere. Tetrahydrofuran (THF), 1,4-dioxane, and toluene were purified by distillation over sodium-benzophenone ketyl under an argon atmosphere. MAnh was recrystallized in chloroform. Other reagents were used without further purification.

Initiators. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol solution and dried *in vacuo*. Commercially available *n*-butyllithium (*n*-BuLi) (1.6 M *n*-hexane solution) was transferred to an ampule via a syringe under an argon atmosphere. The concentration was determined by double titration.[22] Commercially available trifluoroacetic acid (TFA), titanium tetrachloride ($TiCl_4$) (1.0 M dichloromethane solution), and tin tetrachloride ($SnCl_4$) (1.0 M *n*-pentane solution) were used without further purification.

Homopolymerization of DiPMAn with AIBN. DiPMAn (0.95 mL, 5.0 mmol) and a solution of AIBN in THF (0.1 M, 5.0 mL, 2.0 mol%) were placed in an ampule. The ampule was connected to a high-vacuum system, outgassed by three

freeze-pump-thaw cycles with an oil rotary pump and by three freeze-pump-thaw cycles with an oil diffusion pump, and then sealed under high vacuum. The ampule was immersed in an oil-bath, whose temperature was maintained at 80 °C. After 40 h, the ampule was opened and gel permeation chromatography (GPC) analysis was performed on the polymerization mixture.

Homopolymerization of DiPMAn with *n*-BuLi. A solution of *n*-BuLi in *n*-hexane (1.6 M, 0.1 mL, 2.9 mol%) was added to DiPMAn (1 mL, 5.3 mmol) in a flask fitted with a three-way stop cock under an argon atmosphere at *ca.* 30 °C. After 12 h, methanol (5 mL) was poured into the flask to terminate the polymerization. After evaporation of volatile fractions, a residue was obtained. GPC analysis was performed on the residue.

Homopolymerizations of DiPMAn with Cationic Initiators. A typical polymerization of DiPMAn is described below.

Trifluoroacetic acid (10 μL, 0.13 mmol) was added to a solution of DiPMAn (1.5 mL, 7.9 mmol) in 1,2-dichloroethane (2.5 mL) under an argon atmosphere at 80 °C. At intervals, small parts of the reaction mixture were withdrawn for GPC analyses to determine the conversion of the polymerization and to estimate the molecular weight of the polymer. After 150 h, the solvent was evaporated under reduced pressure and an red-brown residue was obtained. After washing the residue with methanol, poly(DiPMAn) was obtained as yellow powder: yield 250 mg, 10.0 %; mp 250-270 °C (dec.); IR (KBr) 3420 (NH), 1620 (aromatic C=C), 880 (out-of-plane deformation) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.6-1.4 (6H, CH_3), 2.5-3.2 (2H, CH), 3.2-4.0 (CH_2N), 4.0-4.4 (NH), 6.5-7.2 (3H, phenyl). Anal. Calcd for $(C_{13}H_{19}N)_n$: C, 82.48; H, 10.12; N, 7.40. Found: C, 81.93; H, 10.13; N, 7.24.

Copolymerization of DiPMAn and MAnh. A typical copolymerization of DiPMAn and MAnh is described below.

MAnh (98 mg, 1.0 mmol) and 1,4-dioxane (0.5 mL) were placed in an ampule under an argon atmosphere. When DiPMAn (0.19 mL, 1.0 mmol) was added to the solution of MAnh in 1,4-dioxane, the reaction mixture changed from colorless to pale yellow. Then the ampule was sealed under an argon atmosphere. The sealed ampule was immersed in an oil-bath whose temperature was maintained at 80 °C. After 24 h, the ampule was opened and *n*-hexane (5 mL) was poured into the ampule to form precipitate. The precipitate was separated from the solution by centrifugation. Copolymer was obtained as colorless powder by reprecipitation in THF-hexane (1:10): yield 257 mg, 89.5 %; mp 160-165 °C; IR (KBr) 1730 (ester C=O), 1670 (amide C=O), 1155 (ester C-O-C), 950 (ester C-O-C), 810 (out-of-plane C-H), 750 (out-of-plane C-H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0-1.4 (6H, CH_3), 2.9-3.1 (2H, CH), 5.5-5.8 (2H, $COOCH_2NCO$), 5.8-6.3 (2H, CH=CH), 7.1-7.5 (3H, phenyl). Anal. Calcd for $(C_{17}H_{21}NO_3)_n$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.46; H, 7.51; N, 4.59.

Preparation of the Compound Derived from the Adduct of DiPMAn with MAnh. MAnh (981 mg, 10 mmol) was placed in an ampule under an argon atmosphere. DiPMAn (1.9 mL, 10 mmol) was added to the MAnh. Then the ampule was sealed under an argon atmosphere. The sealed ampule was immersed in an oil-bath whose temperature was maintained at 80 °C. After 24 h, the ampule was opened and the reaction mixture was dissolved in THF (10 mL). The THF-solution was poured into *n*-hexane (100 mL) to form precipitate. The solution was separated from the precipitate by centrifugation. After evaporation of the solvents, pale yellow powder was obtained. Colorless crystals were obtained by recrystallization in THF-hexane: yield: 49 mg, 1.8 %; mp 183-184 °C; IR (KBr) 3400 (OH), 3200 (NH), 1700 (C=O), 1630 (aromatic C=C), 790 (out-of-plane C-H), 740 (out-of-plane C-H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (d, 6H, CH_3), 3.0 (m, 2H, CH), 6.4 (d, 1H, CH=), 6.7 (d, 1H,

CH=), 7.2-7.4 (m, 3H, phenyl), 8.5 (s, 1H, NH), 15.8 (s, 1H, COOH). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.72; H, 7.68; N, 5.06. EI-MS [M^+] Calcd 275. Found 275.

Preparation of the Compound Derived from the Adduct of DiPMAn with MAnh in the Presence of Water. DiPMAn (1.9 mL, 10 mmol) was added to the solution of MAnh (981 mg, 10 mmol) in 1,4-dioxane under an argon atmosphere. The reaction mixture was maintained at 80 °C. After 8 h, water (10 mL, 0.56 mol) was added to the reaction mixture. Then the reaction mixture was maintained at 80 °C for 16 h. After evaporation of the solvents, a red-brown residue was obtained. The residue was dissolved in THF (10 mL). The THF-solution was poured into *n*-hexane (100 mL) to form precipitate. The solution was separated from the precipitate by filtration. After evaporation of the solvents, pale yellow powder was obtained. Colorless crystals were obtained by recrystallization in THF-hexane: yield 320 mg, 11.6 %.

Measurements. Gel permeation chromatography (GPC) analyses were performed in THF with a TOSOH CCP & 8010 system by using TSK columns at 40 °C. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. The molecular weights were calibrated by polystyrene standards (TOSOH TSK POLYSTYRENE standard). Vapor pressure osmometry (VPO) measurements were carried out on a Knauer Vapor Pressure Osmometer No. A0280 by using toluene as a solvent at 60 °C. The molecular weights were calibrated by benzil ($C_6H_5COCOC_6H_5$). Infrared (IR) spectra were recorded on a JASCO FT/IR-3 spectrometer. ^1H and ^{13}C NMR spectra were observed on a JEOL JNM-EX270 spectrometer using $CDCl_3$ as a solvent at 30 °C. Mass spectrum was recorded on a JEOL JMS SX-102 mass spectrometer by the electron impact (EI) method. Mass number was calibrated by using cesium iodide (CsI). GC analyses were performed on a Shimadzu GC-8A gas chromatograph with a silicone (DC550, Gasukuro Kogyo Inc.) column.

Results and Discussion

Search for Initiators for the Homopolymerization of DiPMAn. Results of the polymerization of DiPMAn by radical, anionic, and cationic initiators are shown in Table 1. DiPMAn, similarly to azine compounds, could not be polymerized with 2,2'-azobis(isobutyronitrile) (AIBN).[13-16] Although the reaction mixture changed from colorless to pale yellow upon addition of *n*-butyllithium (*n*-BuLi), no polymer was formed and an adduct, *N*-pentylaniline, was quantitatively obtained. Oligo(DiPMAn) ($\overline{M}_w$ ~ 1000) was obtained in a high yield (84.0 %) by trifluoroacetic acid (TFA). Therefore, the polymerization of DiPMAn was also investigated with other cationic initiators.

Table 1. Homopolymerizations of DiPMAn

DiPMAn, mmol	initiator (mol%)	solvent (M)	temp., °C	time, h	conv.,[a] %	$\overline{M}_w$[a]
5.0	AIBN (2.0)[b]	THF (1.0)	80[c]	40	~0	-
5.3	*n*-BuLi (2.9)[d]	-	30	12	10.2	280
7.9	TFA (1.6)[d]	CH_2Cl_2 (2.0)	30	47	84.0	1000

[a] By GPC. [b] Under high vacuum. [c] Temperature of the oil-bath.

[d] Under an argon atmosphere.

Homopolymerization of DiPMAn by Cationic Initiators. Table 2 shows the results of the polymerizations of DiPMAn with cationic initiators at 25, 50, 80, 100, and 120 °C. The product, which has a higher molecular weight than the monomer, was obtained in each case. In the case of the polymerization by TFA, the polymer of molecular weight higher than 10000 was obtained when the polymerization was carried out under optimum conditions. It was found that the optimum concentration of initiator and monomer and polymerization temperature were 0.14 mol%, 2.0-3.0 M, and 80 °C, respectively.

Table 2. Polymerizations of DiPMAn with Cationic Initiators[a]

DiPMAn, mL (mmol)	initiator	mol%	solvent (M)	temp., ℃	time, h	conv.,[b] %	polymer yield,[c] %	$\overline{M}_{nGPC}$ [b]	$\overline{M}_{nVPO}$ [d]
1.5 (7.9)	TFA	1.6	$CHCl_3$ (2.0)	25	36	71.7	-	1000	-
1.5 (7.9)	TFA	1.6	$CHCl_3$ (2.0)	50	36	83.5	-	1200	-
1.5 (7.9)	TFA	1.6	CH_2ClCH_2Cl (2.0)	80	36	94.0	-	1900	-
2.5 (13.2)	TFA	0.14	CH_2ClCH_2Cl (1.0)	80	168	~ 100	2.4	4600 [c]	-
2.5 (13.2)	TFA	0.14	CH_2ClCH_2Cl (2.0)	80	168	~ 100	10.0	5200 [c]	10600 [c]
2.5 (13.2)	TFA	0.14	CH_2ClCH_2Cl (3.0)	80	168	~ 100	8.8	5100 [c]	12900 [c]
2.5 (13.2)	TFA	0.14	$CH_2ClCH_2CH_2Cl$ (1.0)	100	168	~ 100	-	1300	-
2.5 (13.2)	TFA	0.14	$CH_2ClCH_2CH_2Cl$ (1.0)	120	168	~ 100	-	1500	-
1.5 (7.9)	$TiCl_4$/TFA	1.2/1.6	$CHCl_3$ (2.0)	25	36	90.3	-	1500	-
1.5 (7.9)	$TiCl_4$/TFA	1.2/1.6	$CHCl_3$ (2.0)	50	36	91.7	-	2100	-
1.5 (7.9)	$TiCl_4$/TFA	1.2/1.6	CH_2ClCH_2Cl (2.0)	80	36	94.5	-	1600 [e]	-
2.5 (13.2)	$TiCl_4$/TFA	0.14/0.14	CH_2ClCH_2Cl (2.0)	80	168	~ 100	10.4	3200 [c]	3900 [c]
1.5 (7.9)	$SnCl_4$/TFA	1.2/1.6	$CHCl_3$ (2.0)	25	36	84.1	-	1600	-
1.5 (7.9)	$SnCl_4$/TFA	1.2/1.6	$CHCl_3$ (2.0)	50	36	87.8	-	1800	-
1.5 (7.9)	$SnCl_4$/TFA	1.2/1.6	CH_2ClCH_2Cl (2.0)	80	36	82.5	-	1300	-

[a] Under an argon atmosphere. [b] By GPC. [c] Methanol-insoluble fraction. [d] By VPO. [e] THF-soluble fraction.

In the polymerization by $TiCl_4$-TFA, no polymer whose molecular weight was higher than 10000 was obtained, although the yield of the polymer formed by $TiCl_4$-TFA (10.4 %) was similar to that of TFA (10.0 %).

As an example, Figure 1 shows the time conversion plots for the polymerization of DiPMAn with $TiCl_4$-TFA at 50 °C. The monomer was rapidly consumed in the early stage of the polymerization (4.4 h, 84.1%-conversion).

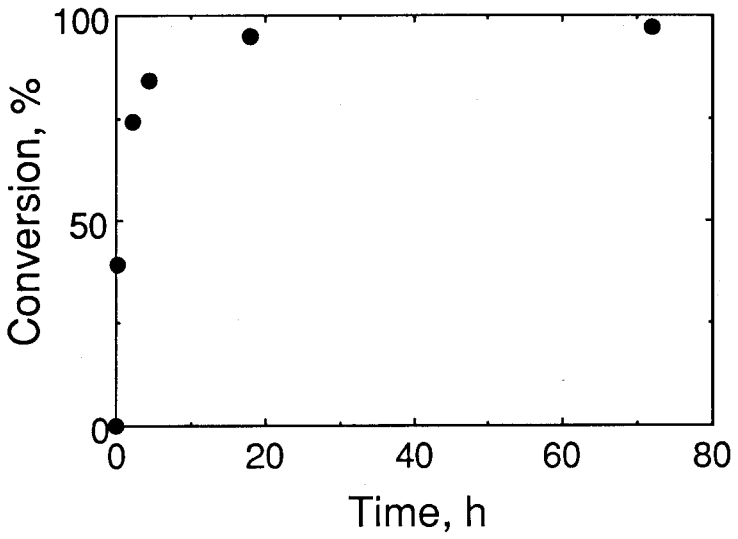


Figure 1. Time conversion of the polymerization of DiPMAn with $TiCl_4$-TFA at 50 °C.

The relationship between the molecular weight of the obtained polymer and the conversion is shown in Table 3. As shown in Figure 2, the molecular weight of the obtained polymer rapidly increases from about 80 %-conversion. These results suggest that poly(DiPMAn) is formed through a step-wise polymerization.

Table 3. Relationship between the Molecular Weights of the Polymers and Conversion for the Polymerization of DiPMAn with $TiCl_4$-TFA at 50 °C

conversion %	$\overline{M}_w$ [a]
0.0	120
39.3	262
74.0	508
84.1	741
94.9	1567
97.3	2261

[a] By GPC.

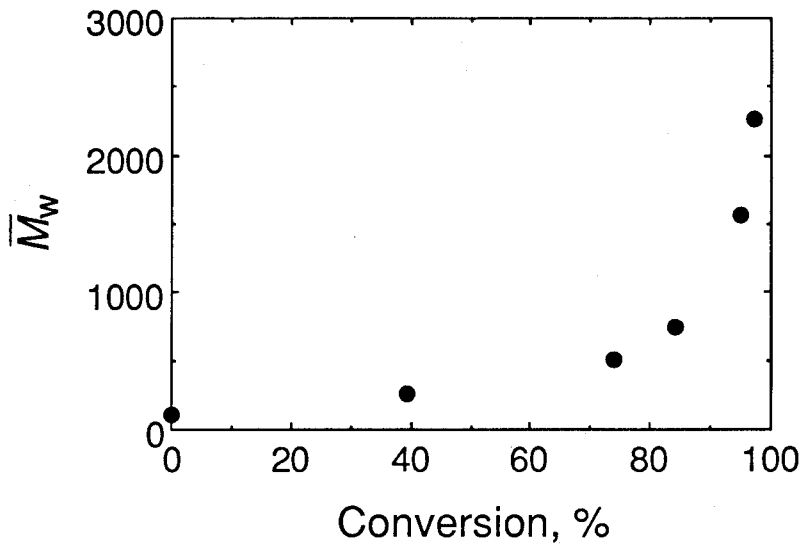


Figure 2. Relationship between the molecular weight of the polymer and the conversion of the polymerization of DiPMAn with $TiCl_4$-TFA at 50 °C.

In the case of the polymerization with $SnCl_4$-TFA, the optimum temperature was 50 °C, suggesting that a part of the active intermediate for the polymerization was decomposed above 50°C.

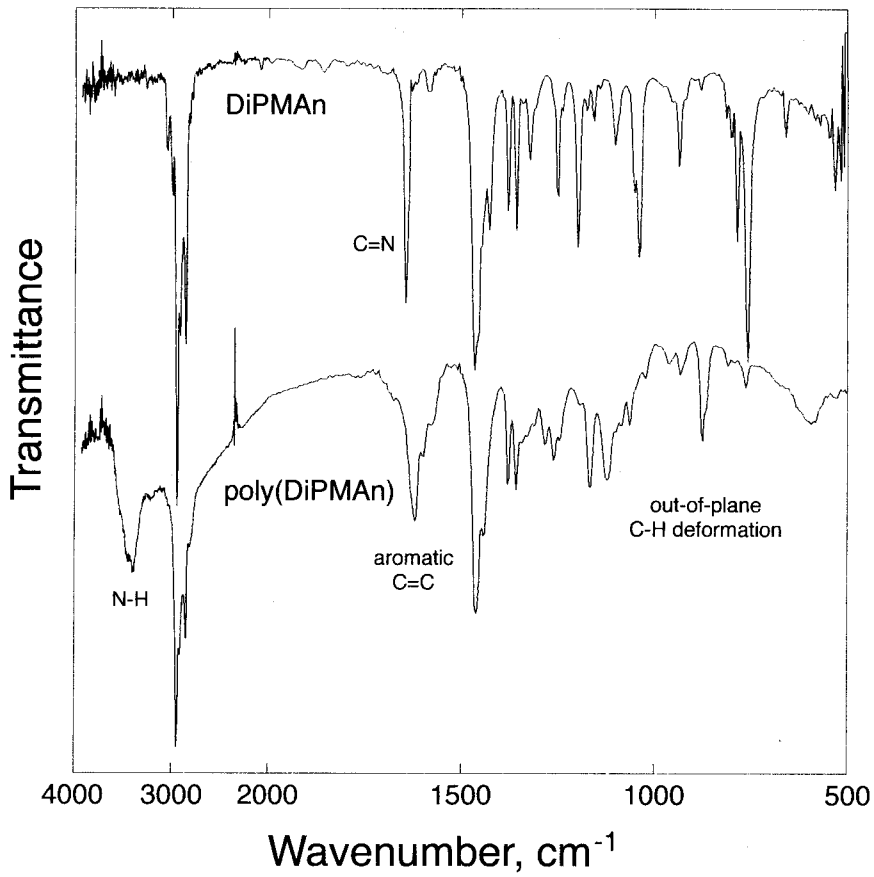


Figure 3. IR spectra of DiPMAn (NaCl) and poly(DiPMAn) (KBr).

The polymerization solution became highly viscous in the last stage of the polymerization at 50, 80, 100, and 120 °C. This suggests that a high yield of the polymer could not be attained due to the high viscosity of the polymerization system.

Structure of the Polymer. The C, H, and N contents of the polymer agreed with those of DiPMAn (Experimental Section). The result shows that the polymer is formed by addition polymerization of DiPMAn.

The IR spectra of the monomer and the polymer are shown in Figure 3. In the spectrum of the monomer, the absorption band assignable to the stretching vibration of the C=N double bond is observed at *ca.* 1650 cm^{-1}; and in the spectrum of the

obtained polymer, there is no peak due to the stretching vibration of the C=N double bond.[23] In the spectrum of the polymer, the absorption band, which is observed at *ca.* 1620 cm^{-1}, can be assigned to the stretching vibration of the aromatic C=C double bond, since the IR spectra of substituted anilines show the absorption bands assignable to the C=C double bond in this region.[24] Furthermore, the absorption band due to the stretching vibration of the N-H bond is observed at *ca.* 3420 cm^{-1}.[23] These results suggest that the polymer is formed through addition of a proton to the nitrogen of the C=N double bond and through opening of the C=N double bond. In addition, the absorption band assignable to the out-of-plane de-formation vibration of the tetra-substituted benzene is observed at *ca.* 880 cm^{-1}.[23] The result suggests that DiPMAn undergoes a substitution reaction during the polymerization.

The 270 MHz ^1H NMR spectra of the monomer and the polymer are shown in Figure 4. Although the AB type of the absorption bands due to the methylene protons of the C=N double bond are observed in the region of 7.3-7.4 ppm in the spectrum of the monomer, the absorption bands almost disappear in the spectrum of the polymer, suggesting that the C=N double bond is consumed in the polymerization. In addition, the absorption bands assignable to the aromatic protons are observed at *ca.* 7.2 ppm in the spectrum of the monomer; and in the spectrum of the obtained polymer, these absorption bands shift to a higher magnetic field (6.5-7.2 ppm). Furthermore, the integral of the peaks due to the aromatic protons became smaller from 3H (in the spectrum of the monomer) to 2H (in that of the polymer). These results suggest that an electron-donating group was introduced to the aromatic ring during polymerization.[25]

On the basis of these results, it is deduced that the polymer has the structure (**5**) shown in Scheme 1.

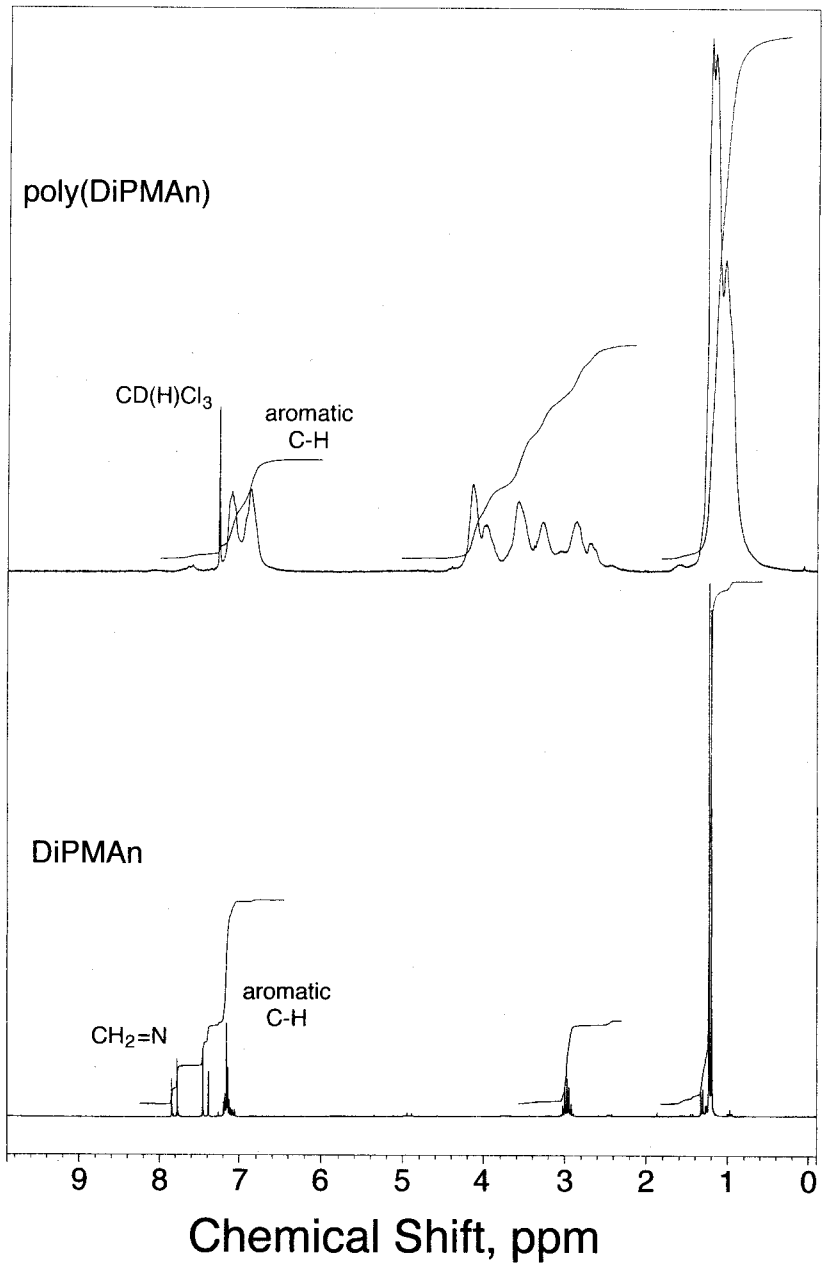
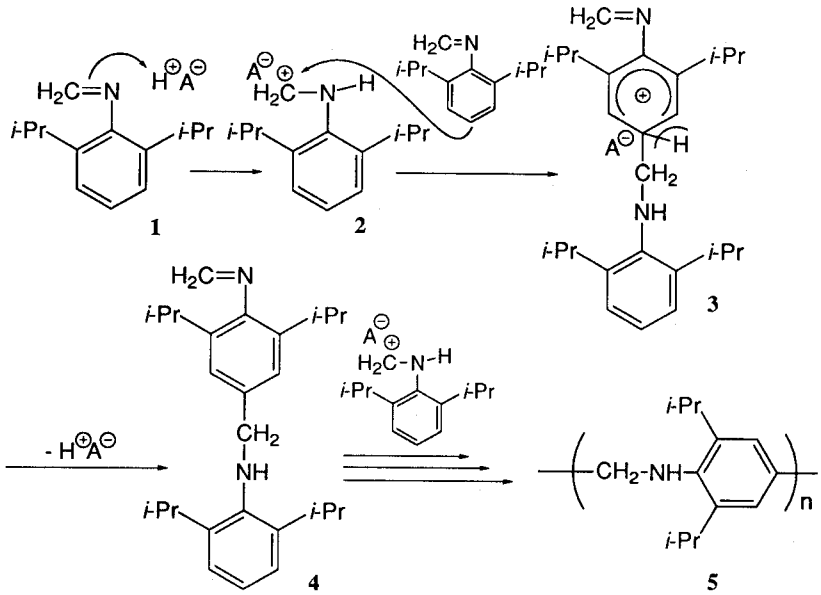


Figure 4. 270 MHz ^{1}H NMR spectra of DiPMAn and poly(DiPMAn) ($CDCl_3$).

Scheme 1. Tentative Mechanism for the Homopolymerization of DiPMAn



Tentative Mechanism for the Hompolymerization of DiPMAn. A tentative mechanism for the homopolymerization of DiPMAn with cationic initiators is shown in Scheme 1. The proton released by an initiator attacks the nitrogen of the C=N double bond to form a carbenium ion, which corresponds to an activated monomer (step **1** to **2**). Since a DiPMAn molecule is substituted by two isopropyl groups at the *ortho*-positions, the carbenium ion attacks the aromatic ring in the *para*-position (step **2** to **3**), followed by an electrophilic substitution (step **3** to **4**). When the electrophilic substitution reaction is repeated, the 1,6-addition polymer of DiPMAn is formed (step **4** to **5**).

Copolymerization of DiPMAn with MAnh. Results of the copolymerization of DiPMAn with MAnh are shown in Table 4. In each case, copolymer was obtained in a high yield (70-90 %). Copolymer of molecular weight as high as 10000 was obtained under a neat condition. The number-average molecular weights estimated by VPO were nearly equal to those determined by GPC. A higher yield of the copolymer was obtained in 1,4-dioxane than in toluene.

Table 4. Copolymerization of DiPMAn with MAnh

DiPMAn, mmol	MAnh, mmol	solvent (M)	temp., °C	time, h	yield, %	$\overline{M}_w$ [a], x 10^3
10.0 [b]	10.0	-	80	8	72.5	9.7
1.0 [c]	1.0	-	80	24	86.1	6.9
1.0 [c]	1.0	toluene (4.0)	80	24	78.7	5.7
1.0 [c]	1.0	1,4-dioxane (4.0)	80	24	89.5	7.8
10.6 [c]	10.6	THF (4.0)	25	60	84.5	7.6

[a] Determined by GPC, calibrated by standard polystyrene. [b] Under high vacuum. [c] Under an argon atmosphere.

In order to obtain the information on the type of the copolymerization, a continuous variation method was carried out. The result is shown in Figure 5. A maximum of the yield of the copolymer is observed at the mole fraction of DiPMAn of 0.5. Figure 6 shows the dependence of the mole fraction of DiPMAn in copolymer on the composition of the charged comonomer. Figure 6 shows that the mole fractions of DiPMAn in copolymer are almost the same (~0.5), being independent of the composition of the charged comonomer. These results suggest that the copolymer was formed by alternating copolymerization.

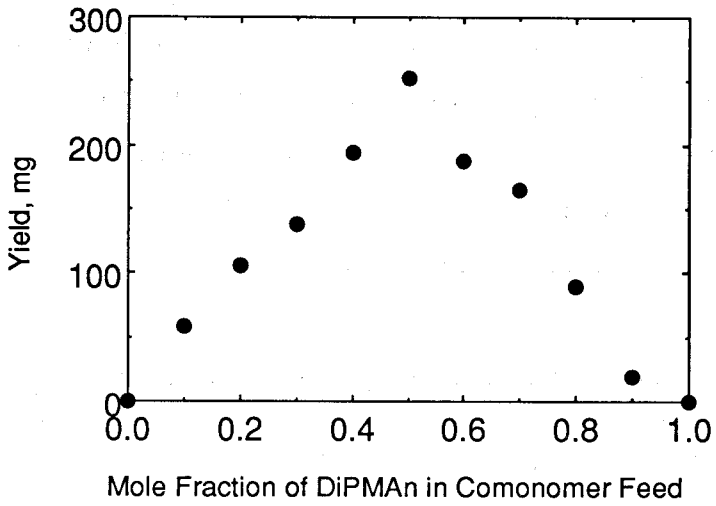


Figure 5. Continuous variation plots for the copolymerization of DiPMAn with MAnh in 1,4-dioxane under an argon atmosphere at 80 °C.

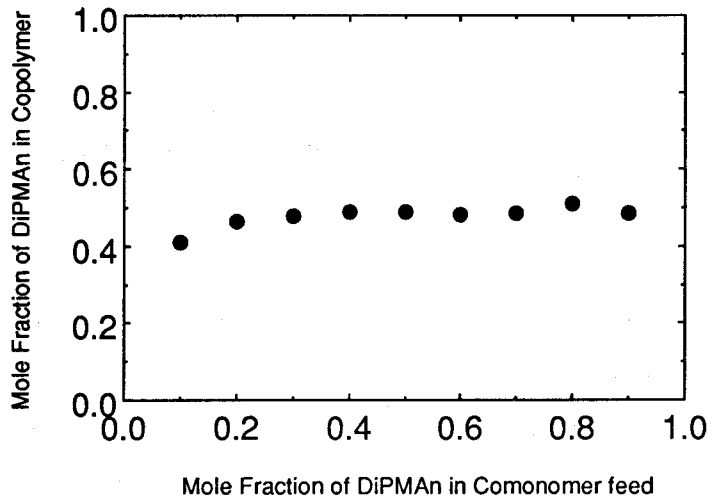


Figure 6. Dependence of the mole fraction of DiPMAn in the copolymer on the mole fraction of DiPMAn in the comonomer feed.

Structure of the Copolymer. The IR spectrum of the copolymer is shown in Figure 7 (lower). In the spectrum of the copolymer, the absorption bands assignable to the stretching vibration of the C=O double bonds of the ester and amide groups are

observed at *ca.* 1740 and 1670 cm^{-1}, respectively.[23] The absorption band due to the stretching vibration of the aromatic C=C double bond is observed at *ca.* 1630 cm^{-1} in the spectrum of the copolymer.[24] Furthermore, the absorption bands due to the symmetric and anti-symmetric stretching vibrations of the C-O-C bonds of the ester group are observed at *ca.* 950 and 1160 cm^{-1} in the spectrum of the copolymer, respectively.[23] These results suggest that esterification and amidation took place during the copolymerization. In addition, in the IR spectrum of the copolymer, the absorption band assignable to the stretching vibration of the O-H bond is observed at *ca.* 3400 cm^{-1}.[23]

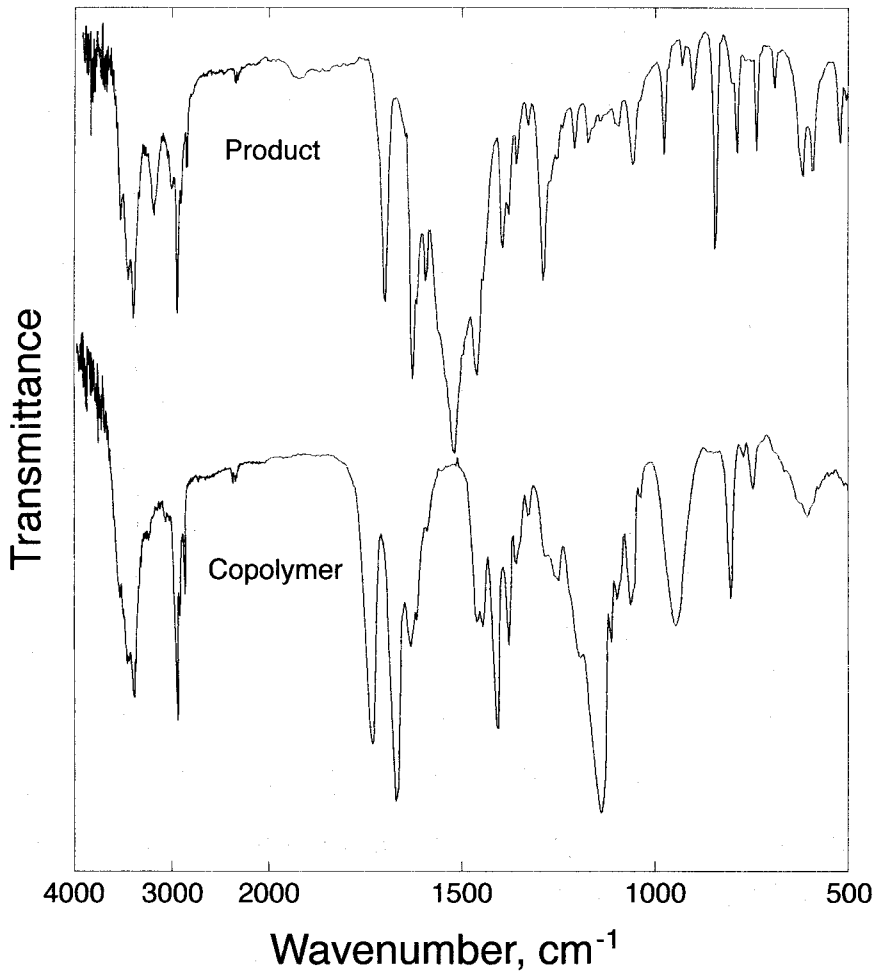


Figure 7. IR spectra of the copolymer (lower) and the crystalline product (upper) (KBr).

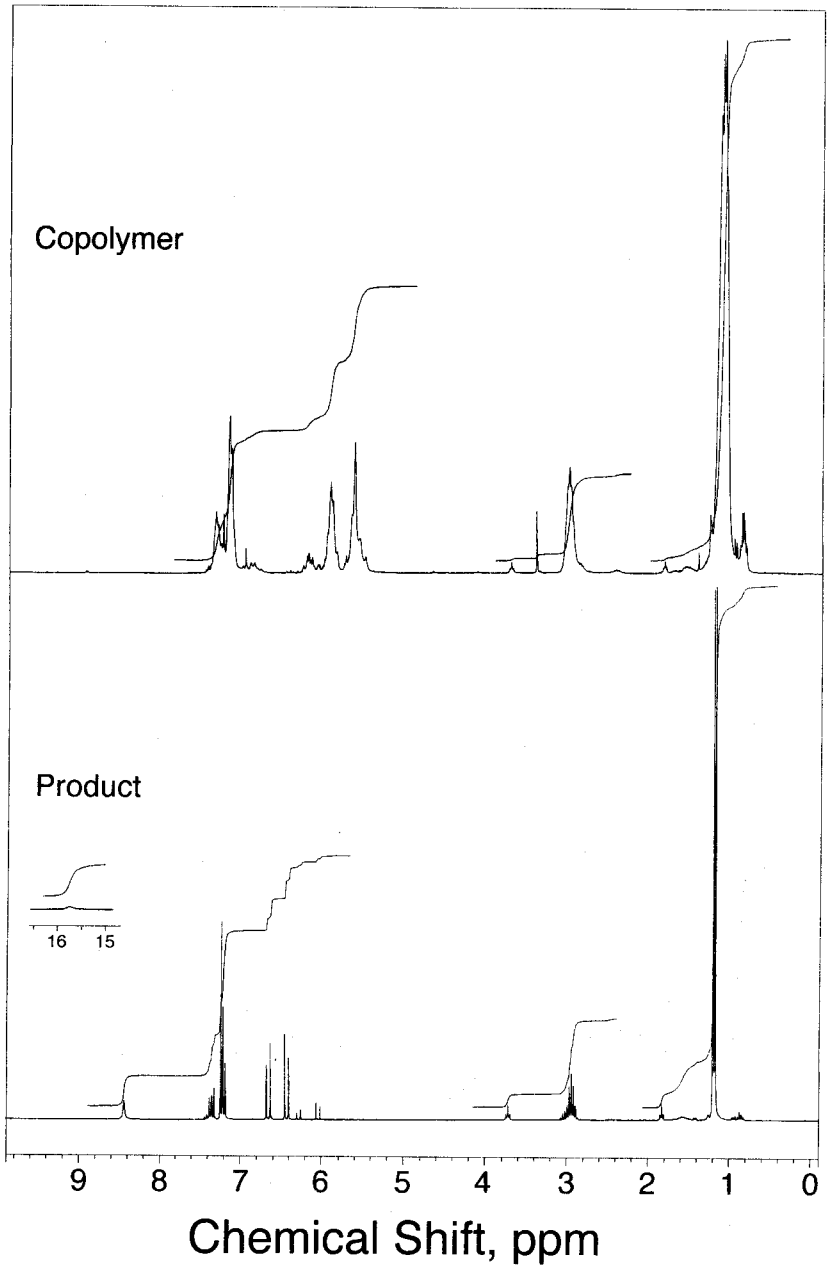


Figure 8. 270 MHz ^{1}H NMR spectra of the copolymer (upper) and the crystalline product (lower) ($CDCl_3$).

A 270 MHz ^{1}H NMR spectrum of the copolymer is shown in Figure 8 (upper). The absorption band due to the protons of the CH=CH is observed at 5.8-6.2 ppm.[25]

This result suggests that the C=C double bond derived from MAnh remains after copolymerization.

On the basis of these results, it can be deduced that the obtained copolymer is composed of the structure (**9**) shown in Scheme 2. The absorption band, observed at *ca.* 3400 cm^{-1} in the IR spectrum of the copolymer, can be ascribed to the carboxyl group of the chain end.

Confirmation of the Zwitterion. Colorless crystals were isolated from the copolymerization system. The chemical structure of the crystalline product was investigated by elemental analysis, EI-mass, IR, and ^{1}H and ^{13}C NMR spectroscopies.

The C, H, and N contents of the crystalline product agree with those of $C_{16}H_{21}NO_3$. The result suggests that the product is the adduct of 2,6-diisopropylaniline with MAnh.

The EI-mass spectrum of the crystalline product showed a signal at m/z = 275 as a molecular ion peak. It is assignable to $[C_{16}H_{21}NO_3]^+$. The result also supports the idea that the crystalline product is the adduct of 2,6-diisopropylaniline (MW = 177) with MAnh (MW = 98).

The IR spectrum of the crystalline product is shown in Figure 7 (upper). The absorption band due to the stretching vibration of the C=O double bonds of the carboxylic acid and amide are observed at *ca.* 1700 and 1630 cm^{-1}, respectively.[23] The absorption bands observed at *ca.* 3200 and 3400 cm^{-1} are assignable to the stretching vibration of the N-H and O-H, respectively.[23]

A 270 MHz ^{1}H NMR spectrum of the crystalline product is shown in Figure 8 (lower). In the spectrum, the AB type of absorption bands observed at 6.5-6.7 ppm are assignable to the protons of the CH=CH.[25] The absorption band due to the proton of the carboxylic acid is observed at *ca.* 15.8 ppm.[25] The absorption band due to the amide proton is observed at *ca.* 8.5 ppm.[25] The signals due to the phenyl protons are observed at *ca.* 7.0 ppm.[25] The absorption bands due to the methine and methyl

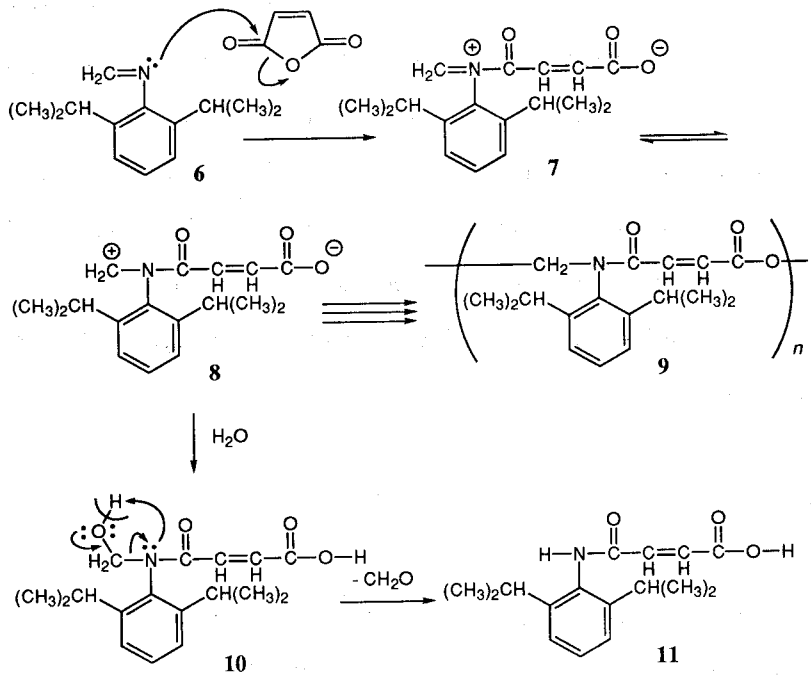
protons of isopropyl groups are observed at 1.5 and 2.5 ppm, respectively.[25] Additional signals are observed at 6.15 and 6.72 ppm, suggesting that *cis-trans* isomerization takes place.

From these results, it is concluded that the product is composed of the structure (**11**) in Scheme 2.

Tentative Mechanism for the Copolymerization of DiPMAn with MAnh. A tentative mechanism for the copolymerization of DiPMAn with MAnh is shown in Scheme 2. The lone pair of the nitrogen of DiPMAn attacks the carbon of the C=O of MAnh to form a zwitterion (step **6** to **8**). The alternating copolymer of DiPMAn with MAnh is formed by the coupling reactions between the zwitterions (step **8** to **9**). Similarly, Saegusa *et al.*[26] reported the alternating copolymerization between *N*-benzylideneaniline and succinic anhydride via the zwitterion mechanism.

The crystalline product is formed by the reaction of the zwitterion with water, accompanied by the elimination of formaldehyde (step **8** to **11**). The product (**11**) can be produced by the reaction of MAnh with 2,6-diisopropylaniline,[27] which is produced by the hydrolysis of DiPMAn. In this case, however, the copolymerization system should not contain 2,6-diisopropylaniline. This is because the purity of DiPMAn was checked by GC and ^{1}H NMR spectroscopy, and the copolymerization was carried out under water-free conditions. This mechanism was confirmed by the fact that the yield of the product increased upon addition of water to the polymerization system in the process of the copolymerization (from 1.8 to 11.6 %). These results also support the zwitterion mechanism.

Scheme 2. Tentative Mechanism of the Copolymerization of DiPMAn with MAnh



From these results, it is concluded that the copolymerization proceeds via the zwitterion (**8**) and that the copolymer is composed of the structure (**9**).

Conclusion

The polymerizability of an azastyrene derivative, DiPMAn, was studied. Although DiPMAn could not be polymerized by radical and anionic initiators, it was polymerized with cationic initiators, such as trifluoroacetic acid (TFA), $TiCl_4$-TFA, and $SnCl_4$-TFA. The structure of the polymer was investigated by means of IR and ^1H NMR spectroscopies. The results suggest that the polymer is formed by 1,6-addition with electrophilic substitution of an activated monomer in the *para*-position of the aromatic ring.

DiPMAn was copolymerized with MAnh in the absence of initiator. The result of the continuous variation method suggested that alternating copolymerization took place. The structure of the copolymer was investigated by elemental analysis, IR, Raman and ^{1}H and ^{13}C NMR spectroscopies. The results suggested the copolymer was formed via a zwitterion. In the course of the purification of the copolymer, a crystalline product was isolated from the copolymerization system. The structure of the product was investigated by elemental analysis, EI-mass, IR, Raman and ^{1}H and ^{13}C NMR spectroscopies. The crystalline product was found to be formed by the reaction of the zwitterion with water. The result supports the proposed mechanism via the zwitterion.

References

(1) Robinson, G. C. *J. Polym. Sci.,. Chem. Ed.* **1964**, *2*, 3901.

(2) Goodwin, A.; Novak, B. M. *Macromolecules* **1994**, *27*, 5520.

(3) Shasoua, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 3159.

(4) Shasoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866.

(5) Patten, T. E.; Novak, B. M. *Macromolecules* **1993**, *26*, 436.

(6) Hall, H. K., Jr. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 73.

(7) Neureiter, N. P. *J. Am. Chem. Soc.* **1959**, *81*, 2910.

(8) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(9) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(10) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232.

(11) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(12) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(13) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(14) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931.

(15) Kamachi, M.; Kajiwara, A.; Hashidzume, A. to be published.

(16) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(17) For example: Bailey, W. J.; Hartz, R. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1968**, *9*, 404.

(18) Distefano, G.; Giumanini, A. G.; Modelli, A.; Poggi, G. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1623.

(19) For example: (a) Miller, J. G.; Wagner, E. C. *J. Am. Chem. Soc.* **1932**, *54*, 3698. (b) Scheele, W.; Steike, L. *Kolloid-Z.* **1941**, *97*, 176.

(20) Verardo, G.; Cauci, S.; Giumanini, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1787.

(21) Giumanini, A. G.; Verardo, G.; Poiana, M. *J. Prakt. Chem.* **1988**, *330*, 161.

(22) Gulman, H.; Houbein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515

(23) Socrates, G. "Infrared Characteristic Group Frequencies"; John Wiley: Chichester, 1994.

(24) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules"; Academic: Boston, 1991.

(25) Emsley, J. W.; Feeney, J.; L. H. Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon: Oxford, 1966; Vol. 2.

(26) Saegusa, T.; Ikeda, H.; Fujii, H. *Macromolecules*, **1972**, *5*, 354.

(27) Cava, M. P.; Deana, A. A.; Muth, K.; Mitchell, M. J. *Org. Synth.* **1961**, *41*, 93.

Chapter 8

Radical Polymerizability of an Azastyrene Derivative. Direct Estimation of Rate Constant for Addition Reaction of Diphenylphosphonyl Radicals to 2,6-Diisopropyl-*N*-methyleneaniline

Introduction

Since radical polymerization is most useful for polymer preparation, there have been many papers on radical polymerization.[1] Recently, the elementary reactions of radical polymerization of vinyl and diene monomers have been investigating in detail by ESR spectroscopy. Consequently, the rate constants of the initiation[2] and the propagation[3] of various vinyl monomers have been determined.

However, few papers have been published on the radical copolymerization of vinyl monomers with imines.[4,5] The results suggest that the imines function as retarders in the radical polymerizations. Furthermore, 2,3-diaza-1,3-butadiene and azastyrene derivatives could not be polymerized by radical initiators.[6-15] It is not clear why these monomers containing the C=N double bond can not polymerize in the presence of radical initiators. In order to obtain some information on the radical reactivity of the C=N double bond, the addition reaction of diphenylphosphonyl radical to 2,6-diisopropyl-*N*-methyleneaniline (DiPMAn) was investigated.

In this chapter, the rate constant for the reaction of diphenylphosphonyl radical with DiPMAn will be estimated by using time-resolved ESR spectroscopy, and the obtained value of DiPMAn will be compared with those of vinyl monomers.

Experimental Section

Materials. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TMDPO) was provided by BASF and Nippon Kayaku Co., Ltd. TMDPO was purified by

recrystallization from ethanol before use. DiPMAn was prepared from 2,6-diisopropylaniline and paraformaldehyde according to the method of Verardo *et al.*[16] DiPMAn was isolated by successive distillations over calcium hydride and stored under an argon atmosphere.

Measurements of Time-Resolved ESR Spectroscopy. A solution of TMDPO in benzene (0.10 M) containing various concentrations of DiPMAn was placed in a flat ESR sample cell. Laser pulses were irradiated by using a Q-switched Nd:YAG laser (Quantaray DCR-2) operated at the third harmonic (54 mJ/flash at 355 nm with a 6-ns fwhm). For the measurements of the time-resolved ESR, a JEOL JES-FE1X spectrometer was operated without magnetic field modulation, and the data were stored in a LeCroy 7200 transient memory at a sampling rate of 10 ns/word. Magnetic fields at resonance signals were determined by an Echo Electronics ES-FC5 NMR field meter. A block diagram of time-resolved ESR measurements is shown in Figure 1.

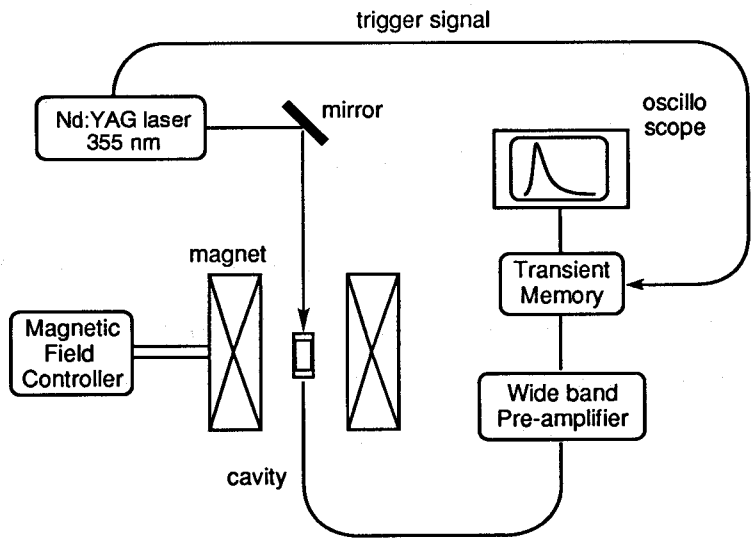


Figure 1. Schematic diagram of the system for time-resolved ESR spectroscopy.

The diphenylphosphonyl radicals generated by the laser pulse irradiation were observed at magnetic fields of 315.0 and 350.2 mT, whose separation corresponded to the hyperfine splitting constant of the diphenylphosphonyl radical with a phosphorus nucleus.[17] The decay of the ESR signals at 350.2 mT was recorded over a period of 40 μs after laser pulse irradiation.

Results and Discussion

Decays of ESR signals due to the diphenylphosphonyl radicals in the laser photolysis of TMDPO in the presence of varying concentrations of DiPMAn are shown in Figure 2. The decays became faster with increasing concentration of DiPMAn. The first-order plots for the signal intensities gave linear relationships in both the absence and the presence of DiPMAn (Figure 3). The apparent first-order rate constant (k') increased with increasing monomer concentration. The plots of the k' value against the monomer concentration yielded linear relationships as shown in Figure 4. Accordingly, k' follows

$$k' = k_1 + k_2[\mathrm{M}]$$

where k_1 is the first-order decay constant in the absence of the monomer, and k_2 is the bimolecular rate constant for the reaction of the diphenylphosphonyl radical with DiPMAn. From the slope of the line shown in Figure 4, the k_2 value for DiPMAn was estimated to be $(1.2 \pm 0.2) \times 10^6$ s^{-1} M^{-1}.

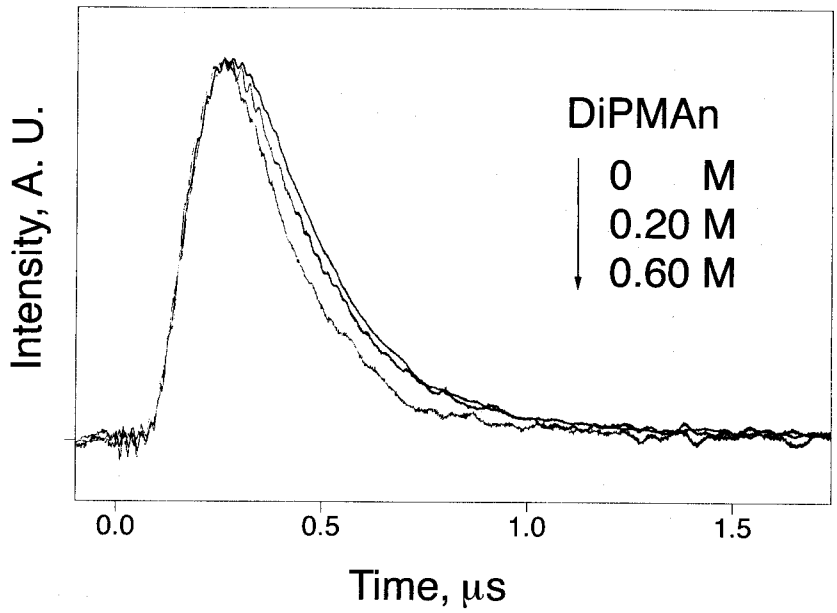


Figure 2. Time profiles of ESR signal intensities due to the diphenylphosphonyl radicals in the presence of varying concentrations of DiPMAn (0, 0.20, and 0.60 M).

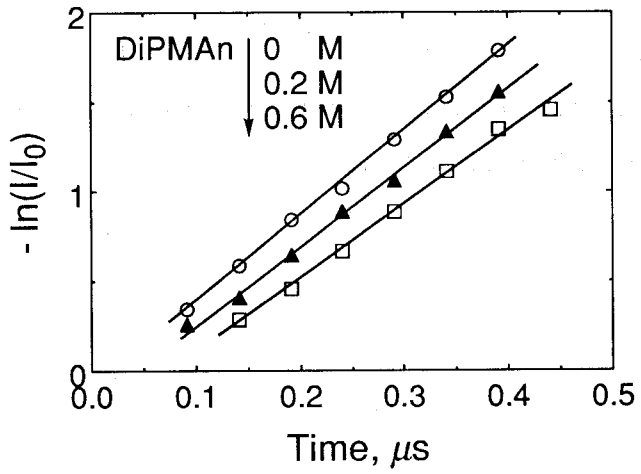


Figure 3. First-order plots for the decays of the diphenylphosphonyl radicals in the presence of varying concentrations of DiPMAn (0, 0.20, 0.60 M).

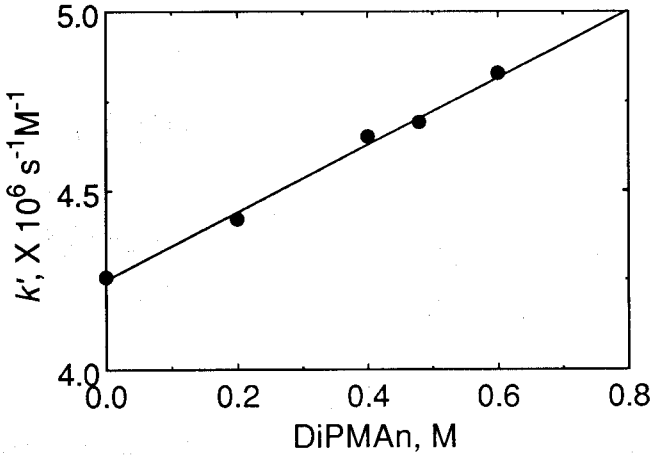


Figure 4. Plots of k' versus the concentration of DiPMAn.

Table 1 shows the initiation rate constants of various vinyl monomers estimated by Kajiwara *et al.*[2] with time-resolved ESR spectroscopy. The obtained rate constant for DiPMAn (1.2×10^6 s^{-1} M^{-1}) is similar to those for vinyl ethers, which cannot be polymerized with radical initiators. Judging from the cases of vinyl ethers,[18] the nitrogen centered-radical generated may be so reactive as to cause side reactions in preference to propagation, although the addition reaction of diphenylphosphonyl radical to the C=N double bond of DiPMAn seems to be possible. This speculation can be confirmed by the ESR spectrum of the radical produced by the reaction of diphenylphosphonyl radical with DiPMAn.

Table 1. Rate Constants on Addition Reactions of the Diphenylphosphonyl Radical to DiPMAn and Vinyl Monomers[a]

monomer	initiation rate constant, s^{-1} M^{-1}
DiPMAn	$(1.2 \pm 0.2) \times 10^6$
1,1-diphenylethylene	$(2.4 \pm 0.2) \times 10^7$ [b]
di-*n*-butyl itaconate	$(1.9 \pm 0.1) \times 10^7$ [b]
N-methylacrylamide	$(1.6 \pm 0.2) \times 10^7$ [b]
methyl methacrylate	$(1.6 \pm 0.4) \times 10^7$ [b]
1-acetoxybutadiene	$(1.5 \pm 0.2) \times 10^7$ [b]
α-methylstyrene	$(1.4 \pm 0.2) \times 10^7$ [b]
styrene	$(1.1 \pm 0.2) \times 10^7$ [b]
ethyl vinyl ether	$(1.5 \pm 0.3) \times 10^6$ [b]
n-butyl vinyl ether	$(4.4 \pm 0.3) \times 10^6$ [b]
i-butyl vinyl ether	$(2.5 \pm 0.2) \times 10^6$ [b]
n-decyl vinyl ether	$(3.1 \pm 0.2) \times 10^6$ [b]
phenyl vinyl ether	$(2.6 \pm 0.2) \times 10^6$ [b]

[a] In benzene at 20 °C. [b] These data from ref. 2.

Conclusion

The rate constant of the reaction of DiPMAn with diphenylphosphonyl radical was estimated to be $(1.2 \pm 0.2) \times 10^6$ s^{-1} M^{-1} by time-resolved ESR spectroscopy. The estimated value is as low as those of vinyl ethers, which cannot be polymerized with radical initiators.

References

(1) Odian, G. "Principles of Polymerization", 3rd ed.; John Wiley: New York, 1991.

(2) Kajiwara, A.; Konishi, Y.; Morishima, M.; Schnabel, W.; Kuwata, K.; Kamachi, M. *Macromolecules* **1993**, *26*, 1656.

(3) For example: Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.

(4) Ferruti, P.; Audisio, G.; Cottica, G.; Feré, A. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 451.

(5) Barson, C. A.; Bevington, J. C., Hunt, B. J. *Eur. Polym. J.* **1995**, *31*, 249.

(6) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 295.

(7) Kamachi, M.; Murahashi, S. *Polym. J.* **1974**, *6*, 302.

(8) Kamachi, M.; Murahashi, S. *Makromol. Chem.* **1968**, *119*, 232.

(9) Kamachi, M.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2890.

(10) Kamachi, M.; Murahashi, S. *Polym. J.* **1973**, *4*, 651.

(11) Harada, A.; Fujii, H.; Kamachi, M. *Macromolecules* **1991**, *24*, 5504.

(12) Harada, A.; Kajiwara, A.; Fujii, H.; Kamachi, M. *Polymer. J.* **1992**, *24*, 931.

(13) Kamachi, M.; Kajiwara, A.; Hashidzume, A. to be published.

(14) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(15) Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromol. Rapid Commun.* **1996**, *17*, 529.

(16) Verardo, G.; Cauci, S.; Giumanini, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1787.

(17) Roberts, B. P.; Singh, K. *J. Organomet. Chem.* **1978**, *159*, 31.

(18) Sandler, S. R.; Karo, W. "Polymer Syntheses", 3rd ed.; Academic: New York, 1977; Vol. II, Chapter 7.

Summary and Conclusions

In **Part 1** of this thesis, the preparation, reactivity, and polymerization of 2,3-diaza-1,3-butadiene derivatives (azine compounds) were described.

In **Chapter 2**, trifluoroacetaldehyde azine (TFAcAz) was prepared to avoid the chain transfer reaction observed in the polymerization of alkyl azine compounds. Its chemical reactivity was investigated. TFAcAz reacted with triethylamine at 20-30 °C to form a cyclic dimer, and with protic compounds to form 1,2-adducts.

In **Chapter 3**, the polymerizability of TFAcAz was discussed. TFAcAz was polymerized by triethylamine at -20 °C to form 1,2-polymer, although alkyl azine formed 1,4-polymer. The results suggest that the nature of azine compounds depends on their substituents at the carbons of C=N-N=C.

In **Chapter 4**, *n*-butyl glyoxylate azine (BgAz), which has an *n*-butyl ester group, was prepared to obtain information on the proposition that the chemical reactivities and polymerizabilies of azine compounds are dependent on the nature of their substituents. BgAz was readily oligomerized by anionic and cationic initiators. In addition, BgAz reacted with alcohols to form 1,2-adducts.

In **Chapter 5**, the copolymerization of acetaldehyde azine (AcAz) with maleic anhydride (MAnh) was studied. It was found that copolymer was formed by the addition polymerization of the adduct, which had a pyrazoline ring, mainly through the C=C double bonds.

In **Part 2**, the preparation, reactivity, and polymerizability of azastyrene (*N*-methyleneaniline) and its derivatives were described.

In **Chapter 6**, the preparation, stability, and chemical reactions of azastyrene (*N*-methyleneaniline, MeAn) were dealt with. MeAn was prepared by the pyrolysis of a cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine, and isolated as a THF-solution. MeAn was found to be stable in THF below -40 °C, and existed in dilute solution (~ 100 mM) even at 30 °C under acid-free conditions. The cyclic trimerization was found to be caused by a small amount of the acid produced by pyrolysis. Furthermore, MeAn

reacted with nucleophiles to form aniline derivatives. In this chapter, the polymerizability of MeAn was also discussed. MeAn was polymerized under concentrated conditions to form insoluble polymer in a relative high yield. The polymer was found to be composed of 1,2-units.

In **Chapter 7**, the polymerizability of 2,6-diisopropyl-*N*-methyleneaniline (DiPMAn), which had been reported to be a stable derivative of azastyrene, was investigated. DiPMAn could not be polymerized by radical or anionic initiators. However, DiPMAn was polymerized by cationic initiators to form 1,6-addition polymer through aromatic electrophilic substitution. In this chapter, the copolymerization of DiPMAn with MAnh was also investigated. Copolymer was obtained when DiPMAn was added to MAnh. The copolymer was found to be formed by alternating copolymerization via a zwitterion mechanism.

In **Chapter 8**, the radical polymerization of DiPMAn was examined. The rate constant of the reaction of diphenylphosphonyl radical with DiPMAn was estimated to be $(1.2 \pm 0.2) \times 10^6$ s^{-1} M^{-1} by time-resolved ESR spectroscopy. The estimated value was as low as those of vinyl ethers, which are known not to be polymerized by radical initiators.

List of Publications

(1) Preparation and Chemical Reactions of Trifluoroacetaldehyde Azine (1,1,1,6,6,6-Hexafluoro-3,4-diaza-2,4-hexadiene)

Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M.; Kusunoki, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2025.

(2) Polymerization of Trifluoroacetaldehyde Azine (1,1,1,6,6,6-Hexafluoro-3,4-diaza-2,4-hexadiene)

Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromolecules* **1995**, *28*, 417.

(3) Polymerization of an Azastyrene Derivative, 1. 1,6-Addition polymerization of 2,6-Diisopropyl-*N*-methyleneaniline

Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M. *Macromol. Rapid. Commun.* **1996**, *17*, 529.

(4) Polymerization of Azastyrene Derivatives, 2. Copolymerization of 2,6-Diisopropyl-*N*-methyleneaniline with Maleic Anhydride

Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M., to be submitted for publication in *Macromolecules*.

(5) Polymerization of Azastyrene Derivatives, 3. Preparation and Polymerization of *N*-Methyleneaniline

Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M., to be published.

(6) Polymerization of Azastyrene Derivatives, 4. Radical polymerizability of 2,6-Diisopropyl-*N*-methyleneaniline (DiPMAn). Direct Estimation of Rate Constant for Addition Reaction of Diphenylphosphonyl Radicals to DiPMAn

Hashidzume, A.; Kajiwara, A.; Harada, A.; Kamachi, M., to be published.