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Fullerene-containing Polymethacrylate:
Synthesis, Properties, and Its Potential Application to
Organic Photovoltaics

VIKO LADELTA

MARCH 2015

Fullerene-containing Polymethacrylate:
Synthesis, Properties, and Its Potential Application to
Organic Photovoltaics

A dissertation submitted to
THE GRADUATE SCHOOL OF ENGINEERING SCIENCE
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DOCTOR OF PHILOSOPHY IN ENGINEERING

BY
VIKO LADELTA

MARCH 2015

Abstract of Thesis

An active layer of organic photovoltaics (OPVs) generally comprises of an electron-donor such as poly(3-hexylthiophene) (P3HT) blended with an acceptor material, typically [60]fullerene (C_{60}) and its derivatives. C_{60} has superior optoelectronic properties such as high electron-acceptability, slow back-electron-transfer, small rearrangement energy, and allow the formation of triplet exciton. However, C_{60} and its derivatives have some drawbacks: limited solubility, poor morphology and lifetime stability in the blend with the polymeric donor, P3HT.

In order to overcome such problems, polymeric acceptors carrying C_{60} moieties in the side groups of polymethacrylates were designed and synthesized. First, copolymers of 6-chlorohexyl methacrylate, a monomer possessing flexible alkyl spacer, and methyl methacrylate were prepared. The subsequent azidation and 1,3-dipolar cycloaddition of azide yielded polymerthacrylates bearing C_{60} moieties. *Atactic* polymethacrylate (**at-PF**) was prepared by radical polymerization, while *syndiotactic* (**st-PF**) and *isotactic* (**it-PF**) were obtained by stereospecific anionic polymerization. The controlled molecular weight with narrow distribution by living anionic polymerization allowed the clear observation of molecular weight changes before and after the C_{60} -addition, which revealed a side reaction, *i.e.* the multi-additions of azides to a C_{60} moiety, resulting insoluble fractions due to the cross-linking. Nevertheless, the obtained **at-PF** and **st-PF** exhibited high solubility in tetrahydrofuran, chloroform and toluene with high C_{60} content up to 41.4 wt%, which is the highest C_{60} content among the reported polymethacrylates. In contrast, **it-F** exhibited relatively low solubility and was only partly soluble in chloroform. The lowest unoccupied molecular orbitals (LUMOs) of **at-PF** and **st-PF** were comparable to that of soluble C_{60} derivative, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), enough low to allow charge transfers from P3HT. The results suggest that **at-/st-PFs** are excellent electron-acceptors for OPVs. This fact was also supported by the almost quantitative fluorescence quenching (94-98%) of the polymers in the blend with P3HT. AFM phase images revealed that the **st-PF** forms a much finer microphase separation in the blend with P3HT than **at-PF**, suggesting the control of stereoregularity and molecular weight had significant effects. The OPV devices prepared from the blends of **at-/st-PF** with P3HT exhibited high open-circuit voltages (V_{oc} s, **at-PF**: 0.73 V, **st-PF**: 0.89 V), although the short-circuit currents (J_{sc} s) and fill factors (FFs) were almost zero. The results indicate that the morphology must be improved to achieve bicontinuous percolation network of donor and acceptor materials.

Although the electron-acceptor polymers with good photoelectric properties

were obtained in the previous chapters, the poor device performance implied the problem of their morphology. A diblock copolymer composed of donor and acceptor segments may form self-assembly of donor and acceptor moieties in nano scales so as to better function as a single molecular device. Toward such a block copolymer, the synthesis and modification block copolymer composed of independently clickable segments were investigated. Anionic copolymerizations of silyl-protected propargyl acrylate and CHMA were conducted in the presence of a bulky aluminum additive. The sequential monomer addition resulted in a relatively wide molecular weight distribution, while the one-shot monomer injection allowed a monomer-selective polymerization to afford block copolymer with narrow molecular weight distribution. The subsequent polymer modification revealed that each segments could be independently functionalized via double click chemistry. This result will provide a facile method for the preparation of block copolymer bearing functional moieties such as an electron-donor and an acceptor for OPV application.

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General Introduction

Organic photovoltaics (OPVs)

1. Photovoltaics

Solar light is the most abundant clean and renewable energy in our planet. It exists all year round particularly in tropical countries in constant intensity. Harvesting the energy from solar light has become one channel to overcome the high demand of energy with maintaining sustainability of environments. Photovoltaic (PV) is a prospective method of exploiting the sunlight energy. PV devices (solar cells) are peculiar in viewpoint that they directly convert the incident solar radiation into electricity, without noise, pollution or moving parts, making them robust, reliable and long lasting.

Historically, principle of PV was proposed by A. E. Becquerel in 1839,¹ and the first photoelectric conversion was found by C. Fritts in 1884.² The breakthrough in this field is the innovation of single-crystal silicon PVs in 1954,³ which opens the practical use of PVs in daily life. Nowadays, various kinds of PV devices have been extensively studied. They can be roughly categorized to inorganic and organic PVs (**Table I**).

In majorities of inorganic PVs, they are classified into silicon based and rare-earth metals based PVs. The former includes single crystalline, polycrystalline, amorphous, and thin-layer silicon. Among them, single-crystalline and polycrystalline are current majorities in commercial use, of which power conversion efficiency (PCE) are 15-20% and 13-18%, respectively. However, the high costs of super-pure silicon still remain as a great issue. Among the latter, rare-earth based PVs, indium-gallium-arsenic (InGaAs) PVs exhibit excellent PCE (~36%), although they cost more than

Table I. Categories and features of photovoltaics

Material	Category		PCE	Problem
Inorganic	Silicon based	Monocrystalline silicon	20-25%	Expensive
		Polycrystalline silicon	15-20%	
		Amorphous silicon	ca.10%	Preparation technique
		Thin-layer silicon	ca.15%	
	Semiconductor based	InGaAs	36%	Very expensive
		CIGS / CZTS / CdTe	11-20%	Still in research
Hybrid	Dye-sensitizer		~11%	Low PCE
Organic (OPV)	Organic-thin-film		~12%	Low PCE

silicon-based PVs. Therefore, novel PVs based on other rare-earth metals such as copper-indium- gallium-selenium (CIGS), copper-zinc-tin-sulfur (CZTS), and cadmium-tellurium (CdTe) have been investigated as promising alternatives. An inorganic-organic hybrid PV, perovskite/dye-sensitizer PV, is also gained the researcher's attention.

Dye-sensitizer PVs are typically composed of organic dye and titanium oxide. Although some literatures categorized dye-sensitizer PVs as organic photovoltaics (OPVs), in this thesis, OPVs means organic-thin-film PVs unless otherwise stated. Recently, OPVs has attracted much interest from basic research to application which bring on the fast growing in the past decade.⁴ Compared with other PVs, particularly silicon-based PVs, OPVs have gained much interest for many reasons; low cost, light-weight, solution processing, good mechanical flexibility and a very high speed of processing.⁵⁻⁷ However, the PCEs of OPVs are ~12% at maximum, and the improvements are still required. Furthermore, the development of manufacturing OPVs in large area is also desired in order to realize mass production.

2. Structure and preparation of OPVs device

An OPV device generally comprises a transparent substrate such as a glass, a transparent electrode of indium tin oxide (ITO), a hole buffer layer, an active layer, an electron buffer layer (LiF), and an aluminum (Al) electrode (**Figure I**).⁸ A typical hole buffer layer consists of a blend of poly(3,4-dioxythiophene) (PEDOT) and poly(styrenesulfonate) (PSS), *i.e.* PEDOT:PSS. An active layer comprises electron-donor (*p*-type semi-conductor) and acceptor (*n*-type semi-conductor) materials. As described later, the choice of donor and acceptor is one of the most significant factors to determine the OPV performance.

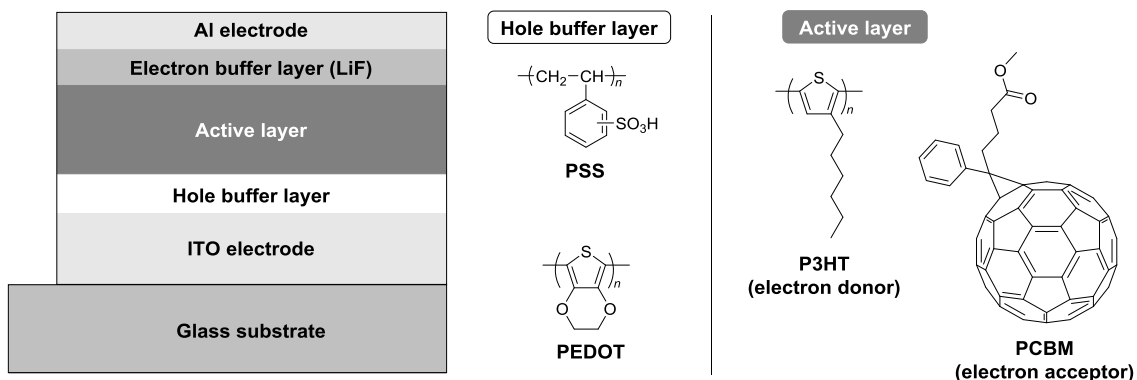


Figure I. Structure of OPV device.

Figure II describes a typical process to prepare the OPVs device.^{8, 9} On a pre-cleaned ITO electrode, an aqueous suspension of PEDOT:PSS is spin-coated under air. Subsequently, the blended solution of a donor, *e.g.* poly(3-hexylthiophene) (P3HT), and an acceptor, *e.g.* [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), is spin-coated under N₂ atmosphere. After vacuum deposition of aluminum, the device is sealed with a glass substrate. Since this conventional device fabrication method is not suitable for mass production, alternative methods have been investigated. The details are described

later.

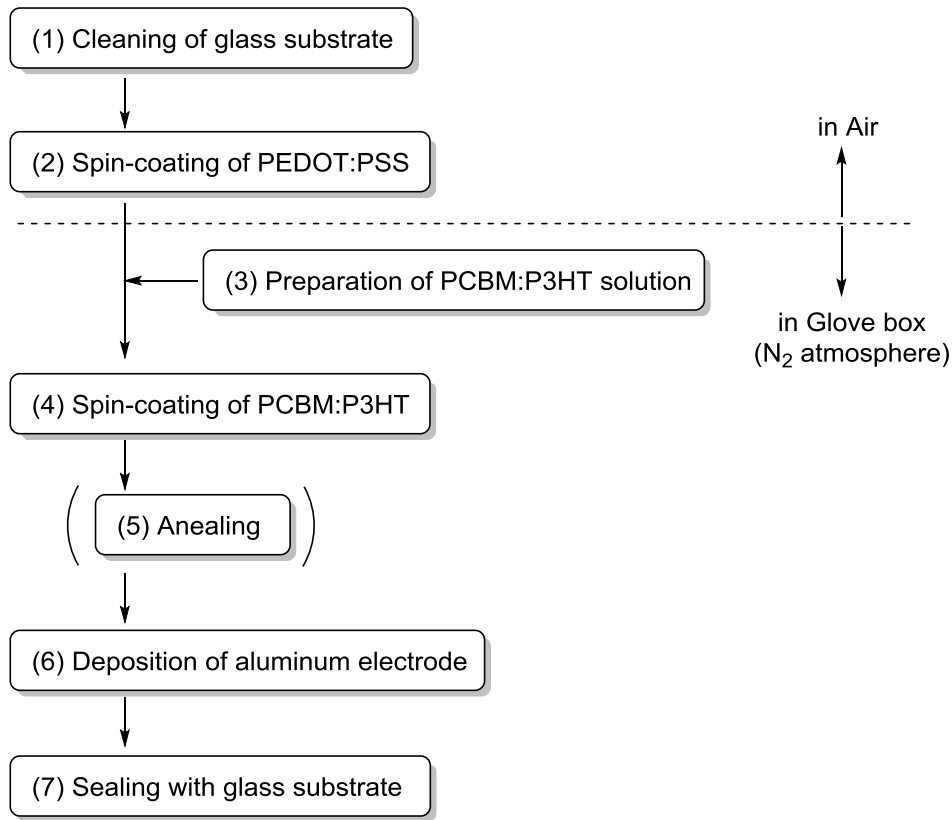


Figure II. Preparation of OPVs devices.

3. Mechanism of power generation in OPVs

Power generation mechanism of OPVs is described in **Figure III**: (1) After the light absorption by electron-donor, (2) the formed exciton diffuses to the interface with acceptor, and (3) electron transfer follows. The anion and cation are (4) formed and (5) move to each electrode, and then (6) the current flows from there. Heeger explained that the mechanism requires 3 steps of consecutive processes:¹⁰ (i) Absorption of photon energy from the solar light, (ii) photo-induced charge generation and charge transfer (in form of electron and hole mobile carriers) and (iii) collection of electron at one electrode and hole at the opposite electrode.

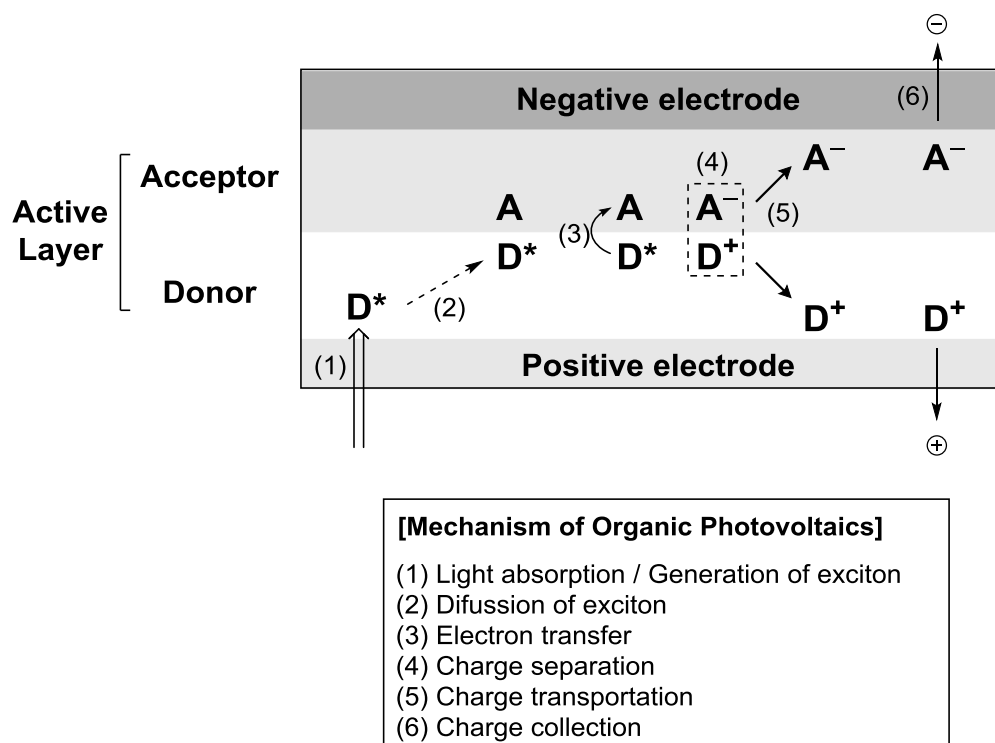


Figure III. General mechanism of power conversion from solar light in an OPVs device.

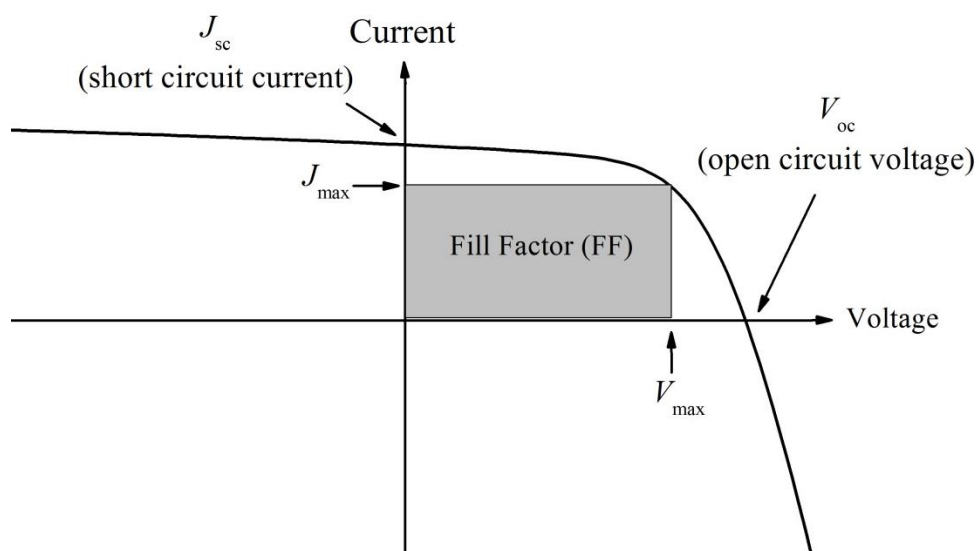


Figure IV. Current-voltage characteristics in OP

4. Evaluation of OPVs performance

The performance of an OPV is generally indicated by a J - V curve, the record

of current that flows from the OPV device which is obtained by sweeping applied voltage under light irradiation. A typical J - V curve is shown in **Figure IV**. Characteristics of current and voltage of an OPVs device can be evaluated by 4 factors as defined by Heeger:¹⁰

(i) Short circuit current (J_{sc}) is the current that flows when there is no external field applied. This is determined by the number of photon absorbed (photoexcitations), the quantum efficiency for charge separation and transport of charge carriers through the donor and acceptor materials.

(ii) Open circuit voltage (V_{oc}) is the voltage where the current is zero. This is a maximum voltage generated by a device. V_{oc} is dependent on the difference of the highest occupied molecular orbital (HOMO) level of donor and the lowest unoccupied molecular orbital (LUMO) level of acceptor.

(iii) Fill factor (FF) is the third parameter, which is given according to the following equation;

$$FF = (J_{max} \times V_{max}) / (J_{sc} \times V_{oc})$$

Here, J_{max} and V_{max} are respectively the current and voltage at the maximum power point where the product of current and voltage becomes the maximum. FF means the balance of the effective maximum power to ideal maximum power, thus an excellent OPV device should have FF more than 0.7. FF is governed by the competition between sweep out of photogenerated carriers and the recombination of the carriers to the ground state.

(iv) Power conversion efficiency (PCE) is constructed by three factors as:

$$PCE (\eta) = (J_{sc} \times V_{oc} \times FF / P_{inc}) \times 100\%$$

Here, P_{inc} is the energy of incident light. The incident solar light power for device

evaluation is standardized as 100 mW cm^{-2} . The solar spectrum also needs to be standardized for evaluating the performance of PVs because the solar spectrum changes with time and location. In the field of PVs, air mass (AM) 1.5 solar spectrum, *i.e.*, the solar irradiance with the sun 48.2° above the horizon where the radiation received on the ground surface (AM 1.0 means the air thick on the equator where the sun light passes toward the ground surface, is commonly used. Thus AM 1.5 corresponds to that in Japan and USA).¹¹ Given this standard, PCE can be rewritten as

$$\text{PCE } (\eta) = J_{\text{sc}} \times V_{\text{oc}} \times \text{FF} = J_{\text{max}} \times V_{\text{max}}$$

5. Problems of OPVs and their solution

[1] Power conversion efficiency

The critical problem of OPVs is the low PCE. While the silicon-based PVs have PCEs of 13-20%, those of OPVs are less than 12%.⁴ It should be noted that PCEs of OPVs were ca. 1% until 2000.¹² In the last decade, several important discoveries have been made, which realized the PCEs of more than 10%. Nowadays, PCE of 15% has been recognized as the next challenge to achieve the industrial use of OPVs.

As described in the previous section, PCE of OPVs is given by;

$$\text{PCE } (\eta) = J_{\text{sc}} \times V_{\text{oc}} \times \text{FF}$$

Thus, to improve PCEs, increases of V_{oc} and FF are effective. The former can be achieved by the design of energy levels of the active layer materials, an electron-donor and an electron-acceptor, while the control of morphology of the active layer is effective for the later.

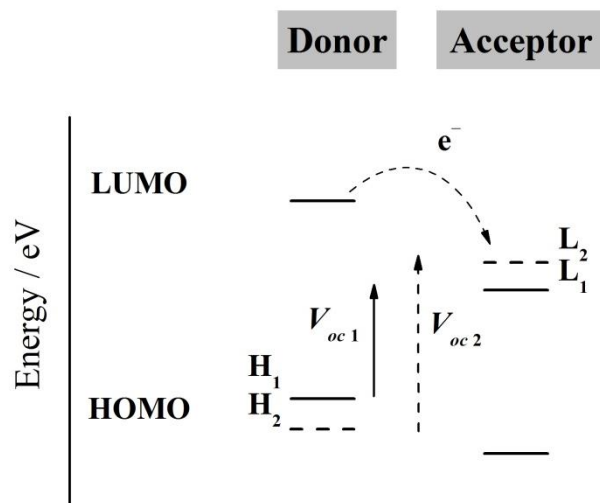


Figure V. Schematic energy alignment of donor and acceptor electrons in OPVs.

In general, V_{oc} has a correlation with the energy differences between the LUMO level of acceptor and HOMO level of donor. As described in **Figure V**, if the LUMO level of an acceptor increases from L_1 to L_2 and if the HOMO level of a donor decreases from H_1 to H_2 , the V_{oc} is expected to increase from V_{oc1} to V_{oc2} under ideal condition. However, the high LUMO level of an acceptor does not simply mean a good performance. Smooth electron transfer from a donor to an acceptor is required for charge separation, which is driven by a downhill energy exceeding the exciton binding energy. The binding energy is a coulombic attraction of a bound electron-hole pair at the interface, and typical values are estimated to be 0.4 – 0.5 eV.⁸ Thus, LUMO level of acceptor must be at least 0.3 eV lower than that of donor.⁸

FF is dependent on the morphology of an active layer. Even if the donor and acceptor have an ideal electronic relationship, the device does not work as an OPV unless it has appropriate morphology. The most ideal structure of active layer is an interpenetrating structure of donor and acceptor materials (**Figure VI**). However,

formation of such morphology is still challenging. Microphase separation of block copolymers composed of donor and acceptor segments is a possible strategy to prepare interpenetrating structure, although it is still at a fundamental research level.¹³ Alternatively, bulk-heterojunction (BHJ) constructions are widely adopted as an ideal morphology. The state-of-the-art is defined by Thompson as a bicontinuous composite of a donor and an acceptor with a maximum interfacial area for exciton dissociation and with an average domain size commensurate with the exciton diffusion length (5–10 nm).⁸ In addition, the donor and acceptor should form phase-segregation on a suitable length scale to allow maximum ordering within each phase and perform effective charge transport in continuous pathways to the electrodes with minimum recombination of free charges.¹⁴

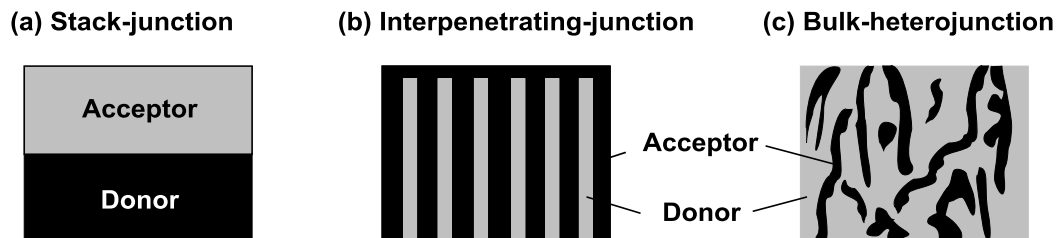


Figure VI. Type of junctions between the donor and acceptor in the active layers.

According to the strategies for the improvements of OPVs as described above, the developments of donor and acceptor materials are important. Electron-donor materials are mainly developed from the class of conjugated polymers¹¹ and at present efficiencies of more than 11% have been obtained.¹⁵ Another developed electron-donor materials comprise porphyrin¹⁶ and phthalocyanine derivatives⁹. On the contrary, an electron-acceptor is mainly supplied as fullerene C₆₀ derivatives,¹⁷ Although there have been some reports on perylene diimide¹⁸ and diketopyrrolopyrrole (DPP)¹⁹ derivatives,

as electron acceptors.

[2] Mass production

As described previously, the conventional device fabrication methods of OPVs are spin-coating and high-vacuum thermal evaporation. However, they are not suitable for mass production. Recently, a new alternative method with high output production performed in a continuous process, called roll-to-roll (R2R) process, has emerged in the industrial application of OPVs. In the R2R process, the device is printed layer by layer continuously from solution processable materials (**Figure VII**).²⁰ For example, Schrödner *et al.* have reported the R2R preparation of OPV device composed of common composites, *i.e.* a hole buffer layer of PEDOT:PSS and an active layer of P3HT:PCBM.²¹ The authors printed the blended materials for each layer stepwise onto the ITO substrates on poly(ethylene terephthalate) (PET) film (width: 5 cm) through a continuous line (printing rate: 1 mm min⁻¹) (**Figure VIII**). The maximum PCE by the optimized printing conditions reached to 1.37%, while that by conventional methods is 3-4%. Furthermore, they have prepared an OPV with 3.20% PCE through the R2R process by using P3HT and other fullerene derivatives, 1',1'',4',4''-tetrahydro-di[1,4]methanonaphthaleno-[1,2:2',3',56,60:2'',3''] [5,6]fullerene-C₆₀ (ICBA) for the active layer.²¹

For the R2R process, the solubilities of donor and acceptor materials are important to print them uniformly to the substrate film. In particular, it is reported that the solvents of donor and acceptor materials in the R2R process affect the OPV device performance.²¹ Thus, the development of such materials with good solubility in common organic solvents is required.

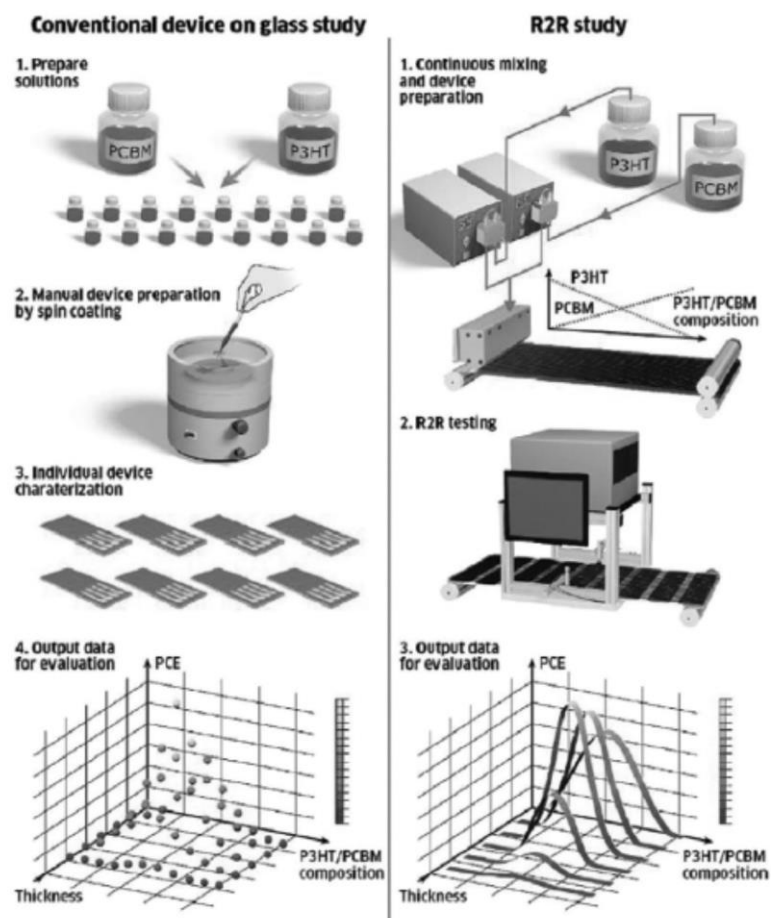


Figure VII. Comparison between conventional spin-coating and differentially pumped roll-to-roll coating.²⁰

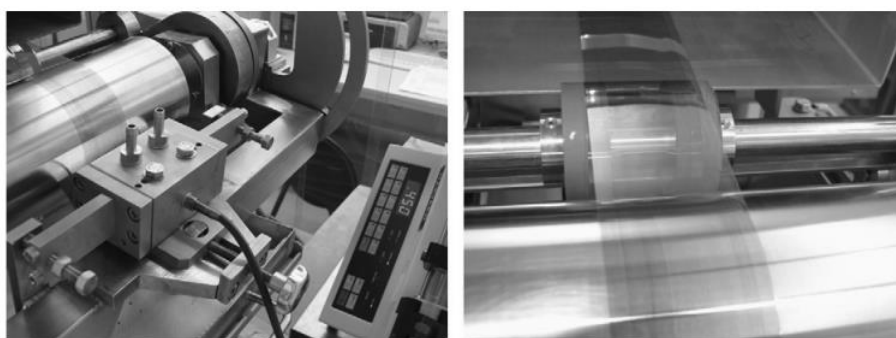


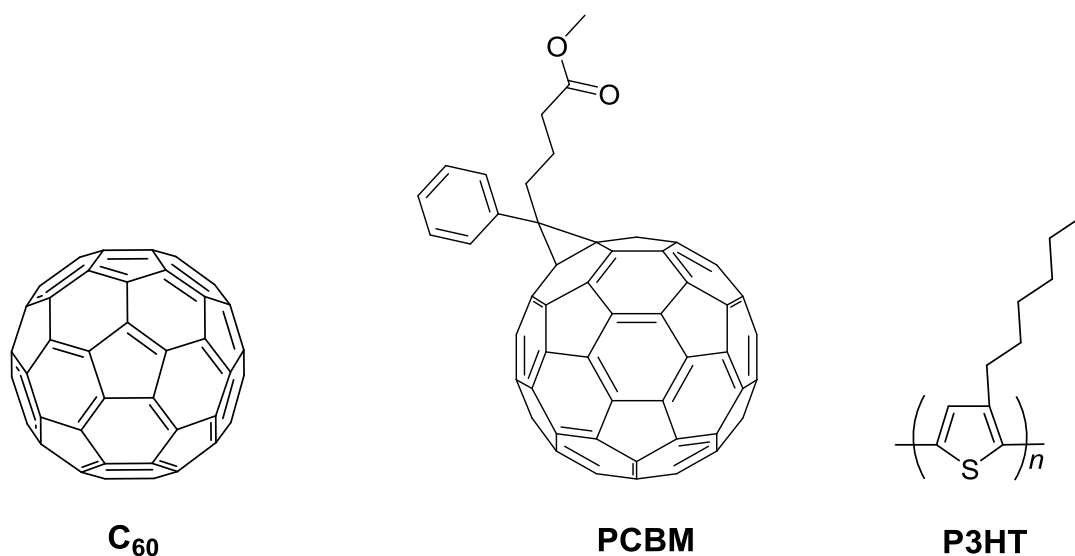
Figure VIII. Preparation of OPV by R2R process (slot-die coating).²¹

Fullerene-containing polymers: Synthesis and application to OPVs

1. Fullerene

As described above, buckminsterfullerene, *i.e.* [60]fullerene, and its derivatives exhibit excellent properties as acceptor materials for OPVs. Fullerene C₆₀, a kind of carbon allotrope was discovered in 1985 by H. W. Kroto, R. F. Curl and R. E. Smalley,²² who were awarded the Nobel Prize in Chemistry in 1996 due to this invention. In 1990, C₆₀ became available in multigram amounts with the preparation procedure by Kratschmer and Huffman.²³ The multigram availability of fullerenes has provided the opportunity for extensive investigation of their functionalization as advanced materials.

Functional C₆₀s can maintain the superior characteristics of pristine C₆₀, such as high electron affinity, small reorganization energy, and superior ability for electron transport, while at the same time they provide desirable processability.¹⁷ For example, PCBM is soluble in common organic solvent and maintain the electronic properties of C₆₀, so that it is widely used as electron acceptor blended with poly(3-hexylthiophene) (P3HT) in BHJ-OPV (**Figure IX**). However, unavoidable drawbacks of PCBM are its morphology, low V_{oc} and stability against long-time light exposure and heat damage.



2. C₆₀-containing polymers: Classifications and application to OPVs

Incorporation of C₆₀ to a polymer, *i.e.* a covalent attachment of C₆₀ moieties to polymer chain, is a promising way to improve the morphology of donor-acceptor blend and to achieve the long lifetime stability of the device.²⁴ This is supported by the fact that chemically-modified C₆₀ derivatives still maintain the electron accepting properties, while the thermal stability increase. Moreover, by the combination of C₆₀ moieties with a donor polymer through covalent linkers, the resulting polymers often exhibit self-assembly and microphase segregation.²⁵⁻²⁷

There are several types of C₆₀-containing polymers (**Figure X**): All carbon, main chain-type, side-chain type, crosslinked-type, and others such as star-shaped and dendrimer-type.²⁸ Among them, side-chain type C₆₀-containing polymer is the most well-known type of C₆₀-containing polymers with potential application to an electron-acceptor for OPVs.

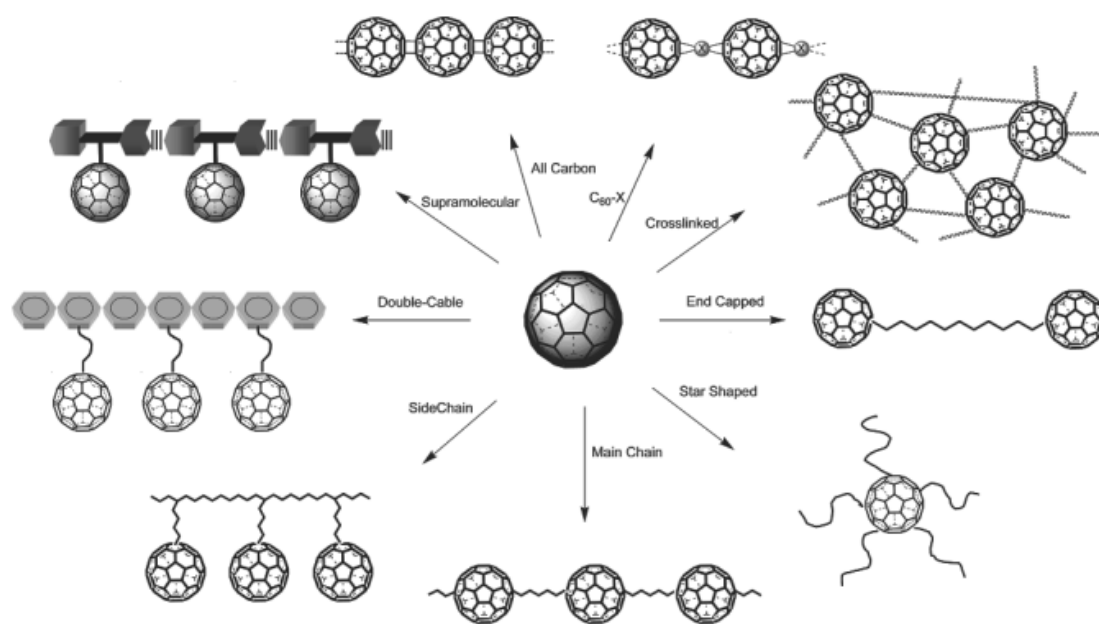


Figure X. Categories of C_{60} -containing polymer.²⁸

The synthetic strategies for the preparation of side-chain type C_{60} -containing polymer are summarized by Giacalone *et al.* in two different approaches:²⁸ (a) Direct introduction of C_{60} or its derivative into a preformed polymer and (b) synthesis of a C_{60} derivative that can be homo- and/or co-polymerized together with other monomers. The approach (a) has been widely explored for the modification of C_{60} , and it is more preferable than the approach (b) to avoid any side reactions during polymerization. For the polymeric backbone, π -conjugated polymers are often selected to prepare a single molecular OPVs device. This molecular design is called “double-cable”, where π -conjugated polymers (donor cable) are covalently bound to C_{60} moieties (acceptor cable). On the other hand, non-conjugated vinyl polymers such as polystyrene and poly(meth)acrylate bearing C_{60} moieties are also reported (**Figure XI**).

There are several reactions to incorporate C_{60} moieties into the polymer side groups. Grafting of C_{60} via Friedel-Crafts reaction onto phenyl pendants of a

polystyrene affords a higher molecular weight polymer (**1**) than expected, because the reaction accompanies crosslinking by multi-substitution to C₆₀.²⁹ Stalmach *et al.* performed atom transfer radical addition (ATRA) catalyzed by CuBr/bipyridine to incorporate C₆₀ into chloromethyl pendant groups of poly(4-chloromethylstyrene) (**2**).³⁰ Thermogravimetric analysis (TGA) revealed that the efficiency of ATRA was 50% so that one C₆₀ moiety was incorporated into two repeating units on average. Wang *et al.* employed [4+2]cycloaddition reaction between C₆₀ and benzocyclobutenone moieties on the side groups of polymethacrylamide (**3**).³¹ In this reaction, a reactive diene might be generated as an intermediate to react with C₆₀. Geckeler and Hirsch synthesized C₆₀-containing polymers (**4** and **5**) by the addition of amine pendant to aromatic double bonds of C₆₀.³² They reported that the reaction was conducted by titration of C₆₀ with poly(ethyleneimine) and poly4-[(2-aminoethyl)imino]methylstyrene. The obtained polymer (**5**) was soluble in carbon disulfide (CS₂) and toluene, which was the first report of soluble C₆₀-containing polymer.

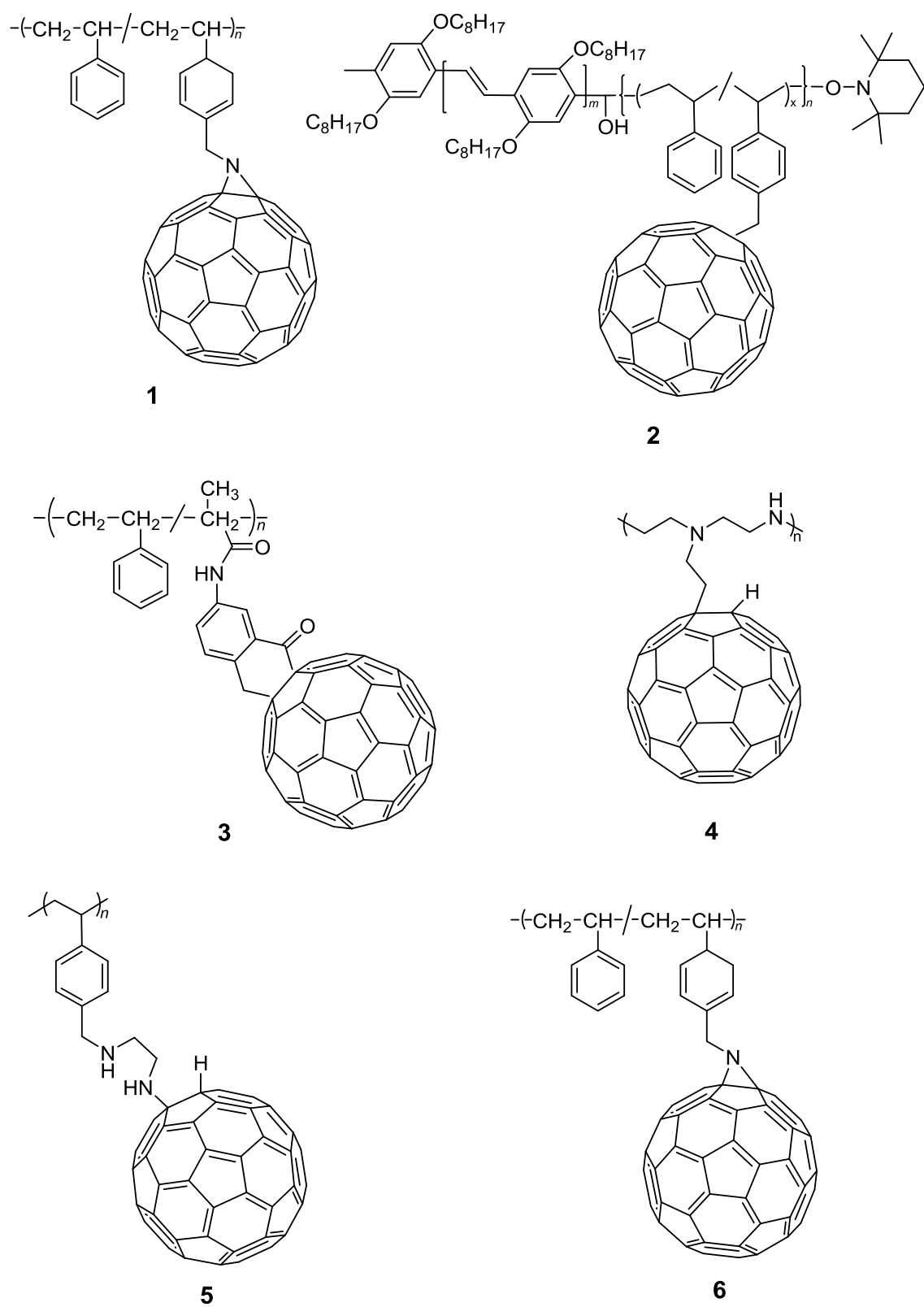


Figure XI. Various types of C₆₀-containing polymers

In 1992, Wudl *et al.* reported the 1,3-dipolar cycloaddition between azide and C_{60} to afford an azafulleroid (**Figure XII**).³³ This is the first example of the reaction between C_{60} and azide. Soon after that, Prato reported the mechanism on the formation of an iminofullerene and the possibility of the isomeric products.^{34, 35} In 1994, Hawker showed that the addition of azides onto C_{60} yields mono-adduct as a main product together with a little amount of multi-adducts.³⁶ Since the mono-adduct is dominant, the reaction can be applied to the preparation of copolymers with a high C_{60} content (**6**, C_{60} content: 29 wt%). The modification of C_{60} with azide-containing polymers has many advantages in comparison to other reactions, such as quantitative yield, facile procedure, and high selectivity. In addition, for OPV application, the absence of metal-catalyst is very favorable, because metal impurity strongly affects the OPVs device performance. Furthermore, recent reports by Park *et al.*³⁷ and Yang *et al.*³⁸ mentioned that the electronic properties of C_{60} derivatives modified by azide groups are conserved well to be used as electron acceptors for OPVs.

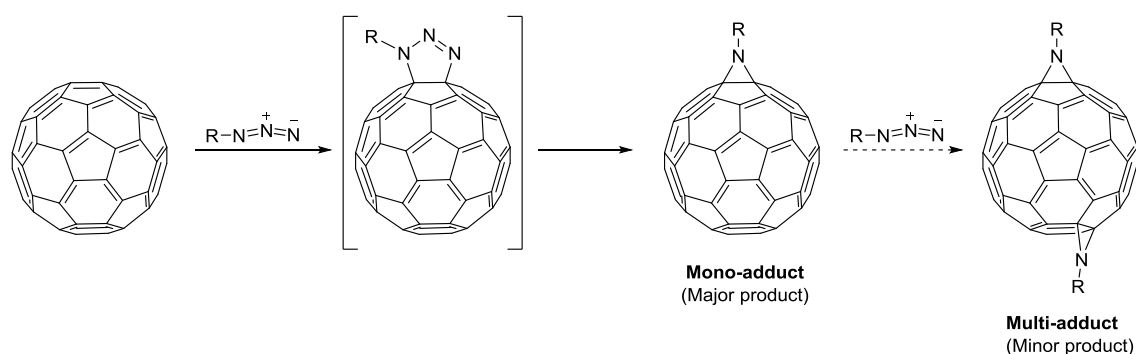
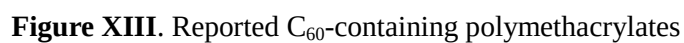


Figure XII. 1,3-Dipolar cycloaddition of azide to C_{60} .

In 2011, Perine *et al.*³⁹ prepared a polystyrene derivative (**6**) similar to that reported by Hawker³⁶ with higher C_{60} contents (~50 wt%).³⁹ However, only the

copolymers whose C₆₀ content was ~40 wt% were truly processable by solution process to prepare OPVs devices.⁴⁰ The optical band gap decreases significantly with the increase of fullerene contents in the polymers. The results demonstrate an insulator to semi-conductor transition by the incorporation of a small amount of C₆₀. A percolation threshold of semiconductor was observed around 5 wt% of C₆₀ content. Nourdine *et al.* measured the electronic properties of these polymers.³⁹ The HOMO level was found to be much lower than that of PCBM, while LUMO was slightly lower. The electron mobility of the polymers was 10 times higher than that of polystyrene:PCBM physical blends. The polymer film formed percolating network, enabling the formation of more homogeneous conduction paths. However, heterogeneous aggregations of C₆₀ moieties induce the rough surface morphology.



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via azide addition, whose maximum C₆₀ content was 13.5 wt%.⁴¹ The resulting C₆₀-containing polymethacrylates has good solubility in common organic solvents such as chloroform (CHCl₃) and tetrahydrofuran (THF). Lu *et al.* reported other types of C₆₀-containing polymethacrylates (**8**) through group transfer polymerization (GTP) and post-polymerization reaction.⁴² A maximum 14.2 wt% of C₆₀ content was achieved. Goh *et al.* investigated the effects of C₆₀ contents on the solubility and miscibility of C₆₀-containing poly(2-hydroxyethyl methacrylate)s (**9**) with different C₆₀ contents (0.6–3.0 wt%).⁴³ Overall, C₆₀-containing polymethacrylates with high C₆₀ content and good solubility in common organic solvents have not been achieved.

Stereospecific living anionic polymerization of (meth)acrylates

As mentioned above, poly(meth)acrylates have fine properties for the application to OPVs. As is known well, the properties of a polymer is often affected by its primary structure such as molecular weight and its distribution, stereoregularity, and end groups, which can be controlled by stereospecific living anionic polymerization. In other words, polymethacrylates that are prepared by typical radical polymerization do not have precisely controlled structure.

Living polymerization, first reported by Szwarc in 1956,⁴⁴ is the most significant way to control molecular weight and its distribution.⁴⁵ Historically, the anionic polymerizations of methacrylates was known to proceed in an *isotactic*-specific manner in non-polar solvents such as toluene, while the controls of molecular weight and its distribution had been recognized difficult due to the presences of some side reactions in the polymerizations, *e.g.* the attack of anionic species to the carbonyl group.^{46, 47} Therefore, numerous efforts have emerged to achieve the living polymerization of (meth)acrylates.^{48, 49} In 1980s, Hatada *et al.* reported an *isotactic*-stereospecific living polymerizations of methyl methacrylate (MMA) in toluene at $-78\text{ }^{\circ}\text{C}$ by using the Grignard reagent, *t*-butylmagnesium bromide ($t\text{-C}_4\text{H}_9\text{MgBr} / \text{MgBr}_2$), as an initiator.^{50, 51} On the other hand, Kitaura *et al.* demonstrated a highly *isotactic*-specific polymerization of MMA by using a combined anionic initiator comprising α -lithioisobutyrate ($\text{Li-}i\text{PrIB}$) and a large excess of lithium trimethylsilanolate (Me_3SiOLi), which afforded PMMA with a degree of *isotacticity* up to 99.5% (**Figure XIV**).⁵²

Kitayama *et al.* reported the *syndiotactic*-specific living polymerization by a binary initiator, *t*-butyllithium / trialkylaluminium ($t\text{-C}_4\text{H}_9\text{Li} / \text{R}_3\text{Al}$).^{53, 54} Recently,

Nishiura *et al.* reported the *syndiotactic*-specific polymerization of MMA by a similar initiator system in dichloromethane (CH_2Cl_2).⁵⁵ The polymerization proceeded more rapidly than in toluene and yielded *syndiotactic*-(*st*-)PMMA (*rr* content = 90%) with narrow molecular weight distribution. In addition, *heterotactic*-specific living polymerization of primary alkyl methacrylates, initiated by *t*- $\text{C}_4\text{H}_9\text{Li}$ in the presence of methylaluminium bis(2,6-di-*t*-butylphenoxide) [$\text{MeAl}(\text{ODBP})_2$] in toluene at low temperature, was also reported.⁵⁶⁻⁵⁸ The same initiator system gave a highly *syndiotactic*-specific polymerization of a bulky methacrylate.⁵⁹

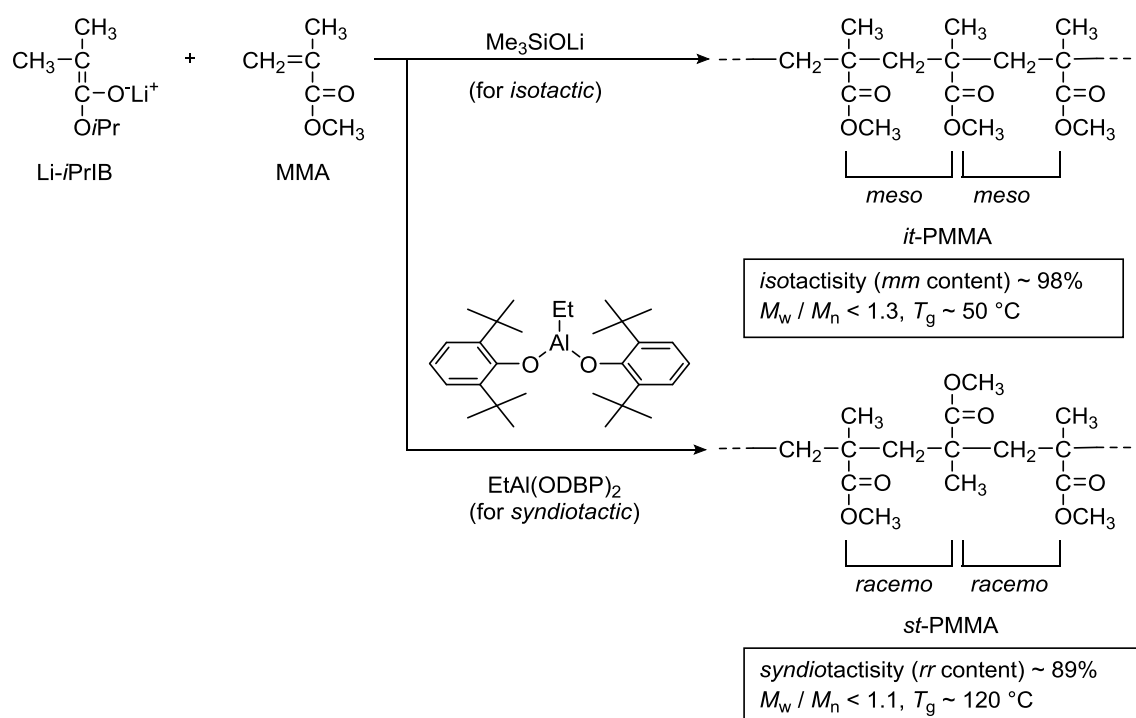


Figure XIV. Stereospecific living anionic polymerizations of MMA with binary initiators.

The combination of *t*- $\text{C}_4\text{H}_9\text{Li}$ / $\text{MeAl}(\text{ODBP})_2$ can also be employed for the polymerization of tertiary alkyl acrylates in a living manner.⁶⁰ Tabuchi *et al.* reported that the polymerization of primary alkyl acrylates initiated by the combination *t*-BuLi /

ethylaluminum bis(2,6-di-*t*-butylphenoxide) [EtAl(ODBP)₂] in toluene proceed in living manner.^{61, 62} The initiator system can also be used for monomer-selective anionic copolymerization of acrylate and methacrylate to yield a block copolymer with a narrow molecular weight distribution.

In this thesis work, these advancements in precision polymer syntheses have been utilized as much as possible for the creation of well-defined OPVs materials.

Outline of this thesis

As mentioned above, novel acceptor materials, *i.e.* fullerene derivatives, with excellent photoelectric properties and good solubilities in common organic solvents are desirable from the viewpoints of the improvements of PCEs and mass production of OPVs. Polymethacrylates bearing C₆₀ moieties are one of the promising candidates, because of the fine properties such as good solubility, high processability, and transparency.

Stereoregularity of polymethacrylates affects the physical properties such as glass transition temperature (T_g),^{48, 52} dielectric constant,⁶³ and crystallization behavior.⁶⁴ Therefore, it is anticipated that C₆₀-polymethacrylates with different stereoregularity might yield different properties in solid state. The control of molecular weight and stereoregularity of precursor polymethacrylates by stereospecific living anionic polymerization is expected to induce regular packing of C₆₀ in thin films and improve the morphology in the blend with P3HT. In this thesis, the author aimed at the synthesis and application of C₆₀-containing polymethacrylates with controlled stereoregularity as potential electron acceptor for OPVs.

The thesis is composed of 4 chapters.

Prior to the control of stereoregularity, the synthesis and fundamental photoelectric properties of C₆₀-containing polymethacrylates are investigated in Chapter 1. The chapter describes the synthesis of C₆₀-containing polymethacrylates which are highly soluble in common organic solvents such as CHCl₃ and THF with high C₆₀ contents (~ 41 wt%) (**Figure XV**). Precursor polymers were prepared by radical polymerization followed by azide modification. 1,3-Dipolar cycloaddition of azide to C₆₀ was employed to incorporate C₆₀ into the side groups of polymethacrylates. The

properties of the obtained polymers relevant to OPVs applications are also investigated.

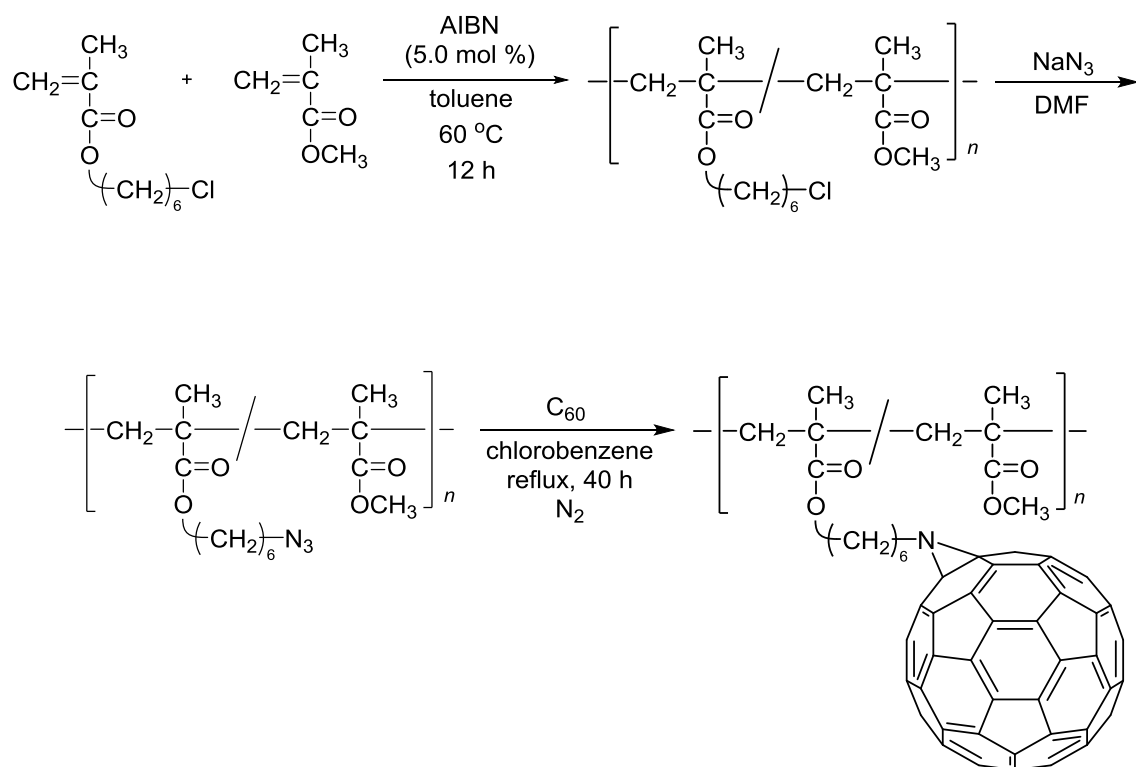


Figure XV. Synthesis of C₆₀-containing polymethacrylates.

In Chapter 2, the synthesis of *stereoregular* C₆₀-containing polymethacrylates according to the molecular design described in Chapter 1 was investigated. Stereospecific anionic (co)polymerizations of 6-chlorohexyl methacrylate (CHMA) and MMA with different CHMA contents were conducted to control the molecular weights and stereoregularities. The subsequent polymer modifications allowed incorporation of C₆₀ moieties into *isotactic* and *syndiotactic* polymethacrylate backbones. The controlled molecular weights with narrow distributions of the precursor polymers also revealed the side reaction, multi-addition of azide to the C₆₀ moieties, which lead to the decreased yield of THF-soluble fractions in the product due to the cross-linking.

In Chapter 3, the comparisons of the photoelectric properties, *i.e.* HOMOs, LUMOs, band gaps and fluorescences, between *atactic* and *syndiotactic* C₆₀-polymethacrylates prepared by radical and anionic polymerizations are presented. It was found that the surface morphology as well as the OPV device performances of the *syndiotactic* polymer was much better than those of *atactic* polymers, suggesting that the controls of stereoregularity and molecular weight had significant effects.

Chapter 4 describes monomer-selective anionic copolymerization to yield a block copolymer comprising two segments which are independently modified quantitatively via click chemistry. The process via monomer-selective block copolymerization by one-shot monomer injection and click chemistry is very unique, convenient, and facile that it is promising to afford block copolymers bearing donor and acceptor moieties on the pendants of each segment, which may function as a single molecular OPVs device.

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Chapter 1

Synthesis and properties of C₆₀-containing polymethacryates through radical polymerization

1.1 Introduction

An active layer of organic photovoltaics (OPVs) generally comprises an electron-donor and an acceptor materials which are either small organic molecules or polymers.¹ Despite of the fast growing research activity on the development of electron-donor materials,¹ relatively limited numbers of electron-acceptor compounds have been explored. Several typical examples that have been well studied are perylene diimide,² diketopyrrolepyrrole (DPP),³ [60]fullerene (C₆₀) and its derivatives.⁴⁻⁶ Among them, C₆₀ is considered as the most promising candidate not only in fundamental research⁷ but also in practical applications,⁸ because C₆₀ has superior optoelectronic properties such as high electron-acceptability, slow back-electron-transfer, small rearrangement energy, and formation of triplet exciton as prerequisites to accept electron.⁹ In fact, combined with donor polymers such as poly(3-hexylthiophene) (P3HT) in the active layer of OPVs, C₆₀ and its soluble derivative, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM),¹⁰ have been demonstrated to improve the overall efficiency.^{11, 12}

Organic thin-film solar cells (OTFSCs) can be prepared by the deposition method or coating method. Although the former provides OTFSCs of highly purified

materials through sublimation process, the expensive cost remains a significant issue.¹³ In contrast, the latter is expected to be able to manufacture OPVs at low cost.¹⁴ Particularly, roll-to-roll (R2R) process is a prospective method toward large area fabrication.¹⁵ R2R process demands both electron-donor and acceptor materials with high solubility as well as good compatibility with buffer layers to form ideal microphase separation in an active layer. There are many candidates for electron donor materials with high solubility, film formability and electronic performance,¹⁶ whereas soluble electron acceptors with high electronic performance, that is, soluble C₆₀ derivatives are, still limited.¹⁷ In fact, PCBM was used as a soluble C₆₀ in the most cases of OPVs prepared by the R2R process.^{15, 18}

As is well known, the incorporation of C₆₀ moieties into a polymeric backbone through a flexible linker improves the solubility of C₆₀.¹⁹ Furthermore, some specific effects, *e.g.* an improvement of electron mobility,²⁰ a change of miscibility / morphology with P3HT,²¹ were reported for C₆₀-bearing polymers. In particular, incorporation of C₆₀ moieties into the side groups of polymethacrylates is an interesting subject, because the fine properties of polymethacrylates such as good solubility, high processability, higher glass transition temperature (T_g) and thermal stability, transparency, and superior weatherability are attractive for the application to OPVs. Furthermore, polymethacrylates with various primary structures can be prepared by stereospecific anionic polymerization to afford high stereoregularity polymethacrylates and controlled molecular weight.²²⁻²⁸ To the best of our knowledge, the first example of polymethacrylate bearing C₆₀ was reported by Lu *et al.* as copolymers with methyl methacrylate (MMA)²⁹ and *n*-butyl methacrylate.³⁰ Later, Goh *et al.* have reported similar copolymers with 2-hydroxyethyl methacrylate (HEMA).³¹ However, the

contents of C₆₀ in such copolymers are still low (< 15 wt%) and their photoelectric properties for OPV application has never been investigated.

In this chapter, the synthesis of polymethacrylates having highly soluble in common organic solvents, such as chloroform (CHCl₃) and tetrahydrofuran (THF), and high C₆₀ contents (~ 41 wt%) is described. Precursor polymers were prepared by radical polymerization followed by azide modification. 1,3-Dipolar cycloaddition of azide to C₆₀ was employed to incorporate C₆₀ into the side groups of polymethacrylates.^{32, 33} This reaction was reported by Hawker as a facile method to afford C₆₀ containing polymers with high C₆₀ content.³² In addition, because the reaction requires no metal catalysts, which often remain in the product and deteriorate the performance of OPVs, the purification of the final product becomes easy. The properties of the obtained polymers relevant to OPV applications are also investigated.

1.2 Experiments

Instruments

^1H NMR spectra were recorded in CDCl_3 (Aldrich) on a JNM-ECS 400 (JEOL) spectrometer. Chemical shifts in ^1H NMR spectra were referred to the signal of tetramethylsilane. Molecular weight and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on a GPC-900 chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm $\times$ 7.5 mm), Polymer Laboratories], using tetrahydrofuran (THF) as an eluent (flow rate = 0.8 mL min $^{-1}$), and calibrated against standard poly(methyl methacrylate) (PMMA) samples (Shodex, MW: 1.25×10^6 , 6.59×10^5 , 1.95×10^5 , 4.96×10^4 , 2.06×10^4 , 6.82×10^3 , 2.00×10^3). IR spectra were recorded in KBr disc with an FT/IR-410 Fourier-transform infrared spectrophotometer (JASCO). Purities of monomers were determined from the gas chromatogram (GC) recorded on a GC-2014 (Shimadzu) equipped with an HP-5 capillary column (Hewlett-Packard). Thermogravimetry / differential thermal analysis (TG/DTA) were performed with an EXSTAR TG/DTA6000 (SII Nano Technology) (scan rate = 20 °C min $^{-1}$) under N_2 atmosphere (flow rate = 100 mL / min). Differential scanning calorimetry (DSC) was recorded on an EXSTAR 6200 (SII Nano Technology) (scan rate = 10 °C min $^{-1}$) under N_2 atmosphere (flow rate = 100 mL min $^{-1}$). HOMO energy was determined by photoelectron spectroscopy (PESA) with an AC2 (Riken Keiki).

Materials

MMA was distilled over CaH_2 under reduced pressure just before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from benzene solution. Silica gel

(Wako Pure Chemical, Wakogel C-400HG) was used for flash column chromatography. C₆₀ (Aldrich, Purity: 98%) and PCBM (Aldrich, Purity > 99%) were used for polymer reaction. P3HT (Aldrich, $M_n = 5.4 \times 10^3 - 7.5 \times 10^3$ g/mol, $M_w / M_n \leq 2.5$) was used as an electron-donor material. Chlorobenzene was purchased from Nacalai Tesque. Tetrahydrofuran (THF), hexane, chloroform (CHCl₃), *N,N* dimethylformamide (DMF), were purchased from WAKO Pure Chemical Industries. All other reagents and solvents were used as received.

Synthesis of 6-chlorohexyl methacrylate (CHMA)

To a mixture of 6-chlorohexanol (25.0 mL, 0.190 mol) and methacrylic acid (66.7 mL, 0.760 mol) *conc.* H₂SO₄ (2.0 mL, 36 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 24 h and poured into *sat.* aq NaHCO₃ (100 mL). The product was extracted with Et₂O (100 mL × 2) and washed with brine (100 mL). The combined organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified on silica gel flash column chromatography [eluent: hexane / ethyl acetate (v / v = 6 / 1, Rf: 0.3)] to give CHMA (27.2 g) as colorless oil. Yield 69.9%; purity 100%; ¹H NMR (400 MHz, 30 °C, CDCl₃): δ 6.09 (m, 1H, *CHH*), 5.56-5.54 (m, 1H, *CHH*), 4.15 (t, *J* = 7.1 Hz, 2H, 1-CH₂), 3.53 (t, *J* = 6.6 Hz, 2H, 6-CH₂), 1.94 (s, 3H, α-CH₃), 1.83-1.76 (m, 2H, 2-CH₂), 1.73-1.66 (m, 2H, 5-CH₂), 1.53-1.46 (m, 2H, 3-CH₂), 1.46-1.38 (m, 2H, 4-CH₂). Density = 1.02 g mL⁻¹.

Copolymerization of CHMA with MMA

A typical procedure (Table 1, Run 1): To a toluene (6.0 mL) solution of MMA

(0.578 mL, 5.40 mmol) and CHMA (0.123 g, 0.600 mmol) was added AIBN (49 mg, 0.300 mmol). The reaction mixture was degassed three times by freeze-pump-thaw, and N₂ gas was introduced. The reaction mixture was heated at 60 °C for 12 h, cooled to room temperature, and poured into hexane (200 mL). The precipitate was collected by centrifugation and dried *in vacuo* to yield the polymer (**PCI-1**, 0.685 g) as a colorless solid.

Azidation of polymethacrylates

A typical procedure: To a solution of **PCI-1** (500 mg, 0.20 mmol per chlorine atom) in DMF (2.0 mL) was added NaN₃ (0.260 g, 4.00 mmol). The reaction mixture was stirred at 60 °C for 24 h and poured into water (40 mL) - CH₃OH (160 mL) cosolvent. The precipitate was collected by filtration, washed with water, and dried *in vacuo* at room temperature for 12 h to yield **PN₃-1** (262 mg, 52.4%).

Synthesis of C₆₀-containing Polymethacrylates

A typical procedure: A solution of **PN₃-1** (80 mg, 62 μmol per azide group) and C₆₀ (24 mg, 33 μmol) in chlorobenzene (27 mL) was degassed three times by freeze-pump-thaw and refluxed for 48 h under N₂ atmosphere. The reaction mixture was concentrated on a rotary evaporator. The residual solids were stirred in THF, and the insoluble fraction was removed by centrifugation. The soluble fraction was poured into hexane (200 mL) to reprecipitate the polymer. This process was repeated several times until no traces of C₆₀ on thin layer chromatography (TLC) plate (eluent: toluene, R_f = 0.9) were observed. The product was dried *in vacuo* at 40 °C for 12 h. For further optoelectronic analysis, the product was purified by preparative SEC on a NEXT (Japan

Analytical Industry) equipped with JAIGEL-ODS-AP-50 column (Japan Analytical Industry) in CHCl_3 as eluent.

Fluorescence quenching measurement

Films of the blend of P3HT:PCBM and P3HT:**PC₆₀-2** (w / w = 1 / 1, per C₆₀ moieties) were spin coated on glass substrates at 800 rpm for 30s from chlorobenzene solution with concentration 1 wt%. All films were excited at wavelength 508 nm and fluorescence emission was recorded over 800-1100 nm on a Fluorolog fluorescence spectrometer (HORIBA).

Cyclic voltammetry

Cyclic voltammetry (CV) measurements were carried out in a solution with a three-electrode cell configuration consisting of a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode at room temperature. Measurements were conducted using a solution of PCBM, **PC₆₀-2** in CH_2Cl_2 and 0.1 M tetrabutylammonium tetrafluoroborate ($\text{Bu}_4\text{N}^+\text{BF}_4^-$) was used as a supporting electrolyte. The reduction potentials were recorded at a scan rate of 10 mV s^{-1} and reported with reference to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

Photoelectron spectroscopy in air (PESA) analysis

ITO-coated substrates having area $1.0 \text{ cm} \times 2.0 \text{ cm}$ (Asahi Glass, $15 \text{ } \Omega/\text{sq}$) were solvent-cleaned in an ultrasonic cleaner by the following sequential manner (each step was 5 minutes); rinsed in distilled water, detergent (2 vol%), flowing tap water, distilled water, acetone, and isopropanol. Subsequently, the substrates were dried and

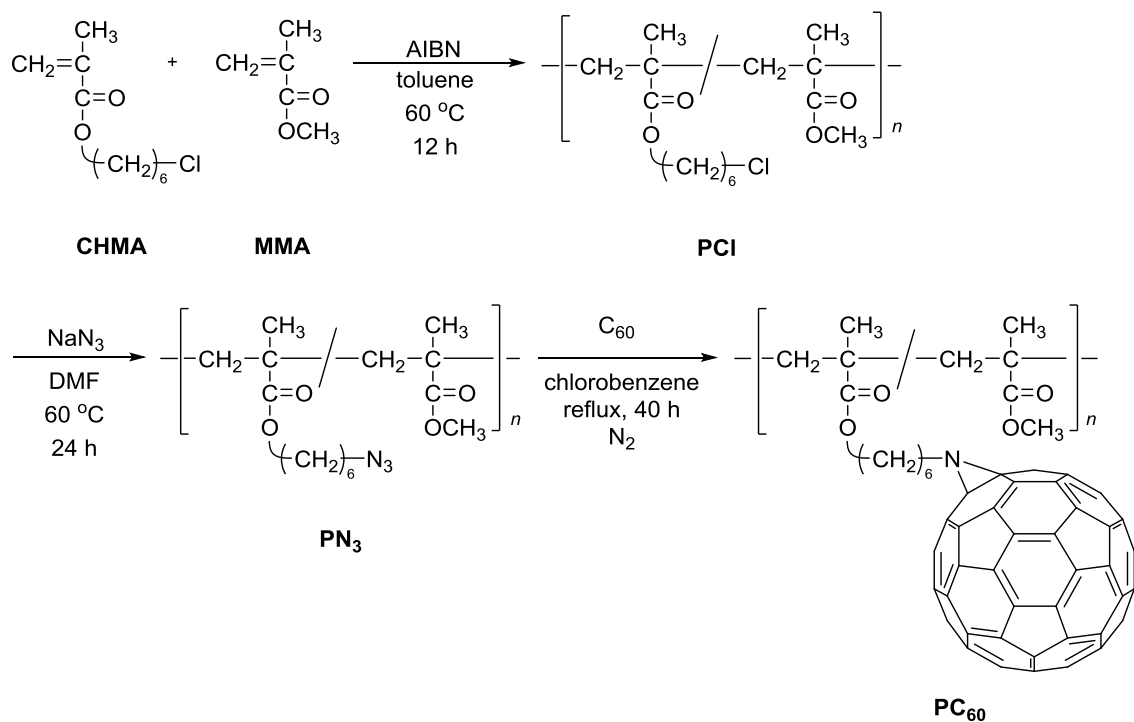
treated with UV-O₃ for 1200 s. A 1 wt% solution of **PC₆₀-2** in CHCl₃ was spin coated on a pre-cleaned glass substrate at the rate of 500 rpm for 30s under N₂ atmosphere. The samples were stored under N₂ atmosphere prior to analysis. HOMO energy was determined by photoelectron spectroscopy (PESA) with an AC2 (Riken Keiki).

1.3 Results and Discussion

1.3.1 Synthesis and characterization of polymethacrylates bearing C_{60}

In order to incorporate C_{60} moieties into polymethacrylate, 1,3-dipolar cycloaddition reaction of azide to C_{60} is known quantitative.³⁴ In fact, the first polymethacrylate bearing C_{60} was synthesized by Lu *et al.* through the 1,3-dipolar cycloaddition reaction of copolymers of 3-azidopropyl methacrylate with MMA, although the C_{60} content was low (~ 13.5 wt%).³⁵ In order to improve the C_{60} content and yield of soluble fraction, 6-azidohexyl methacrylate (AzHMA) was used as a monomeric unit of prepolymer, because flexible hexylene spacer was expected to render more space for C_{60} moieties to be attached as well as to enhance the solubility of the corresponding C_{60} -polymers owing to the higher flexibility of the longer alkyl spacer.

Since a treatment of azide monomer sometimes causes an explosion accident, azide groups are introduced after the polymerization. 6-Chlorohexyl methacrylate (CHMA) was radically copolymerized with MMA in various compositions (**Scheme 1-1**, **Table 1-1**). In any runs, the resulting copolymers have monomer compositions which are in good agreement with the feeds. Subsequently, azidation of the obtained copolymers with NaN_3 was conducted in DMF at $60\text{ }^\circ\text{C}$ for 24 h, yielding the copolymers composed of AzHMA units. In ^1H NMR spectra (**Figure 1-1**), the shift of 6- CH_2 signal from 3.56 ppm to 3.33 ppm was observed after the azidation, indicating quantitative conversion. It was also confirmed by the appearance of azide absorption band (2095 cm^{-1}) in the IR spectrum (**Figure1- 2**).



Scheme 1-1. Synthesis of polymethacrylates bearing C₆₀.

Table 1-1. Copolymerization of MMA with CHMA.^a

Run	Polymer	CHMA content /%		Yield /%	$M_n^c/10^3$ SEC	M_w^c M_n
		Feed	Results ^b			
1	PCI-1	10	8.5	95.3	9.8	2.08
2	PCI-2	20	19	79.2	9.9	2.14
3	PCI-3	50	48	80.5	11.5	2.35
4	PCI-4	80	76	67.0	28.7	1.74
5	PCI-5	100	100	98.7	15.7	2.42

a) Copolymerization was initiated by AIBN (0.30 mmol) with monomers (6.0 mmol) in toluene (6.0 mL) at 60 °C for 1 h.

b) Determined from ¹H NMR spectroscopy (400 MHz, CDCl₃, 55 °C)

c) Estimated by SEC (PMMA standards, THF, 40 °C).

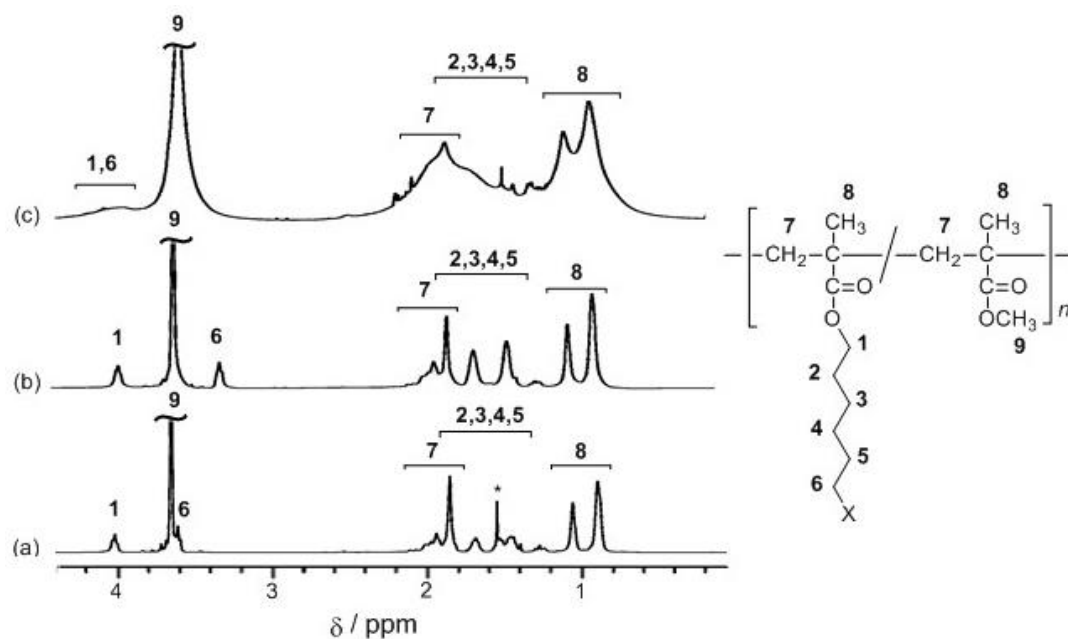


Figure 1-1. ^1H NMR spectra of (a) PCI-2, (b) PN₃-2, and (c) PC₆₀-2 (400MHz, CDCl₃, 55 °C).

o : water

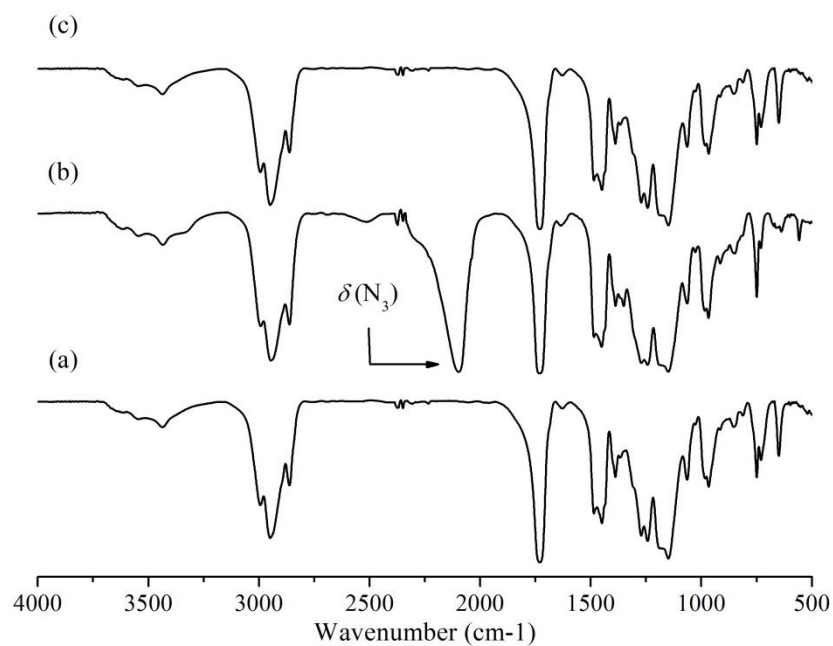


Figure 1-2. IR spectra of (a) PCI-2, (b) PN₃-2, and (c) PC₆₀-2.

C₆₀ was reacted with the obtained (co)polymers in chlorobenzene under reflux for 40 h, and the THF-soluble fractions were extracted from the products. The yields of

the soluble fractions decreased as the composition of AzHMA units in the copolymers increased (**Table 1-2**). In particular, **PN₃-4** with AzHMA unit content of 76 % (Run 4) and the homopolymer, **PN₃-5** (Run 5) yielded no soluble fraction. Aiming at improving the yield of soluble fraction, PCBM, a common fullerene derivative with good solubility, was used instead of C₆₀ (Run 6). However, the reaction of PCBM with **PN₃-2** resulted in a slight decrease of the yield. In ¹H NMR spectra (**Figure 1-1**), the signal assignable to 6-CH₂ group shifted from 3.33 ppm to 3.98 ppm, overlapping with 1-CH₂, which indicates the complete consumption of azide groups. However, the content of C₆₀-methacrylate units in **PC₆₀s** could not be determined precisely from the intensity ratio of these signals to 1-CH₂ signals due to severe broadening of the peaks. The complete proceedings of click reaction was also confirmed by IR spectra (**Figure 1-2c**), where the disappearance of the azide absorption band (2095 cm⁻¹) was evident. UV-vis spectrum in CHCl₃ solution (**Figure 1-3**) exhibited broad band from 300 to 800 nm with a maximum absorption at 330 nm characteristic to C₆₀ moieties.

Table 1-2. Preparation of polymethacrylates possessing fullerene moieties.

Run	Precursor	Product	Azide content	Yield	$M_n^a/10^3$	M_w^a	C ₆₀ content ^b	
			mol %	%	SEC	M_n	wt %	mol % ^c
1	PCI-1	PC₆₀-1	8.5	56	10.6	2.16	27.4	5.5
2	PCI-2	PC₆₀-2	19	67	10.2	2.77	41.4	10.8
3	PCI-3	PC₆₀-3	48	34	23.4	3.13	39.9	10.1
4	PCI-4	PC₆₀-4	76	0	—	—	—	—
5	PCI-5	PC₆₀-5	100	0	—	—	—	—
6	PCI-2	P(PCBM)	19	59	11.5	2.66	37.9	11.0

a) Estimated by SEC (PMMA standards, THF, 40 °C).

b) Residual mass after heating up to 550 °C by TGA.

c) Composition of C₆₀-methacrylate units based on the mono-adduct model as described in **Scheme 1-1**.

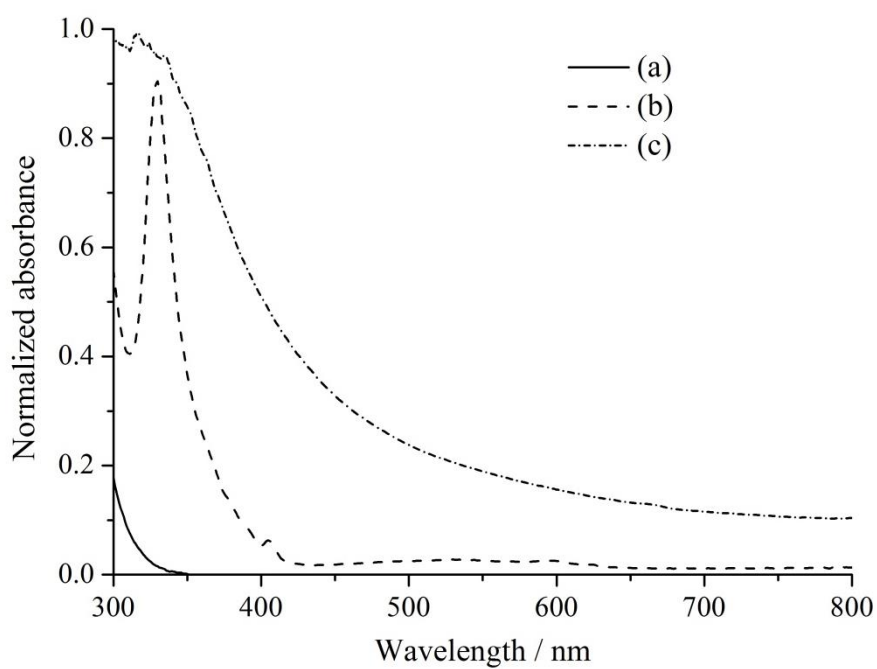


Figure 1-3. UV-Vis spectra of (a) $\text{PN}_3\text{-2}$, (b) C_{60} and (c) $\text{PC}_{60}\text{-2}$ in CHCl_3 .

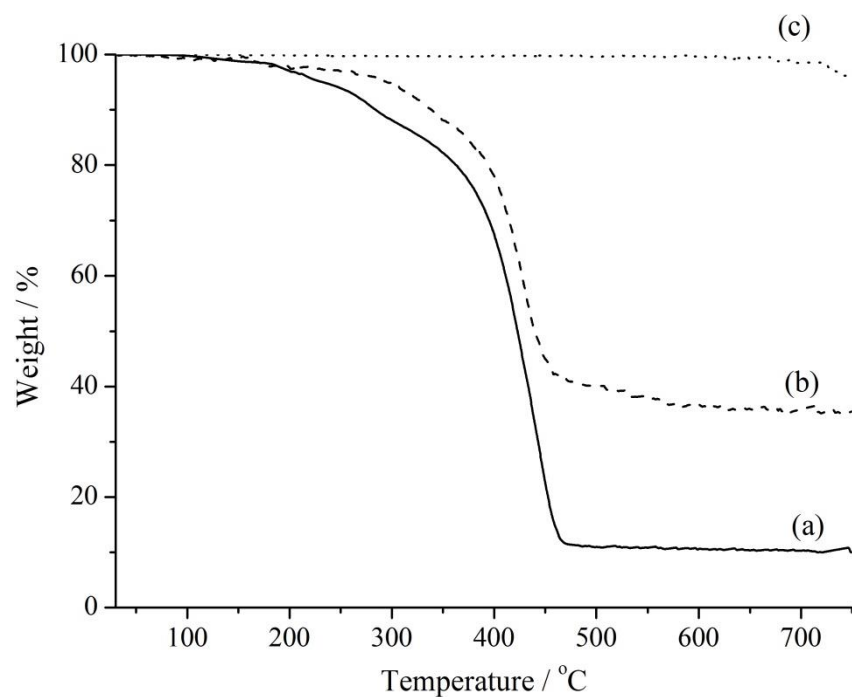
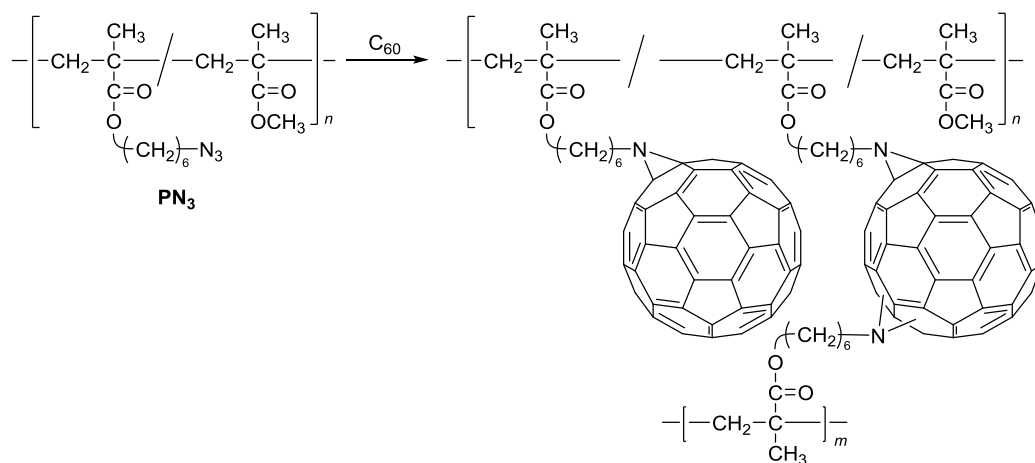


Figure 1- 4. TGA curves of (a) PMMA ($M_n = 5800$, $M_w/M_n = 2.5$), (b) $\text{PC}_{60}\text{-2}$ and (c) C_{60} under N_2 atmosphere.

Since the ^1H NMR spectra of the C_{60} modified polymers are so broad that the compositional analyses were difficult. It is well known that polymethacrylates undergo thermal degradation at temperatures below $400\text{ }^\circ\text{C}$ in an unzipping manner predominantly leaving monomer molecules as a volatile decomposition products,³⁶ while C_{60} is stable under the same condition. Thus, the C_{60} moiety contents in the polymers were estimated by thermogravimetric analysis (TGA) as the degradation residue. **Figure 1-4** shows the TGA curves of PMMA ($M_n = 5800$, $M_w/M_n = 2.5$), C_{60} and **PC₆₀-2** under N_2 atmosphere. While C_{60} does not show weight loss up to $550\text{ }^\circ\text{C}$, PMMA decomposed almost completely at $550\text{ }^\circ\text{C}$. Thus, the weight contents of C_{60} moieties in **PC₆₀-2** were roughly estimated as 41.4 wt% from the residual mass at $550\text{ }^\circ\text{C}$, which might include a small amount of ashes of the polymer backbone. Consequently, the content of C_{60} -methacrylate unit was 10.8 mol%, if we can ignore the contribution of the addition of several azides to a single C_{60} moiety (**Scheme 1-2**). The contents of C_{60} moieties for other copolymers were determined in a similar manner (**Table 1-2**) and were less than those of the AzHMA units in the corresponding azide polymers. In particular, **PC₆₀-2** and **PC₆₀-3** gave only slight different C_{60} content of 10.8 and 10.1 mol%, though their precursor polymers had different compositions.

There are several possibilities to explain these results; (i) the decomposition of azide during the reaction, (ii) the insolubility of macromolecules which have more than 41.4 wt% of C_{60} -methacrylate units in THF, and (iii) the addition of azide at the multi-points on a C_{60} moiety which may cause cross-linking (**Scheme 1-2**). To confirm the stability of the azide group, a control experiment was carried out by using **PN₃-2** under reaction condition similar to the preparation of **PC₆₀-2**. Apparently, azide group of **PN₃-2** endured the reflux condition in chlorobenzene as proved by ^1H NMR spectra

(**Figure 1-5**). The content of azide group remained constant after 40 h. This result confirmed that all azide groups were reacted with C₆₀ molecules. Thus, the possibility (i) is inadequate. In other words, the poor solubility of C₆₀-containing polymethacrylates and/or cross-linking might cause the lower C₆₀-contents than expected. Nevertheless, the C₆₀ content of 41.4 wt% was the highest among reported polymethacrylates.³⁷ In order to improve the solubility of the product, PCBM was used instead of C₆₀ (Run 6). However, the content of C₆₀ moiety did not increase (37.9 wt%).



Scheme 1-2. Possible side-reaction on the incorporation of C₆₀.

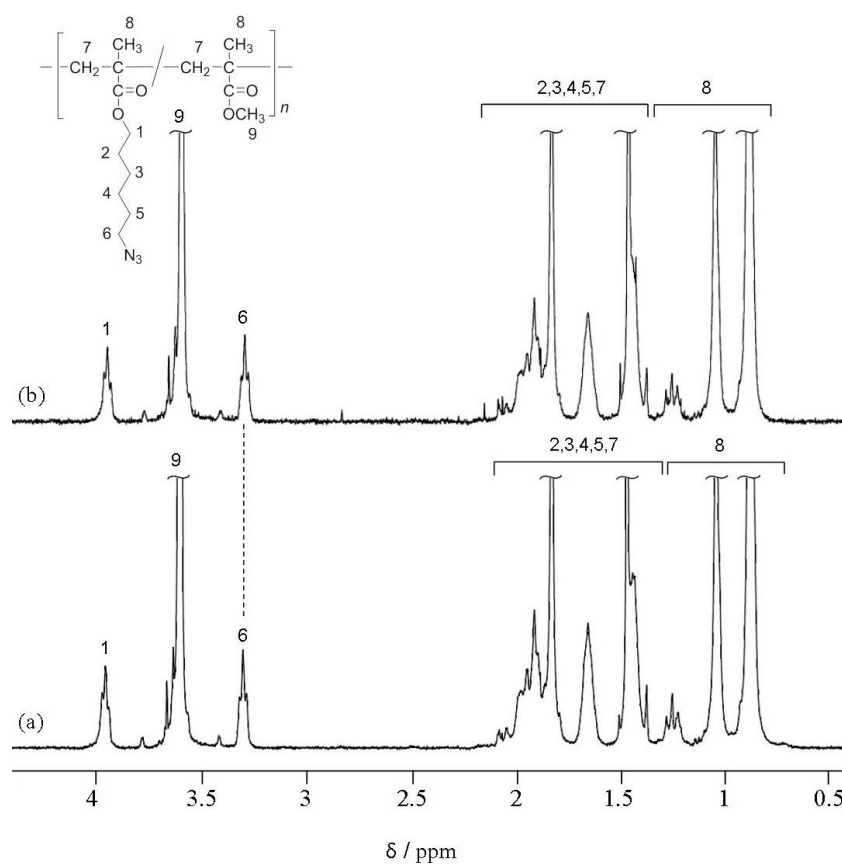


Figure 1-5. ^1H NMR spectra of **PN₃-2** under reflux condition in chlorobenzene for: (a) 0 h and (b) 40 h (400 MHz, CDCl_3 , 55 $^\circ\text{C}$).

It was noteworthy that the obtained C_{60} -containing polymers (**PC₆₀s**) as THF-soluble fractions also exhibited high solubilities in CHCl_3 and toluene which are common solvents for P3HT, a donor polymer. The high contents of C_{60} in the polymers with good solubilities are promising for manufacturing OPVs by a solution process.

SEC traces of **PC₆₀** in THF shifted toward the higher molecular weight region from those of precursor **PCI**'s with broadening (**Figure 1-6**); *e.g.* number-average molecular weight (M_n) and its dispersity (M_w/M_n) of **PC₆₀-2** were 10200 and 2.77, whereas those of the precursor were 9900 and 2.14, respectively. However, considering the content of C_{60} moieties, the observed molecular weight was lower than expected. A similar result was also reported by Krauss and Müllen,³⁸ who attributed the results to the interaction between C_{60} -moieties and SEC packing material (polystyrene gel).

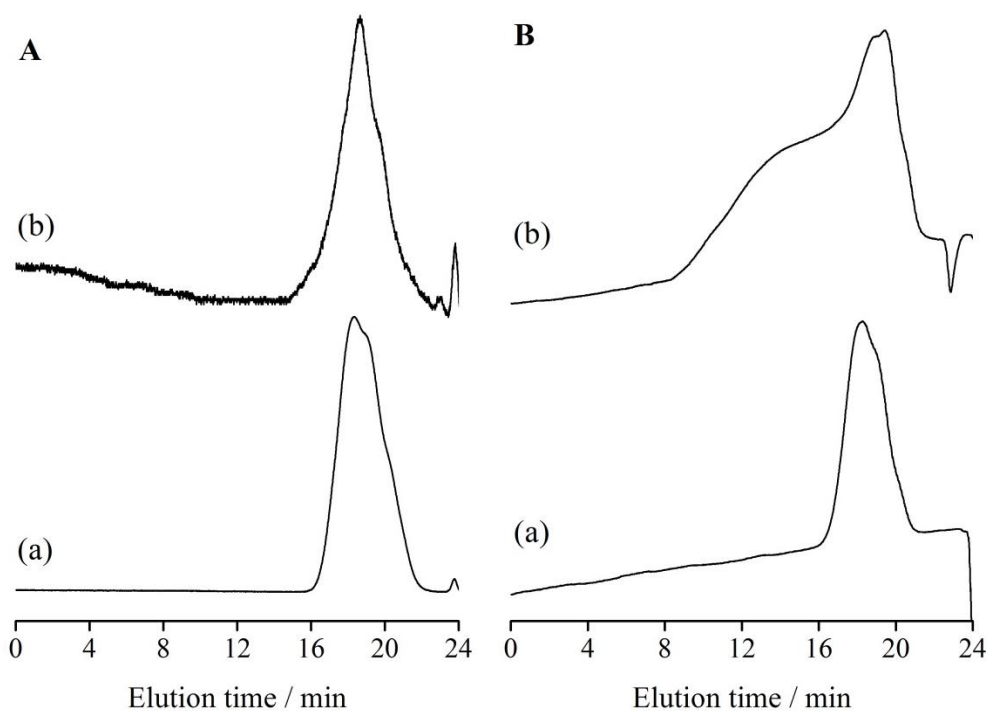


Figure 1-6. SEC traces of (a) **PCl-2**, (b) **PC₆₀-2** in **A:** THF and **B:** CHCl₃, respectively.

Interestingly, SEC traces in CHCl₃ (**Figure 1-6B**) exhibited broad and multimodal peaks spreading over a wide range of molecular weights from exclusion limit of the SEC column employed, suggesting intermolecular self-aggregation in CHCl₃. The SEC traces also spread to the area of lower molecular weight than their precursors. Thus, in addition to inter-chain aggregation, intra-chain aggregation, that is the self-aggregation of C₆₀ moieties on a single macromolecular chain, might occur.³⁹

1.3.2 Photoelectric properties of polymethacrylates bearing C_{60}

As the photoelectric properties are very sensitive to the impurity in fullerene-containing materials,^{40, 41} **PC₆₀-2** was thoroughly purified by preparative SEC. The chromatogram of **PC₆₀-2** after several reprecipitation procedure showed a trace amount of unreacted C_{60} (detailed descriptions are given in Chapter 3, page 100), suggesting that reprecipitation was not enough to remove C_{60} completely.

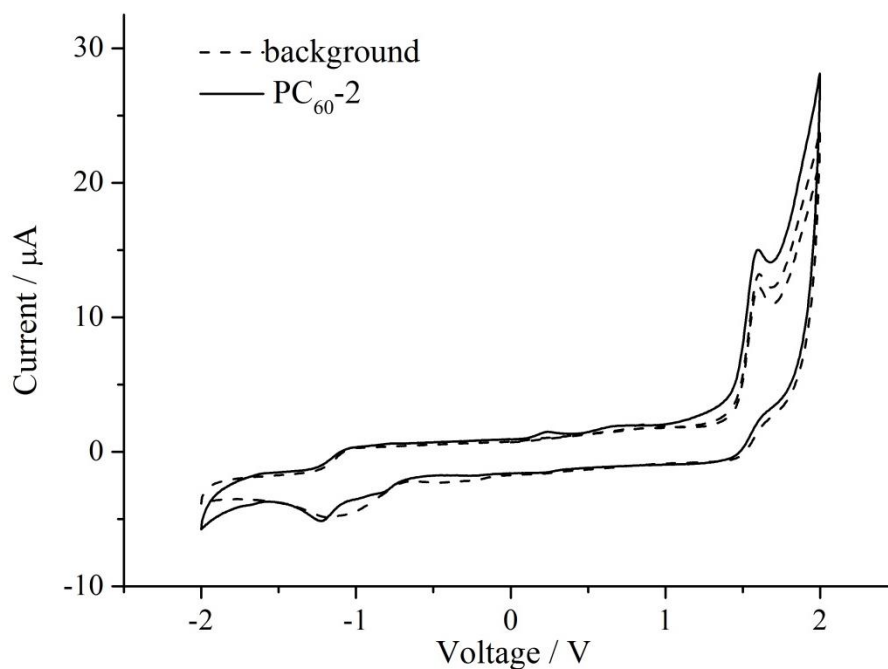


Figure 1-7. Cyclic voltammograms of **PC₆₀-2** in CH_2Cl_2 solution with 0.1 M $Bu_4N^+BF_4^-$ as a supporting electrolyte.

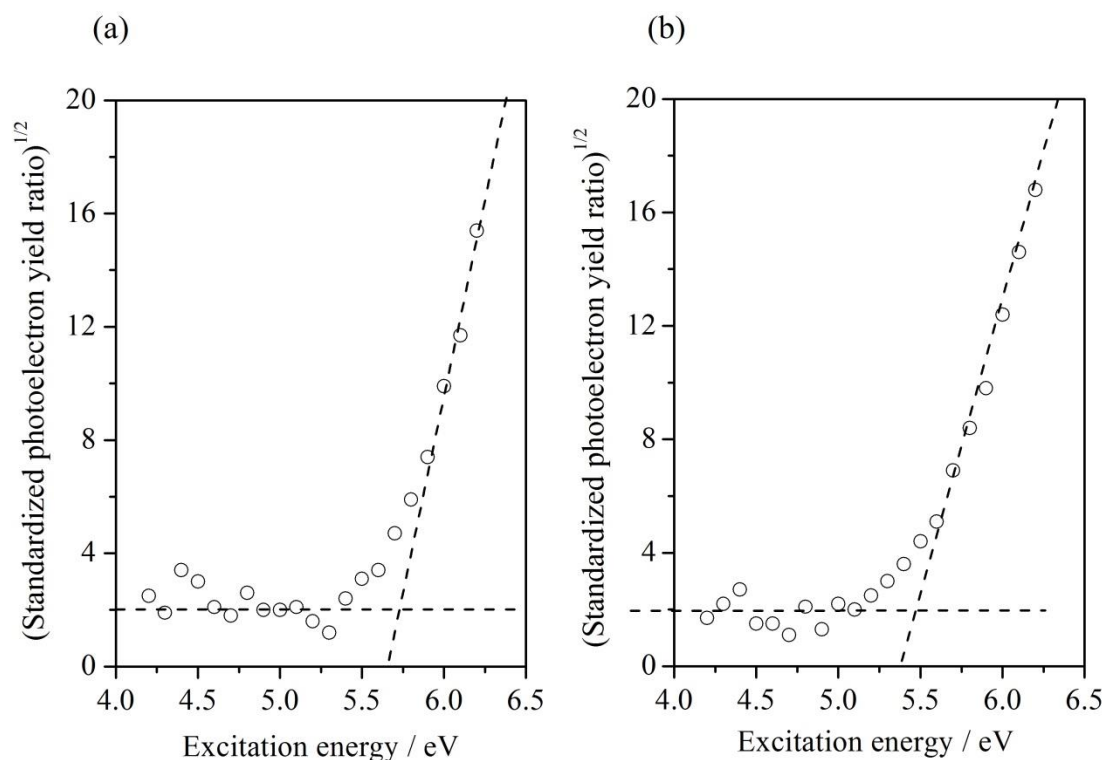


Figure 1-8. Photoelectron spectroscopy analyses in air of **PC₆₀-2** (a) before and (b) after purification.

In order to estimate the HOMO level of **PC₆₀-2**, cyclic voltammetry (CV) measurement was carried out in CH₂Cl₂ solution with 0.1 M Bu₄N⁺BF₄⁻ as a supporting electrolyte (**Figure 1-7**). However, no clear peak was observed. Thus, HOMO level was determined by an alternative way, photoelectron spectroscopy in air (PESA) (**Figure 1-8**). The HOMO level of **PC₆₀-2** after purification by column chromatography was determined to be -5.5 eV from the threshold of PESA, while the value before purification was -5.7 eV. The different values of HOMO energy before and after purification (0.2 eV) are possibly due to the effects of unreacted C₆₀. Hence, thorough purification by preparative SEC gave clear information about the HOMO level of the pure C₆₀-polymethacrylates for OPV application.

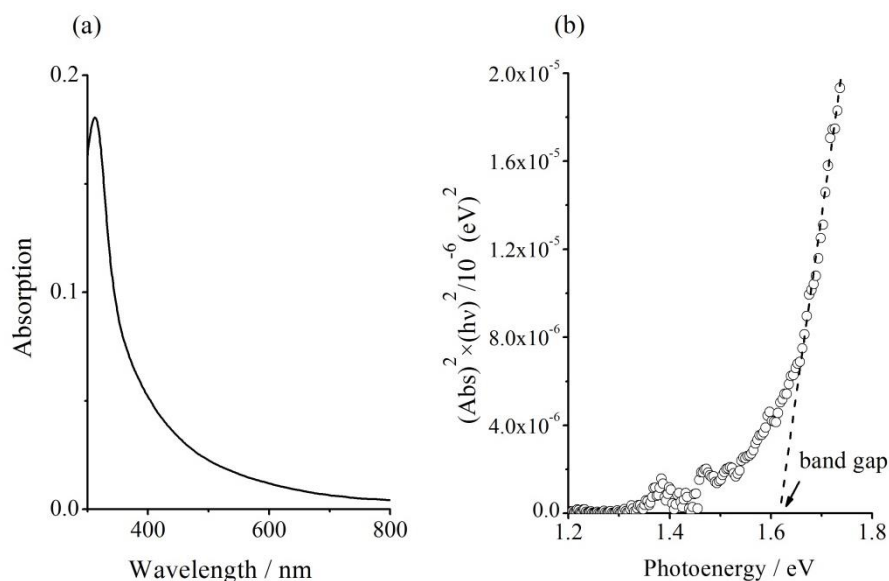


Figure 1-9. (a) UV-Vis spectrum of a **PC₆₀-2** film and (b) plots according to equation (1).

UV-vis spectrum of the purified **PC₆₀-2** film spin-coated from CHCl_3 solution is shown in **Figure 1-9a**. The absorption peak appeared at 330 nm, while no other peaks were observed in visible region, suggesting that perturbation did not occur on the forbidden transition of fullerene. Gartner *et al.* have reported that the electronic band gap (E_g) of solid semiconductor can be estimated from the absorption coefficient (α) according to the following equation:⁴²

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where A is a constant, h is Planck's constant, ν is wavelength, and n is a constant depending on the probability of transition; the n values are 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition gaps, respectively. Since n is determined to be 1/2 from the linear relationship shown in **Figure 1-9 (b)**, the π - π^* transition in conjugated organic materials is categorized as direct allowed transition. The intercept of plots according to equation (1) ($n = 2$) for

PC₆₀-2 (Figure 1-8b) indicates $E_g = 1.6$ eV. Subsequently, according to the definition of E_g ,

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (2)$$

Here, E_{LUMO} and E_{HOMO} are energy level of LUMO and HOMO, respectively. Thus, LUMO level of **PC₆₀-2** was determined as -3.9 eV. The band gap of **PC₆₀-2**, pristine C₆₀, and PCBM are summarized with that of P3HT in **Figure 1-10**. The higher LUMO level of **PC₆₀-2** than that of pristine C₆₀ (-4.2 eV) can be explained by the effects of the strained structure of C₆₀ moieties due to the substitution.⁴³ The HOMO level of **PC₆₀-2** is higher than that of pristine C₆₀ by 0.7 eV and PCBM by 0.2 eV. Nevertheless, LUMO level of **PC₆₀-2** is still lower than the LUMO of P3HT, which is sufficient to generate downhill energetic driving force to avoid binding energy of electron-hole at the donor-acceptor interface. Thus, **PC₆₀-2** has high potential as an electron acceptor for OPVs in combination with P3HT.

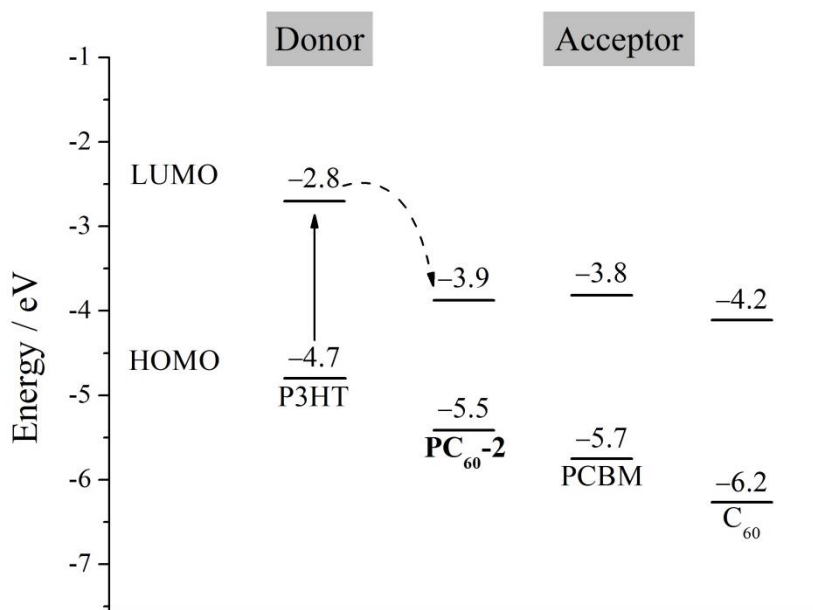


Figure 1-10. Schematic energy diagram of **PC₆₀-2** compared to reference materials for OPVs.

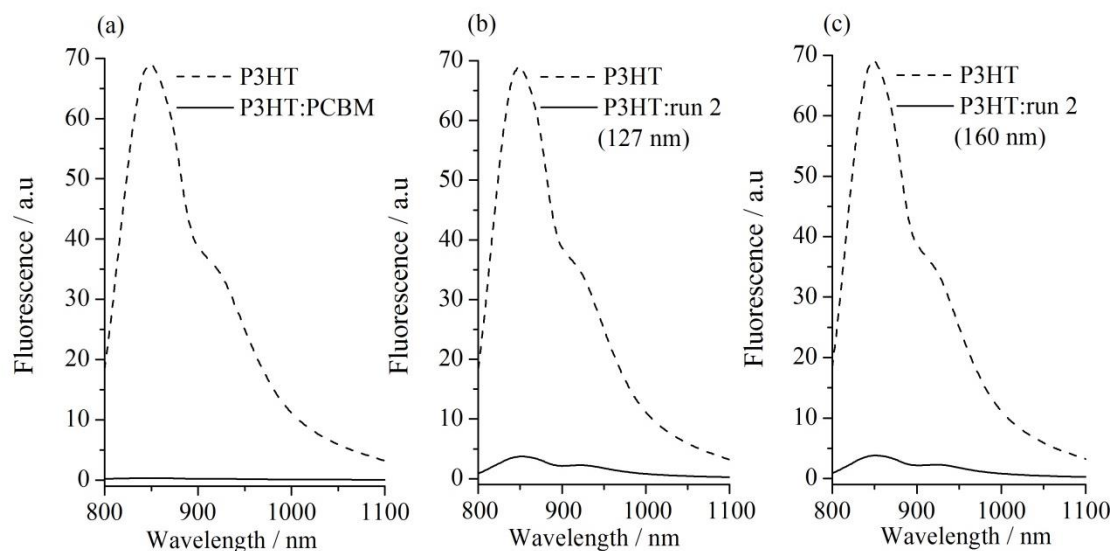


Figure 1-11. Fluorescence spectra of P3HT and its blends with **PC₆₀₋₂** or PCBM in films.

Fluorescence quenching efficiency indicates the charge transfer phenomena at the interface of donor-acceptor. High fluorescence quenching can be ascribed to the LUMO level of acceptor low enough to provide a driving force for charge transfer from exciton (LUMO of donor). **Figure 1-11** shows the fluorescence quenching of P3HT blended with **PC₆₀₋₂** in thin film with different thicknesses. The quenching efficiencies were very high (94%) for both thinner (127 nm) and thicker (160 nm) layers and only 4% lower than the blend with PCBM (98%). The results also imply that **PC₆₀₋₂** is suitable as a polymeric electron acceptor having enough compatibility with P3HT. Analysis of morphology of **PC₆₀₋₂** in the blend with P3HT as well as OPV device performance will be described in Chapter 3.

1.4 Conclusion

Polymerthacrylates bearing C₆₀ moieties were synthesized through the 1,3-dipolar cycloaddition of azide to C₆₀ on the copolymers of MMA and AzHMA. Among the obtained polymers, **PC₆₀-2** exhibited high solubility in CHCl₃ and THF with the highest C₆₀ content (41.4 wt%), while it underwent self-aggregation in CHCl₃ solution. The high solubility of **PC₆₀-2** allowed the facile preparation of polymer blend with P3HT, which exhibited high fluorescence quenching. The HOMO and LUMO levels of **PC₆₀-2** estimated by PESA indicated its potential applicability to an acceptor material for OPVs.

As higher C₆₀ content per polymer chain deteriorates solubility, molecular weight control might be important. In this regard, the radical copolymerization should not be the best process to obtain the precursor copolymers with controlled molecular weight. In addition, bulk properties of polymers, such as thermal properties, miscibility in blends and so on, often depend on stereoregularity of the polymer backbone. As is well known, the synthesis of polymerthacrylates with controlled primary structures, *i.e.* molecular weight and stereoregularity, can be achieved by stereospecific living anionic polymerization.^{25, 44} Thus, solubility of polymer and the morphology in polymer blend are expected to be improved further by the use of polymethacrylates with well-defined structure prepared by the sophisticated polymerization chemistry. The results of this approach as well as the OPV performance with those polymers will be reported later.

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Chapter 2

Precise synthesis of stereoregular C₆₀-containing polymethacrylates with controlled molecular weight

2.1 Introduction

The C₆₀-containing polymethacrylates prepared through the radical copolymerization of 6-chlorohexyl methacrylate (CHMA) with methyl methacrylate (MMA) followed by the azidation and 1,3-dipolar cycloaddition with fullerene C₆₀, have high C₆₀ contents and good solubilities in common organic solvents as described in chapter 1, it has been described that. However, the C₆₀ contents and yields of the soluble fractions were lower than those expected, probably because the azides reacted with C₆₀ moiety at multi-points, which causes inter- and intra-molecular cross-linking. Since the molecular weight distribution of the precursor polymers prepared by radical polymerization was broad, the growth of branching and further cross-linking was difficult to be clearly observed by size-exclusion chromatography (SEC). In other words, the azide polymer with narrow molecular weight distribution is expected to allow the detailed investigation of cross-linking reaction. Furthermore, the control of molecular weight might be significant to unify and control the morphology of the C₆₀-polymethacrylates in the blend with poly(3-hexylthiophene) (P3HT), which is an important factor to determine the performance of the organic photovoltaics (OPVs).

There are several methods to control the molecular weight and its distribution

in the polymerization of methacrylate; controlled radical polymerization (CRP),^{1, 2} coordination polymerization with metal catalysts,³ and living anionic polymerization.^{4, 5} Among them, it is known that anionic polymerization in non-polar solvents proceeds with livingness and high stereospecificity to achieve polymethacrylates with high stereoregularity and narrow molecular weight distribution.⁴ For example, Kitayama *et al.* have reported the *syndiotactic*-specific polymerization of methyl methacrylate (MMA) with a binary initiator of *t*-butyllithium and organoaluminum compounds in toluene at -78°C .⁶ The polymerization is also effective to the polymerization of various (meth)acrylates, such as ethyl methacrylate,⁷ vinyl methacrylate,⁸ and trimethylsilyl methacrylate (TMS-MA).^{9, 10}

Kitayama *et al.* have also reported the *isotactic*-specific living anionic polymerization of MMA by a Grignard reagent, *t*-butylmagnesium bromide. However, the polymerization rate is so slow that the polymer whose molecular weight is higher than 10^4 requires long reaction time to be synthesized. In addition, more importantly, the *isotactic*-specific polymerization by Grignard reagent could not be applied to other methacrylates except MMA. Later, Teyssie *et al.*¹¹ reported the *isotactic*-specific living anionic polymerization initiated by *s*-butyllithium in the presence of a lithium silanolate, prepared *in situ* through the reaction of *s*-butyllithium and hexamethylcyclotrisiloxane. Following this success, Kitaura *et al.*⁵ reported *isotactic*-specific polymerization of MMA initiated by a binary initiator, isopropyl α -lithioisobutyrate (Li-*i*PrIB) / lithium trimethylsilanolate (Me_3SiOLi). This polymerization system gives PMMA with high isotacticity (*mm* triad, 99.5% at -95°C), while molecular weight distribution was relatively narrow ($M_w / M_n = 1.09 \sim 1.3$). Similar to the *syndiotactic*-specific polymerization in the presence of organoaluminums, the *isotactic*-specific

polymerization is also applicable to various methacrylates. Therefore, these stereospecific anionic polymerizations may be effective for the (co)polymerization of CHMA, which has a long alkyl chain and a chlorine atom. It should be noted that alkyl halides are so stable in the stereospecific anionic polymerization system that they do not terminate the polymerization,¹² although enolate anions are known to react with alkyl halides in a S_N2 mechanism. This is because the suppressed reactivity of living anions by the interaction with the counter cations and the additives. In fact, the terminating reaction with allyl halide required the activation of living polymer anion by the additional reagents to dissociate the counter cation and the additives, otherwise no reaction proceeds.¹² Consequently, it is expected that CHMA can be polymerized in such stereospecific anionic polymerization system.

Stereoregularity of polymethacrylates affects the physical properties such as glass transition temperatures (T_g),^{4, 5} dielectric constant,¹³ and crystallization behavior.¹⁴ Therefore, it is anticipated that C_{60} -polymethacrylates with different stereoregularity might yield different properties. That is, the control of stereoregularity of C_{60} -polymethacrylate is also expected important as well as molecular weight and its distribution to control the photoelectric properties and the morphology in a blend with P3HT.

In this chapter, the stereospecific anionic (co)polymerizations of CHMA and MMA with different CHMA contents are investigated to control the molecular weights and stereoregularities. Subsequently, the modifications of the copolymers to incorporate C_{60} moieties are reported.

2.2 Experiments

Materials

Toluene (Aldrich, anhydrous grade) was dehydrated with red colored reaction mixture of butyllithium (*n*-BuLi, 1.64 M hexane solution, Kanto Chemical) and 1,1-diphenylethylene (Acros Organics), and distilled under high vacuum just before use. Dichloromethane (CHCl₂) (Wako Pure Chemical Industry) was distilled over calcium hydride (CaH₂) two times and stored under N₂ atmosphere. Ethylaluminum bis(2,6-di-*t*-butylphenoxide) [EtAl(ODBP)₂] was prepared according to the literature¹⁵ and stored as toluene solutions (1.06 mol/L) under nitrogen atmosphere. MMA (Nacalai Tesque) was distilled two times over CaH₂ and stored under N₂ atmosphere at -20 °C. The monomer was used within 24 h after the distillation. Li-*i*PrIB was prepared and recrystallized in toluene according to the literature.^{16, 17} The initiator was treated as benzene solution (0.401 M) and stored under N₂ atmosphere at -20 °C in frozen state. CHMA was prepared according to the procedure written in Chapter 1 and dried over activated molecular sieves (MS) 4A beads (Aldrich). CHCl₃, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), triethylamine and hexane were purchased from Wako Pure Chemical Industry.

Instruments

¹H NMR spectra were recorded in CDCl₃ (Aldrich) and toluene-*d*₈ (Cambridge Isotopes Laboratories Inc.) on a JNM-ECS 400 (JEOL) spectrometer. Chemical shifts in ¹H NMR spectra were referred to the signal of tetramethylsilane. Molecular weight and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on a GPC-900 chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C

(300 mm $\times$ 7.5 mm), Polymer Laboratories], using THF as an eluent (flow rate = 0.8 mL min⁻¹), and calibrated against standard poly(methyl methacrylate) (PMMA) samples (Shodex, MW: 1.25×10^6 , 6.59×10^5 , 1.95×10^5 , 4.96×10^4 , 2.06×10^4 , 6.82×10^3 , 2.00×10^3). IR spectra were recorded in KBr disc on an FT/IR-410 Fourier-transform infrared spectrophotometer (JASCO). Purities of monomers were evaluated by gas chromatography (GC) recorded on a GC-2014 (Shimadzu) equipped with an HP-5 capillary column (Hewlett-Packard). Thermogravimetry / differential thermal analysis (TG/DTA) were performed with an EXSTAR TG/DTA6000 (SII Nano Technology) (scan rate = 20 °C min⁻¹) under N₂ atmosphere (flow rate = 100 mL min⁻¹).

Polymerization of MMA and CHMA

[Syndiotactic-specific polymerization]

A typical procedure (**Table 2-2**, Run 2): All the polymerization reactions were carried out under dried nitrogen atmosphere in glass ampoules fitted with three-way stopcocks and the solvents and reagents were transferred via hypodermic syringes. To a glass ampoule filled in dried N₂ passed through MS4A at -78 °C, MMA (7.8 mmol), CHMA (2.0 mmol), toluene (5.0 mL), and EtAl(ODBP)₂ (0.5 mmol) were added at room temperature. The reaction mixture was cooled to -78 °C for 30 min, and Li-*i*PrIB (0.1 mmol) was added. The reaction was quenched after 24 h by adding 1 M HCl water-methanol solution. A small fraction of the reaction mixture was sampled for ¹H NMR spectroscopy (400 MHz, 30 °C, toluene-*d*₈). The conversions of each monomer were evaluated from the intensity ratio of the respective vinylidene signals (CHMA: 6.08 and 5.24 ppm, MMA: 6.02 and 5.19 ppm) to the O-CH₂ [CHMA / CHMA units in the polymer at 3.91 / 3.96 ppm] and O-CH₃ [MMA / MMA units in the polymer at 3.34 /

3.36 ppm) signals. The reaction mixture was then concentrated under reduced pressure, and the residue was diluted with CHCl_3 and washed with 1 M aq HCl and water. The organic layer was dried *in vacuo* at 40 °C for 12 h to afford a polymeric product (0.90 g, yield 76.1%).

Note: MMA and CHMA in the reaction mixture can be distinguished by the ^1H NMR spectra in toluene- d_8 but not in CDCl_3 .

[Isotactic-specific polymerization]

A typical procedure (**Table 2-3**, Run 1): To a glass ampoule filled in dried N_2 passed through MS4A at 0 °C, CH_2Cl_2 (5.0 mL), Me_3SiOLi (1.0 mmol) and Li-*i*PrIB (0.1 mmol) were added at room temperature. The reaction mixture was cooled to 0 °C, and a mixture of MMA (7.87 mmol) and CHMA (1.94 mmol) was added. After 1 h, the reaction was quenched by adding 1 M HCl water-methanol solution. A small fraction of the reaction mixture was sampled for ^1H NMR spectroscopy. The conversions of each monomer were evaluated in a similar manner to *syndiotactic*-specific polymerization. The reaction mixture was then concentrated under reduced pressure, and the residue was diluted with CHCl_3 and washed with 1 M aq HCl and water. The organic layer was dried *in vacuo* at 40 °C for 12 h to afford a polymeric product (1.3 g, yield 100 %).

Azidation of Polymethacrylates

A typical procedure: To a solution of the copolymer (**Table 2-7**, Run 2) (200 mg, 0.64 mmol per chlorine atom) in DMF (2.0 mL) was added NaN_3 (0.132 g, 2.02 mmol). The reaction mixture was stirred at 60 °C for 24 h and poured into water (40 mL) - CH_3OH (160 mL) cosolvent. The precipitate was collected by filtration, washed

with water, and dried *in vacuo* at room temperature for 12 h to yield **it-PN₃** (329 mg, 81.8%).

Synthesis of C₆₀-Containing Polymethacrylates

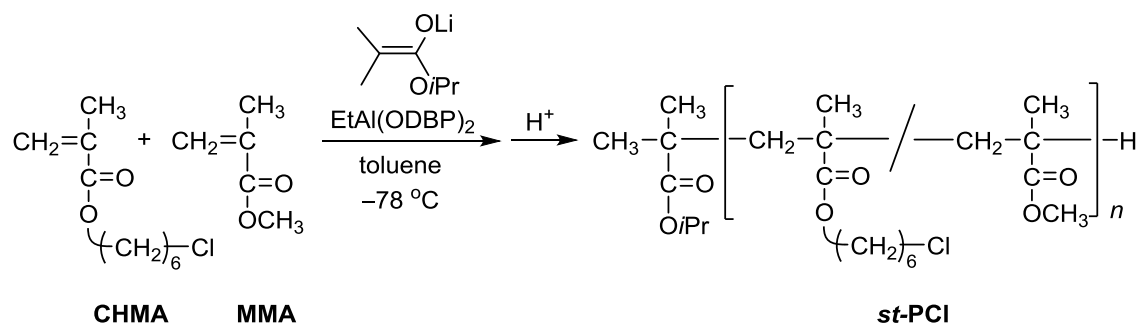
A typical procedure: A solution of **it-PN₃** (50 mg, 80 μ mol per azide group) and C₆₀ (57 mg, 80 μ mol) in chlorobenzene (57 mL) was degassed by freeze-pump-thaw 3 times and refluxed for 48 h under N₂ atmosphere. The reaction mixture was concentrated on a rotary evaporator. The residual solids were stirred in THF, and the insoluble fraction was removed by centrifugation. The soluble fraction was poured into hexane (200 mL) to reprecipitate the polymeric product. This process was repeated several times until no traces of C₆₀ on TLC plate (eluent: toluene, R_f = 0.9) were observed. The product was dried *in vacuo* at 40 °C for 12 h. Yield 30 mg (29%), dark-brown precipitates.

2.3 Results and Discussion

2.3.1 Anionic copolymerization of MMA and CHMA

Syndiotactic-Specific Polymerization

It is known that *syndiotactic*-specific living anionic polymerization of MMA initiated by Li-*i*PrIB/ethylaluminum bis(2,6-di-*t*-butylphenoxide) [EtAl(ODBP)₂] in toluene at -78 °C proceeds smoothly with good control of molecular weight and syndiotacticity.⁴ In the living copolymerization, if the relative reactivities of MMA and CHMA are different, the resulting copolymer should not have constant but gradient monomer sequence. In order to investigate those relative reactivities, copolymerizations were conducted for different reaction times (feed ratios: [MMA]₀ / [CHMA]₀ / [Li-*i*PrIB]₀ = 50 / 50 / 1, **Scheme 2-1**).



Scheme 2-1. Anionic copolymerization of MMA and CHMA

The results of copolymerizations were presented in **Table 2-1**. The copolymerization was not completed within 24 h (Run 4). From the ¹H NMR spectra of the sampled reaction mixture, the conversions of each monomer were evaluated to be 78% for CHMA and 63% for MMA, respectively. The time-conversion plots (**Figure 2-1**) revealed that CHMA was consumed faster than MMA (**Figure 2-1**). The results imply that CHMA has slightly higher reactivity than MMA.

Table 2-1. Copolymerization of CHMA and MMA initiated by Li-*i*PrIB / EtAl(ODBP)₂ at -78 °C^a

Run	Polymerization time	Conversion / % ^b		$M_n / 10^3$		M_w^c
	h	MMA	CHMA	SEC ^c	NMR ^b	M_n
1	3	10	18	4.3	4.4	1.05
2	6	10	26	6.0	6.5	1.06
3	12	20	42	8.2	9.2	1.06
4	24	63	78	12.0	13.6	1.05

a) MMA 2.5 mmol, [MMA]₀ / [CHMA]₀ / [Li-*i*PrIB]₀ = 50 / 50 / 1, toluene 5.0 mL.

b) Evaluated from ¹H NMR spectra (400 MHz, toluene-d₈, 30 °C).

c) Determined by SEC at 40 °C in THF calibrated against PMMA standard samples.

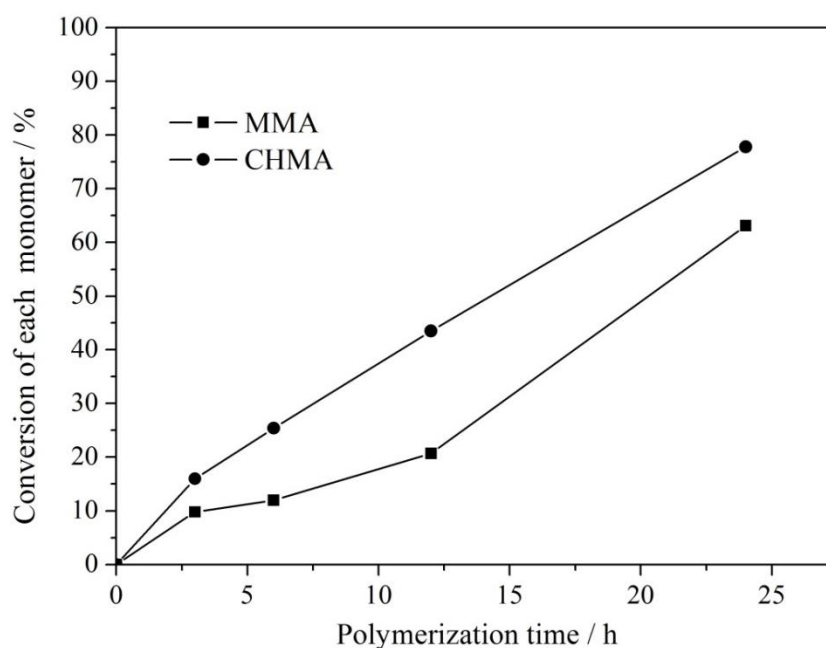


Figure 2-1. Plots of time vs. copolymerization of CHMA and MMA initiated by Li-*i*PrIB / EtAl(ODBP)₂ in toluene at -78 °C.

Molecular weights of the copolymers increased with increasing polymerization time. The molecular weights determined from ¹H NMR and SEC were close to each other, and their distributions were very narrow ($M_w / M_n = 1.05$ - 1.06 , Run 4). In addition, the SEC charts (**Figure 2-2**) show unimodal peak shifting to the higher

molecular weight side with increasing reaction time throughout the whole polymerization process, indicating the livingness of the copolymerization.

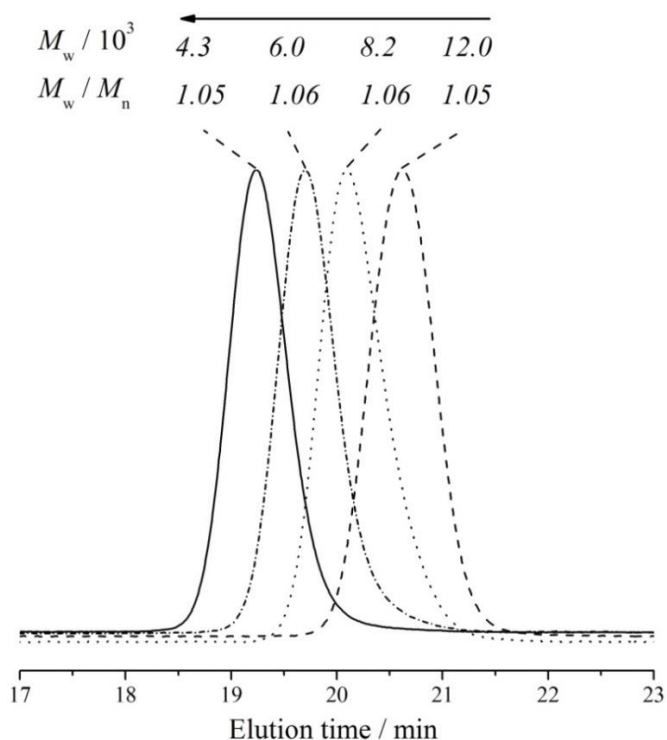


Figure 2-2. SEC charts of the obtained polymers from the copolymerizations of CHMA and MMA initiated by Li-*i*PrIB / EtAl(ODBP)₂ in toluene at -78 °C. From right to left (arrow direction), the reaction times are 3 h, 6 h, 12 h, and 24 h.

Taking into account the reactivities of CHMA and MMA as seen in Figure 2-1, the resulting copolymers might not be completely random copolymers. Since CHMA was consumed faster than MMA, CHMA units were incorporated more than MMA units in the early stage (reaction time $\leq$ 12 h), and the resulting copolymer may have a slightly gradient monomer sequence.

A series of copolymerizations with different CHMA contents were conducted under similar conditions for 36 h. The results are presented in **Table 2-2**. In any feed ratios, the conversions of CHMA were larger than those of MMA, resulting in the formation of the copolymers with larger contents of CHMA units than those expected

from the feed ratios. ^1H NMR spectra of the obtained copolymer (**Table 2-2**, Run 2) is shown in **Figure 2-3**. The signal of *O*-methylene group (signal 3) of CHMA units is observed at 3.55 ppm, while that of *O*-methyl group of MMA units (signal 9) is overlapping with that of chloromethylene group of CHMA units (signal 8) around 3.58 ppm. From their intensity ratio, the content of CHMA units is determined, which agreed well with the estimated value from the feed ratios and conversions. The signals assignable to $\alpha\text{-CH}_3$ (1) were observed from 1.23 to 0.80 ppm, which show splittings owing to the stereoregularity. According to literature,⁴ the stereochemical triad contents were determined to be $mm / mr / rr = 3 / 10 / 87$, respectively. In all the copolymers, rr triad contents were found to be higher than 84%. Thus, it can be concluded that the copolymerization proceeded in high *syndiotactic*-specificity to afford the *syndiotactic* copolymer with controlled molecular weight and its distribution.

Table 2-2. Anionic copolymerization of CHMA and MMA initiated by Li-*i*PrIB / EtAl(ODBP)₂ at $-78\text{ }^\circ\text{C}$ for 36 h^a

Run	Monomer		Conversion		Yield	$M_n/10^3$		M_w^c	CHMA		Tacticity/ % ^d		
	/mmol		/% ^b						content/ % ^d				
	CHMA	MMA	CHMA	MMA		%	SEC ^c		Calcd.	M_n	NMR	<i>mm</i>	<i>Mr</i>
1	1.3	8.9	95	75	76.8	11.6	9.2	1.05	14.1	2	10	88	
2	2.0	7.8	94	76	76.1	12.4	10.1	1.04	24.8	3	10	87	
3	5.1	4.8	93	72	72.8	17.8	13.5	1.09	58.8	5	11	84	
4	2.5	-	94	-	90.2	9.4	9.7	1.07	100	3	6	91	

a) Li-*i*PrIB 0.1 mmol, EtAl(ODBP)₂ 0.5 mmol, toluene 5.0 mL.

b) Determined by ^1H NMR of the sampled reaction mixture (400 MHz, toluene-*d*8, $30\text{ }^\circ\text{C}$).

c) Determined by SEC (THF, calibrated against PMMA standards, $40\text{ }^\circ\text{C}$).

d) Determined by ^1H NMR (400 MHz, CDCl_3 $55\text{ }^\circ\text{C}$).

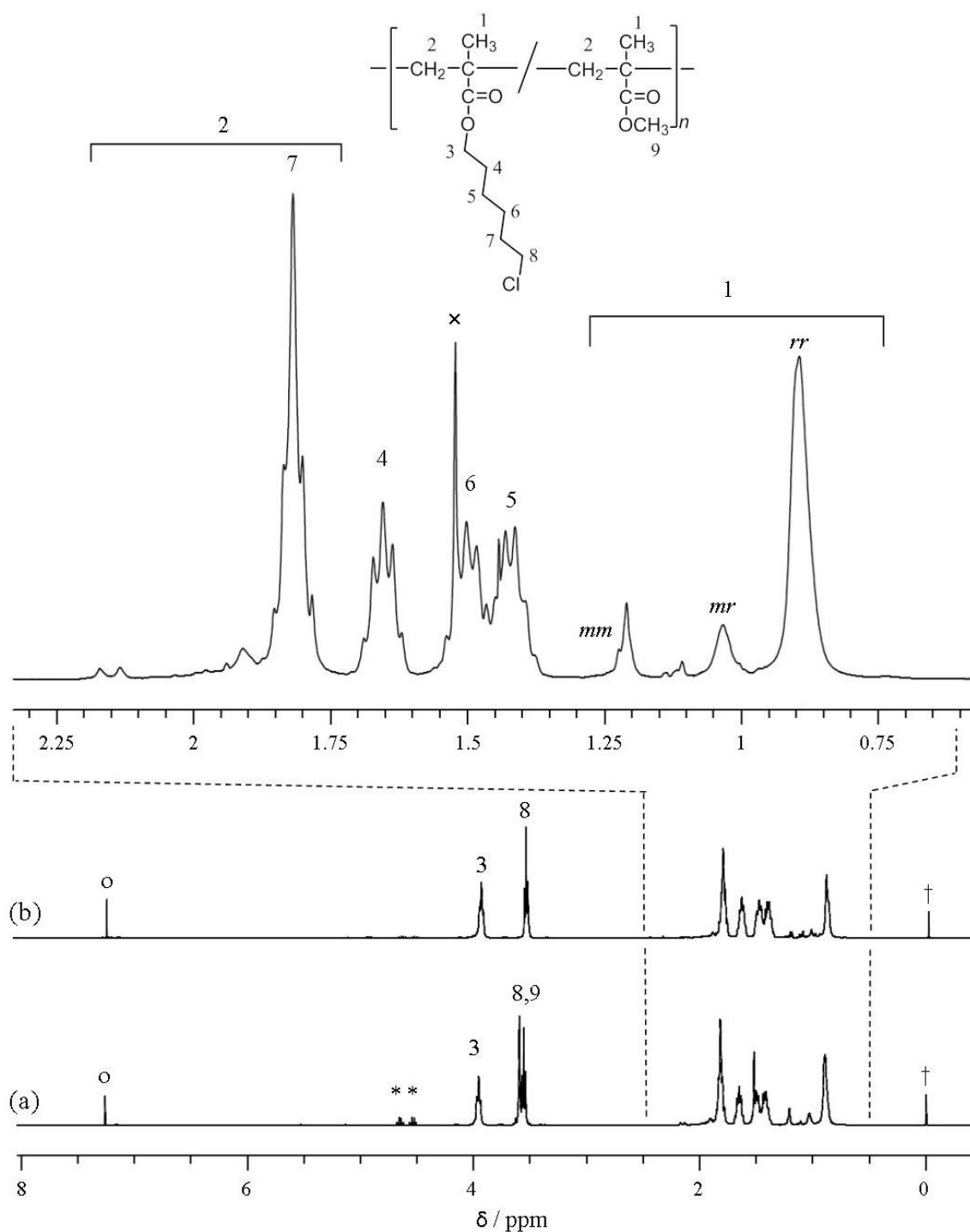
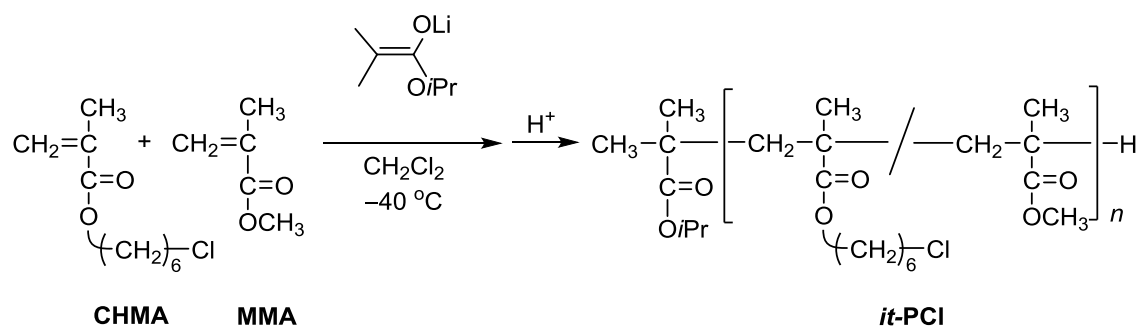


Figure 2-3. ^1H NMR spectra of the resulting copolymers (**Table 2-2**) initiated by Li-*i*PrIB / [EtAl(ODBP) $_2$] in toluene at $-78\text{ }^\circ\text{C}$ (400 MHz, CDCl_3 , $55\text{ }^\circ\text{C}$): (a) Run 2 and (b) Run 4. o CHCl_3 , *1,1,1,2-tetrafluoroethane (vial cleaner), x H_2O , † tetramethylsilane.

Isotactic-specific Polymerization

Copolymerization of MMA and CHMA in CH₂Cl₂ at -40 °C was initiated with a binary initiator, Li-*i*PrIB / Me₃SiOLi (**Scheme 2-2**), which is known effective for *isotactic*-specific living polymerization of MMA as reported by Kitaura *et al.*⁵ The results of copolymerization are summarized in **Table 2-3**.



Scheme 2-2. Isotactic-specific anionic polymerization of CHMA and MMA initiated by Li-*i*PrIB / Me₃SiOLi in CH₂Cl₂.

Table 2-3. Anionic polymerization of CHMA and MMA initiated by Li-*i*PrIB / Me₃SiOLi at -40 °C for 1 h ^a

Run	Monomer		Conversion ^b		Yield	CHMA						
	/mmol		/%			M_n^c / 10 ³		M_w^c	content ^d	Tacticity ^d / %		
	CHMA	MMA	CHMA	MMA		%	SEC ^c	Calcd	M_n	%	<i>mm</i>	<i>mr</i>
1	1.1	11	100	100	89	52.7	12.1	1.40	10.7	95	4	1
2	1.6	8.9	100	100	93	40.5	11.7	1.76	13.5	95	4	1
3	8.6	2.5	100	100	93	50.1	12.9	1.71	19.0	96	3	1
4	7.8	2.7	100	100	100	58.1	12.9	1.72	24.6	96	3	1

a) Li-*i*PrIB 0.1 mmol, Me₃SiOLi 1.0 mmol, CH₂Cl₂ 10 mL

b) Determined by ¹H NMR of the sampled reaction mixture (400 MHz, toluene-d₈, 30 °C).

c) Determined by SEC (THF, calibrated against PMMA standards, 40 °C).

d) Determined by ¹H NMR (400 MHz, CDCl₃ 55 °C).

In contrast to the *syndiotactic*-specific polymerization, the results of the *isotactic* specific polymerization of CHMA and MMA was found to be uncontrolled in

terms of molecular weight distribution. In all Runs, both CHMA and MMA were found to be completely consumed within 1 h, indicating the fast initiation and propagation rate in the *isotactic*-specific polymerization. Molecular weight distributions of all the resulting copolymers were broad. In the case of Run 1 with the lowest CHMA feed, the molecular weight distribution was 1.40, while it increases significantly at the higher CHMA feed. Probably, 6-chlorohexyl chain of CHMA affected the behavior of polymerization. Nevertheless, all copolymers exhibited high isotacticity (**Figure 2-4**) with *mm* triad content ~95%.

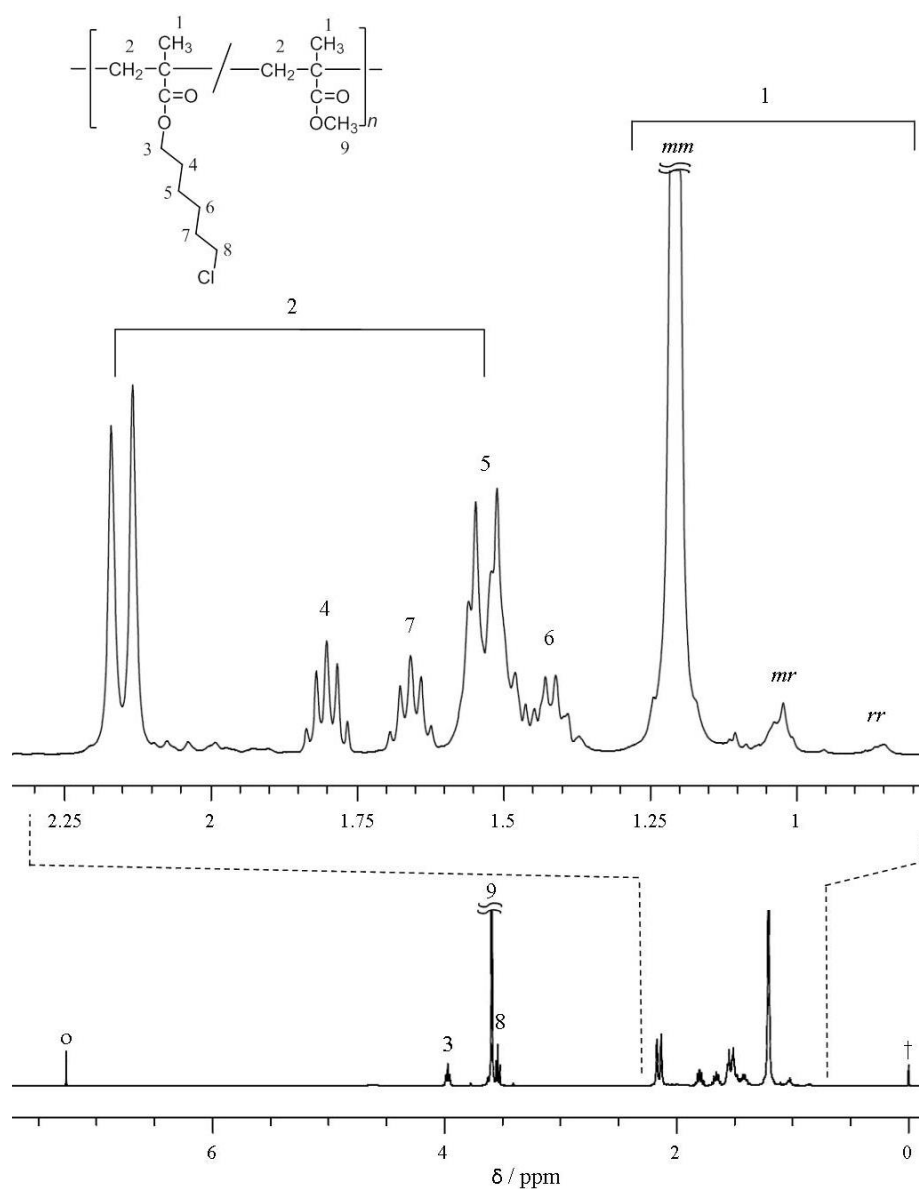


Figure 2-4. ¹H NMR spectra of the resulting copolymers of CHMA and MMA (Run 1, Table 2-3) initiated by Li-*i*PrIB / Me₃SiOLi in CH₂Cl₂ at -40 °C (400 MHz, CDCl₃, 55 °C).

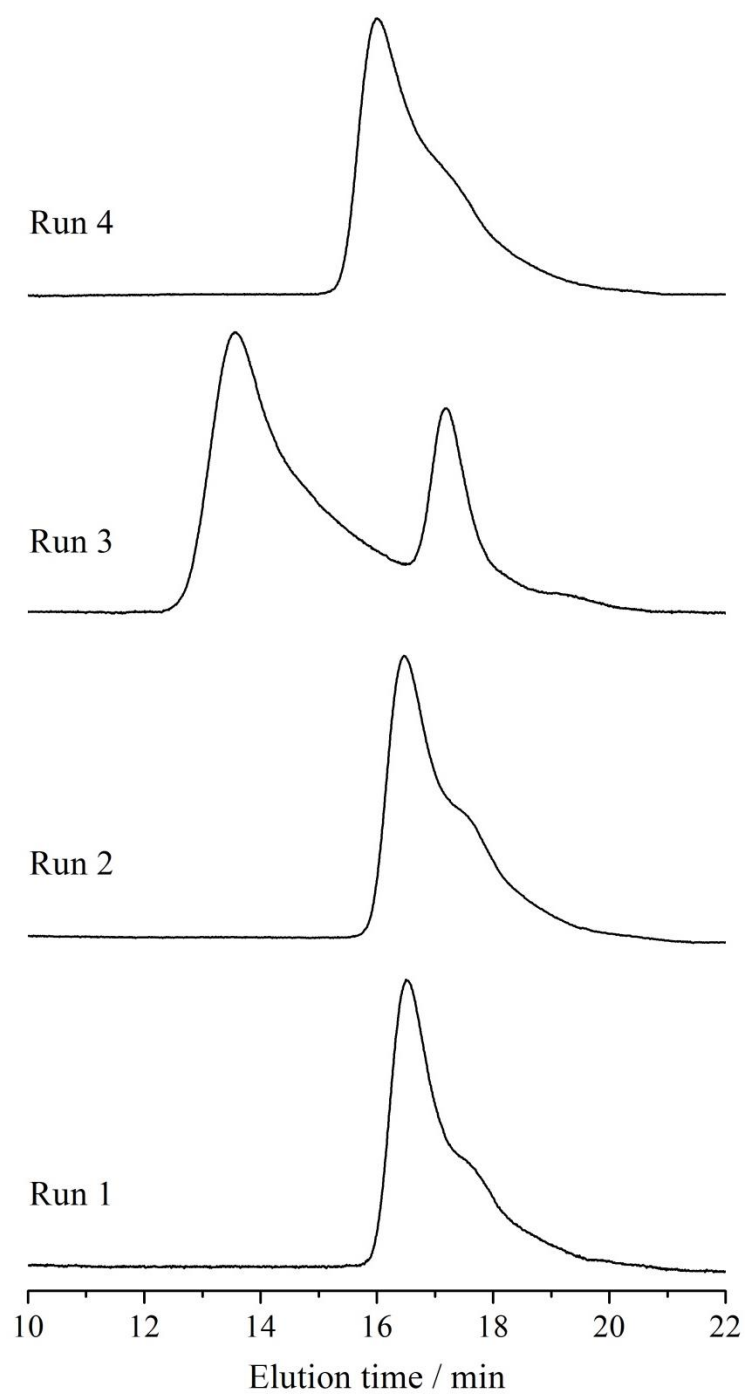


Figure 2-5. SEC charts of the obtained copolymers from *isotactic*-specific anionic polymerization of CHMA and MMA initiated by Li-*i*PrIB / Me₃SiOLi in CH₂Cl₂ at -40 °C.

Table 2-4. Anionic copolymerization of CHMA and MMA initiated by Li-*i*PrIB / Me₃SiOLi at -40 °C for 1 h^a

Run	Monomer		Conversion ^b		Yield	CHMA						
	/mmol		/ %			$M_n^c / 10^3$		M_w^c	content ^d	Tacticity ^d / %		
	CHMA	MMA	CHMA	MMA		%	SEC ^c	Calcd.	M_n	%	<i>mm</i>	<i>mr</i>
1	1.10	11.1	100	100	81	111	12.1	1.98	49.9	96	3	1
2	1.56	–	100	–	93	76.9	11.7	4.16	100	93	5	2
3	–	2.45	–	100	100	32.4	12.9	1.48	–	96	3	1

a) Li-*i*PrIB 0.1 mmol, Me₃SiOLi 1.0 mmol, CH₂Cl₂ 10 mL

b) Determined by ¹H NMR of the sampled reaction mixture (400 MHz, toluene-*d*₈, 30 °C).

c) Determined by SEC (THF, calibrated against PMMA standards, 40 °C).

d) Determined by ¹H NMR (400 MHz, CDCl₃ 55 °C).

In order to investigate the effect of 6-chlorohexyl chain of CHMA on the polymerization behavior, homopolymerization of MMA and CHMA together with their copolymerization were conducted by Li-*i*PrIB / Me₃SiOLi at -40 °C for 1 h (Table 2-4). Copolymerization of CHMA and MMA (Run 1) and each homopolymerization (Run 2 for CHMA and Run 3 for MMA) proceeded completely within 1 h. The molecular weight distribution of Run 2 was broader than Run 3, suggesting that the 6-chlorohexyl group of CHMA makes the control of molecular weight difficult under this condition. Since the *syndiotactic*-specific polymerization using the same grade monomers proceeded in a well-controlled manner as described above, the reason for the broad molecular weight distribution of the copolymers might be ascribed to some specific interaction between CHMA and Me₃SiOLi, though the details are not clear at present.

Kitaura *et al.*⁵ reported that the *isotactic*-specific anionic polymerization of MMA under the current conditions proceeded with good control of molecular weight and its distribution, where monomer was injected into the initiator (Method B). In an

opposite manner, the initiator was injected into the monomers in the above experiments for the reason of convenience to mix the monomers in the reactor (Method A). As the result, even for the polymerization of MMA (Run 3), the molecular weight distribution was broader than reported. Hence, it is suspected that the injection order of reagents may affect the control of molecular weight. In order to confirm the effects of injection order, *isotactic*-specific anionic polymerization of CHMA was conducted with different injection orders of reagents at $-78\text{ }^{\circ}\text{C}$, $-40\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$ (**Table 2-5**).

Table 2-5. Anionic polymerization of CHMA initiated by Li-*i*PrIB / Me₃SiOLi in CH₂Cl₂ at different temperature for 1 h^a

Run	Method ^b	Temp.	Conv. ^c	Yield	$M_n / 10^3$		M_w^d	Tacticity/ % ^e		
		$^{\circ}\text{C}$	%	%	SEC ^e	Calcd	M_n	<i>mm</i>	<i>mr</i>	<i>rr</i>
1	A	0	100	100	16.8	10.4	3.87	87	10	3
2		-40	100	100	39.2	10.4	4.79	88	9	3
3		-78	94.5	91	49.8	9.78	12.4	92	6	2
4	B	0	100	89	32.2	10.4	1.28	89	9	2
5		-40	100	100	69.6	10.4	2.43	93	5	2

a) Li-*i*PrIB 0.1 mmol, Me₃SiOLi 1.0 mmol, CH₂Cl₂ 5 mL

b) See text (p.77-78), A: initiator into monomer and B: monomer into initiator.

c) Determined by ¹H NMR of the sampled reaction mixture (400 MHz, CDCl₃ 30 $^{\circ}\text{C}$).

d) Determined by SEC (THF, calibrated against PMMA standards, 40 $^{\circ}\text{C}$).

e) Determined by ¹H NMR (400 MHz, CDCl₃ 55 $^{\circ}\text{C}$).

In the polymerizations by Method A (initiator into monomer), molecular weight distributions of the obtained polymers were very broad (Runs 1-3). In Method B (monomer into initiator), the polymerization at $0\text{ }^{\circ}\text{C}$ (Run 4) resulted in narrower molecular weight distribution ($M_w / M_n = 1.28$), while the polymerization at lower temperature (Runs 5) led broader molecular weight distribution. **Figure 2-6** displays

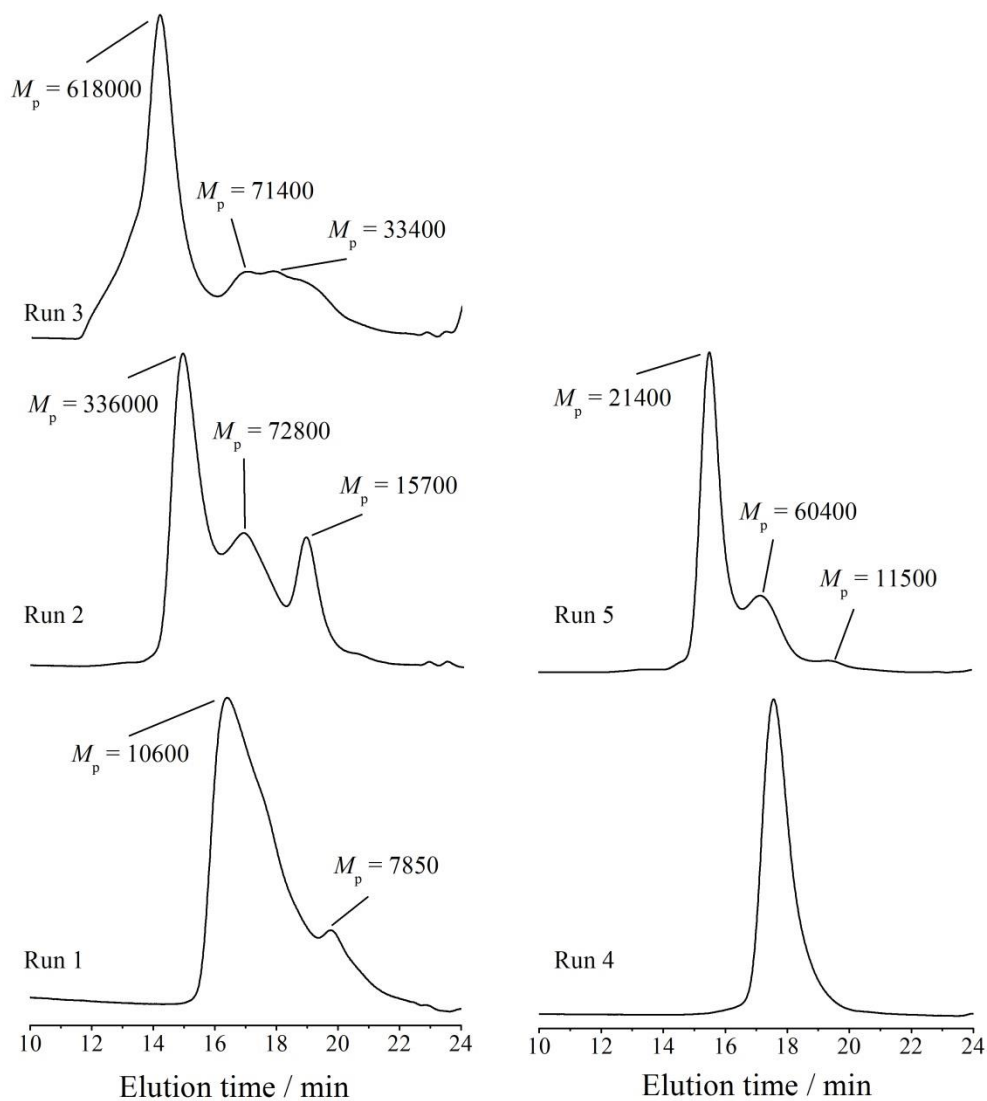
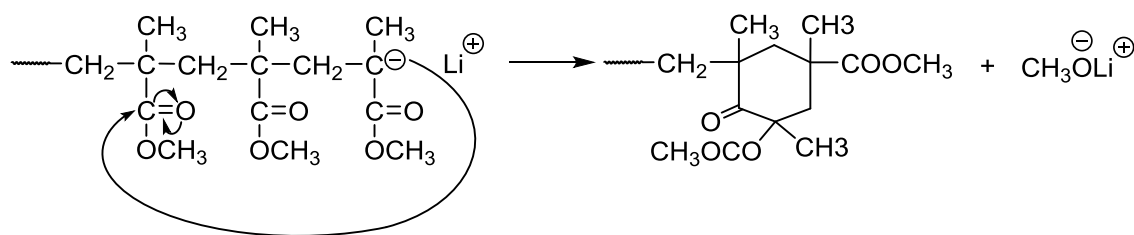


Figure 2-6. SEC charts of the obtained polymers from the *isotactic*-specific anionic polymerizations of CHMA and MMA initiated by Li-*i*PrIB / Me₃SiOLi in CH₂Cl₂ with different orders of reagent injection and temperatures. Run numbers are corresponding to those in **Table 2-5**.

SEC charts of the resulting polymers shown in **Table 2-5**. Broad and multi-modal peaks were observed in Runs 1-3, and 5, indicating the coexistence of several active species with different reactivities in the polymerization system, while their stereospecificity is all *isotactic*-specific. Only Run 4 gave narrow and unimodal SEC chart. Consequently, in order to control the molecular weight, polymerization should be initiated by the addition of monomers to the solution of initiator at 0 °C. It should be noted that the polymerization of MMA at 0 °C causes a back-biting reaction of the living anion to form a 6-membered cyclic ketone unit (**Scheme 2-3**).



Scheme 2-3. Back-biting reaction of PMMA living anion to form 6-membered cyclic ketone unit

This side reaction proceeds slower than the propagation so that the control of molecular weight can be achieved even if the living anion becomes slowly “dead” after the consumption of MMA. Furthermore, the polymerization at 0 °C decreases the isotacticity of the resulting polymers as reported for MMA polymerization.⁵ In fact, the *mm* content of the poly(CHMA) prepared at 0 °C (Run 4, 89%) was lower than that prepared at −40 °C. It should be noted that the polymerization of 2-chloroethyl methacrylate proceeds in a similar behavior to that of MMA; the polymerization at −78 °C by Method B yielded a polymer with small MWD ($M_n = 9300$, $M_w / M_n = 1.26$) and high isotacticity (*mm* content = 94%).¹⁸ Consequently, the presence of a chloro atom in

CHMA might not be a major cause of influencing its polymerization behavior described above. Though the reason for the formation of active species of different activities is not clear at present, the multiplicity of active species was suppressed by elevating the polymerization temperature probably through faster exchange between the species so as to average out the reactivity difference. Nevertheless, *isotactic*-specific anionic polymerization of CHMA should be conducted under the conditions similar to Run 4, if the main purpose is the control of molecular weight.

Table 2-6. Anionic polymerization of CHMA and MMA initiated by Li-*i*PrIB / Me₃SiOLi in CH₂Cl₂ at different temperatures for 1 h. ^a

Run	Monomer		Conversion ^b		Yield	CHMA						
	/ mmol		/ %			$M_n^c / 10^3$		M_w^c	content ^d	Tacticity ^d / %		
	CHMA	MMA	CHMA	MMA		%	SEC ^d	Calcd	M_n	%	<i>mm</i>	<i>mr</i>
1	0.97	8.84	100	100	86	28.9	10.4	1.15	9.82	85	12	3
2	1.94	7.87	92	100	100	59.2	10.4	1.19	19.3	86	9	5
3	2.96	6.71	83	100	86	126	9.78	1.39	29.8	90	8	2

a) Li-*i*PrIB 0.1 mmol, Me₃SiOLi 1.0 mmol, CH₂Cl₂ 5 mL

b) Determined by ¹H NMR of the sampled reaction mixture (400 MHz, 30 °C, toluene-*d*₈).

c) Determined by SEC at 40 °C in THF calibrated against PMMA standards.

d) Determined by ¹H NMR (400 MHz, 55 °C, CDCl₃).

Based on the knowledge of homopolymerization, copolymerizations of CHMA and MMA were conducted at 0 °C by injecting the monomer mixture to the initiator solution (**Table 2-6**). The conversions of each monomer in Run 1 reached 100% within 1 h. On the other hand, CHMA was not completely consumed in Runs 2 and 3, although the feeds of MMA were larger than CHMA. These results indicate that the polymerization rate of MMA is larger than that of CHMA in this polymerization system. It is opposite to the case of the *syndiotactic*-specific polymerization described above. In

the *syndiotactic*-specific polymerization induced by the additive, EtAl(ODBP)₂, it is postulated that methacrylate monomers must be activated through coordination by EtAl(ODBP)₂ to react with the propagating anion stabilized by EtAl(ODBP)₂. In this copolymerization system, the difference in activation acceptability of the comonomers sometimes cause monomer-selective polymerization.¹⁹ Similarly, the higher reactivity of CHMA in the presence of EtAl(ODBP)₂ might have relationship with the activation by EtAl(ODBP)₂. In contrast, the current *isotactic*-specific polymerization system does not require such monomer activation. Thus, the *isotactic*-specific polymerization might proceed according to the inherent reactivity of the monomers, i.e. electron density at vinylidene groups and static hindrance due to the different ester group structures, and MMA exhibited higher reactivity than CHMA under the current conditions.

The molecular weight distributions of the obtained copolymers were narrow and the SEC charts were unimodal as shown on **Figure 2-7**. **Figure 2-8** shows the ¹H NMR spectra of the polymers from Run 4 in **Table 2-5** and from Run 2 in **Table 2-6**. Similar to the results of *syndiotactic* polymers (**Figure 2-3**), the signals of 6-chloromethyl groups of CHMA units (signal 8) and O-methyl groups of MMA units (9) are overlapped with each other, while the O-methylene proton of CHMA unit (signal 3) is observed separately at 3.95 ppm. The CHMA contents of the resulting polymers are determined by their intensity ratios, which agreed well with the initial monomer feed ratios. The splitting of the main chain methylene protons (signal 2) as an AB quartet indicates high isotacticity of the copolymer. In fact, the *mm* triad content determined from the splitting of α-methyl protons (signal 1) is 89% for Run 4 in **Table 2-5** and 86 % for Run 2 in **Table 2-6** respectively.

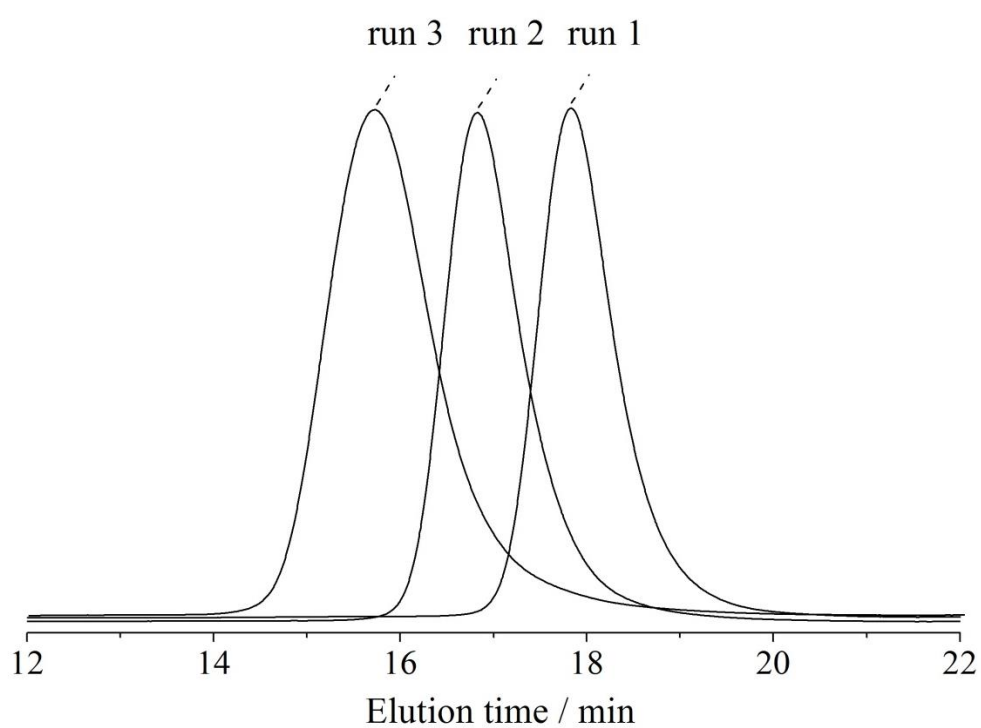


Figure 2-7. SEC charts of the obtained copolymers from the *isotactic*-specific anionic copolymerizations of MMA and CHMA initiated by Li-*i*PrIB/Me₃SiOLi in CH₂Cl₂.

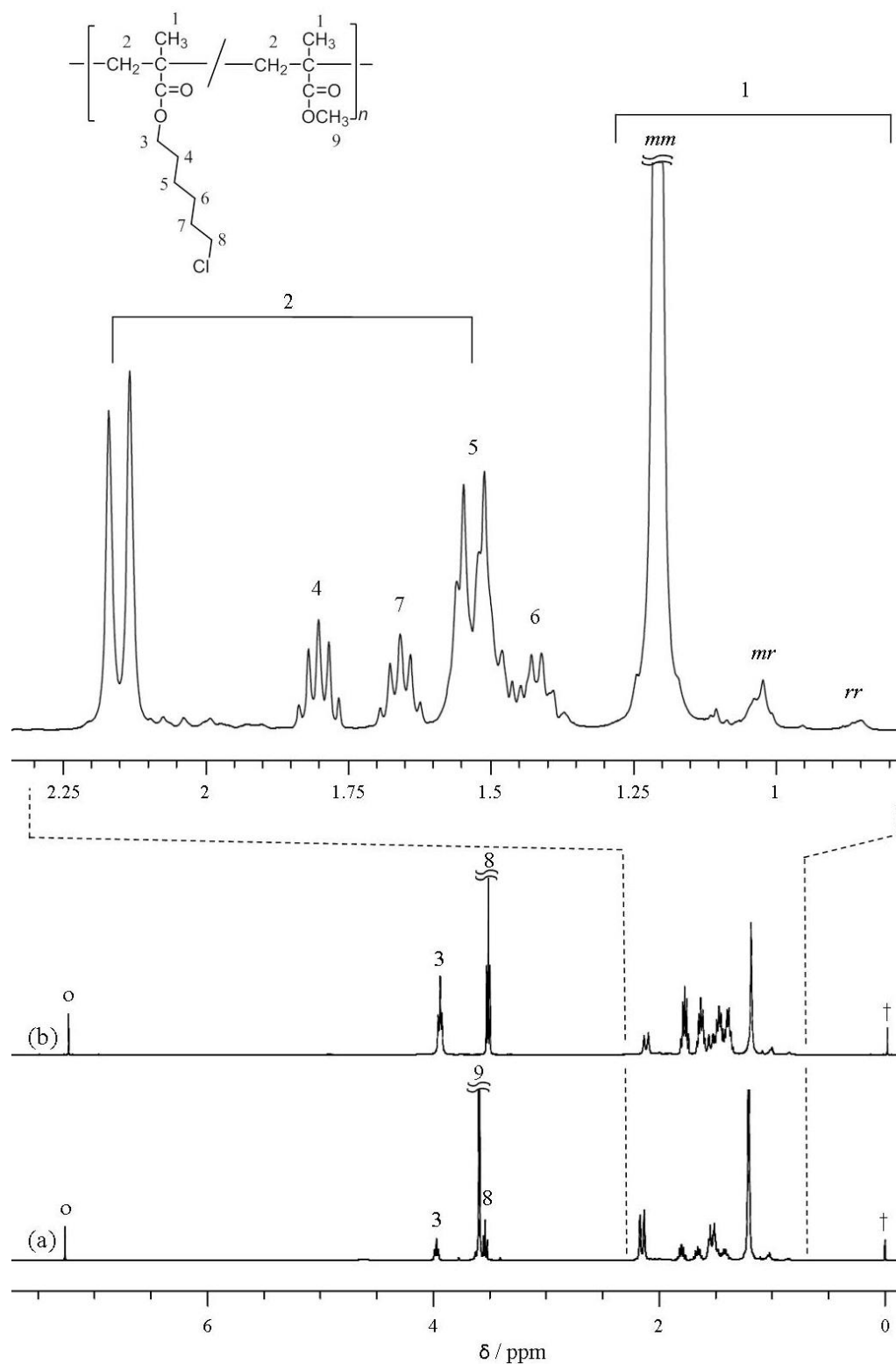


Figure 2-8. ^1H NMR spectra of the resulting polymers of CHMA and MMA initiated by Li-*i*PrIB / Me_3SiOLi in CH_2Cl_2 (400 MHz, CDCl_3 , 55 $^\circ\text{C}$): (a) Run 2 in Table 2-6 and (b) Run 4 in Table 2-5. o CHCl_3 , † tetramethylsilane.

2.3.2 Synthesis of C₆₀-containing stereoregular polymethacrylates

Incorporation of C₆₀ moieties into polymethacrylates were performed in a similar procedure to that described in Chapter 1. The chlorine atoms in the obtained **st-PCI** ($M_n = 17800$, $M_w/M_n = 1.09$, $mm / mr / rr = 3 / 10 / 87$) and **it-PCI** ($M_n = 59200$, $M_w/M_n = 1.19$, $mm / mr / rr = 88 / 10 / 2$) were converted to azide group by the reaction with NaN₃ in DMF at 60 °C to afford copolymer with 6-azidohexyl methacrylate (AzHMA) unit. The reactions proceeded quantitatively as evidenced by ¹H NMR and IR spectra of the products. The resulting azide-containing polymethacrylates were named **st-PN₃** and **it-PN₃**, respectively. Subsequently, C₆₀ was reacted with the copolymers in chlorobenzene under reflux for 40 h, and the THF-soluble fractions were extracted from the products. The results are summarized in **Table 2-7**.

Table 2-7. Preparation of stereoregular polymethacrylates possessing C₆₀ moieties.^a

Run	Azide polymer	Azide content	Yield ^b %	$M_n / 10^3$	M_w^c	C ₆₀ content ^d	
		mol %			M_n	wt %	mol %
1	st-PN₃	19	50	12.3	3.37	33.9	7.7
2	it-PN₃	19	29	49.9	8.26	39.8	10.0

a) [azide group]₀ / [C₆₀]₀ = 1 / 1, [C₆₀]₀ = 1.0 mg/mL, reflux in chlorobenzene under N₂ atmosphere for 40 h.

b) THF-soluble fraction.

c) Estimated by SEC (calibrated against PMMA standards, THF, 40 °C).

d) Residual mass after heating up to 550 °C by TGA.

The yield of the soluble fraction of **st-PF** (50 %) was found to be higher than that of **it-PF** (29%) even though the initial AzHMA content was the same. In fact, some sticky precipitates were readily observed in the reaction of **it-PN₃** with C₆₀ in chlorobenzene after 36 h. In ¹H NMR spectra (**Figure 2-9**), the signal assignable to

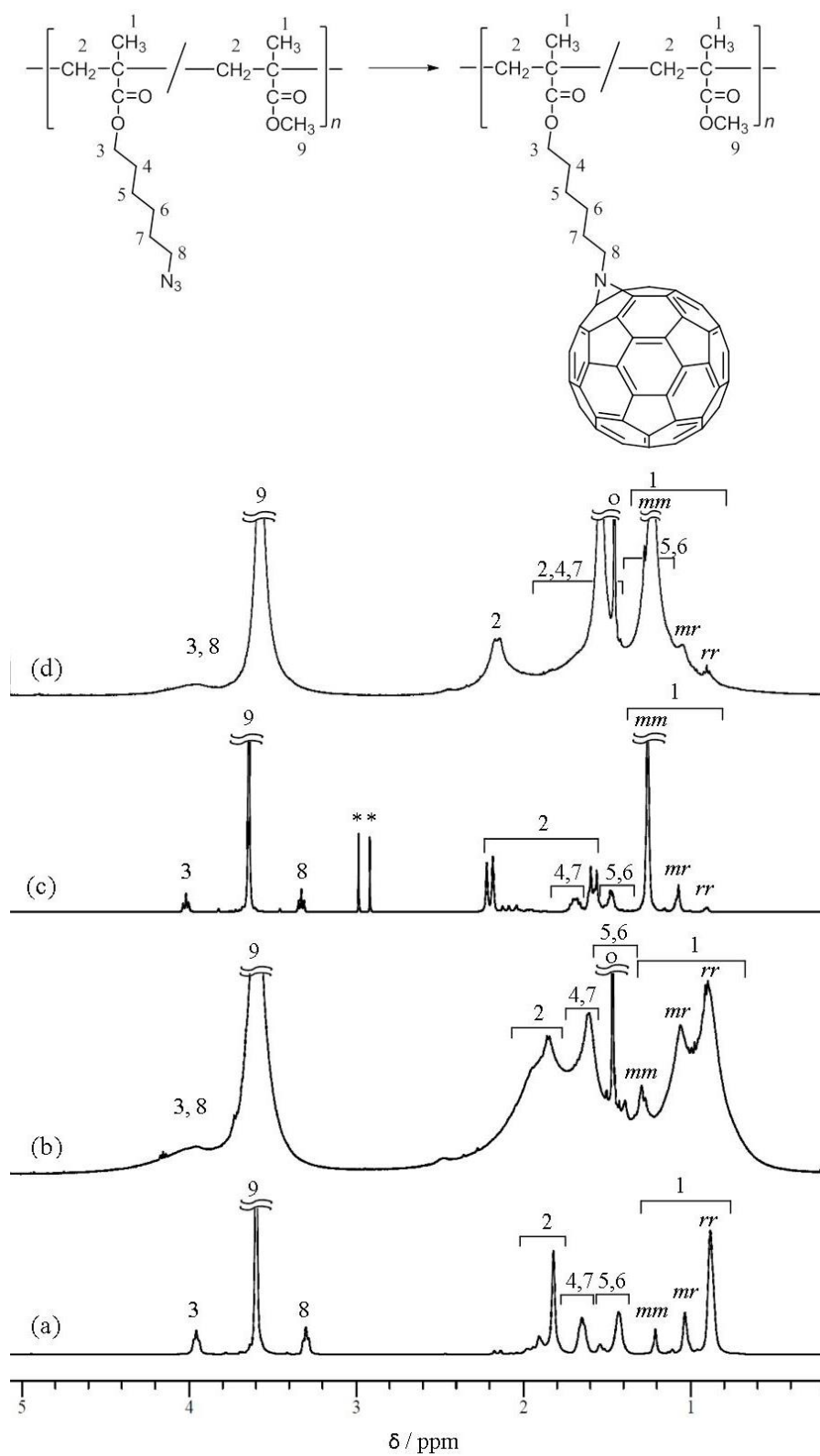


Figure 2-9. ¹H NMR spectra of (a) *st*-PN₃, (b) *st*-PF, (c) *it*-PN₃, and (d) *it*-PF (400MHz, CDCl₃, 55 °C). * DMF, ○ H₂O

N_3 -CH₂ protons (signal 8) at 3.33 ppm disappeared after the reaction and shifted to 3.98 ppm, over-lapping with O-CH₂ (signal 3), which indicates the complete consumption of azide groups. The completion of the cycloaddition was also confirmed by IR spectra (**Figure 2-10**), where the disappearance of the azide absorption band (2095 cm⁻¹) was observed.

While the precursors for both *st*- and *it*-PFs have narrow molecular weight distribution ($M_w/M_n = 1.05$ for *st*-PCI and $M_w/M_n = 1.19$ for *it*-PCI, respectively), the C₆₀-incorporated polymers exhibited broad and multi-modal molecular weight distribution (*it*-PF are much broader than *st*-PF) (**Figure 2-11**). As described in Chapter 1 for *atactic* C₆₀-polymethacrylate prepared through radical polymerization, the aggregation of C₆₀ moieties might not occur in THF for *st*- and *it*-PFs. Thus, the broad and multi-modal peaks indicates that branching of macromolecular chains occurred to increase the molecular weight, probably due to the addition of azide groups onto more than one point of single C₆₀ moieties. The low yield of THF-soluble fraction can be explained by the same reason; that is, the growth of branching causes cross-linking, and the cross-linked macromolecules became insoluble and was removed in the extraction procedure as an insoluble fraction.

The soluble yield of *it*-PF was lower than *st*-PF. There are two possible reasons for this result. First, based on the result on **Table 2-6**, MMA showed the tendency to have higher reactivity than CHMA in *isotactic* copolymerization. Thus, MMA was consumed faster than CHMA so that at the final stage only CHMA remained for polymerization. In such case, *it*-PCI might form CHMA rich segments at the final stage of polymerization. During the reaction of *it*-PN₃ with C₆₀, this structure will increase the probability of multi addition due the close distant of azide groups. The

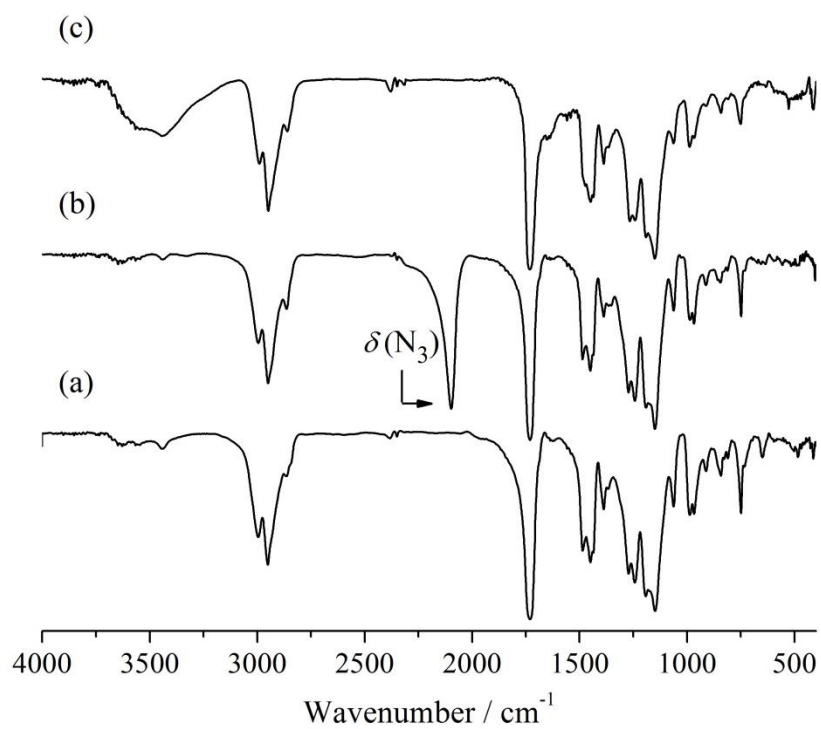


Figure 2-10. IR spectra of (a) Run 2, **Table 2-2**, (b) *st*-PN₃, (c) *st*-PF.

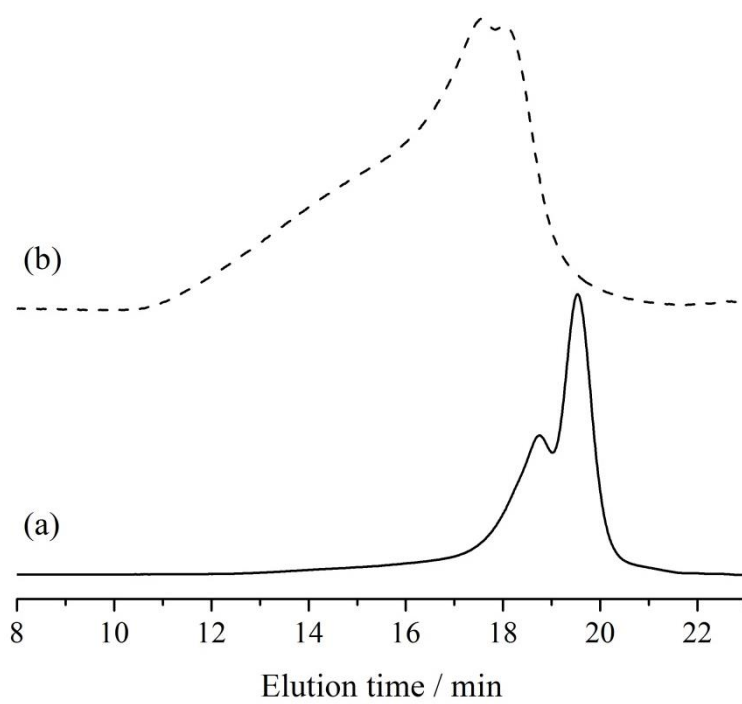


Figure 2-11. SEC charts of (a) *st*-PF, (b) *it*-PF in THF

second reason is the molecular weight of the precursor polymer. **it-PCI** has much higher molecular weight than **st-PCI**, led to high azide content on **it-PN₃**. Therefore, one macromolecular chain on **it-PF** will have much higher C₆₀ content than **st-PF**, and yielded as insoluble fractions after the reaction.

Interestingly, considering the contents of C₆₀ moieties, the observed molecular weights were much lower than expected. Similar results were also observed for the radically prepared *atactic* C₆₀-polymethacrylate as described in Chapter 1. It might be due to the interaction between C₆₀-moieties and SEC packing material (polystyrene gel).²⁰

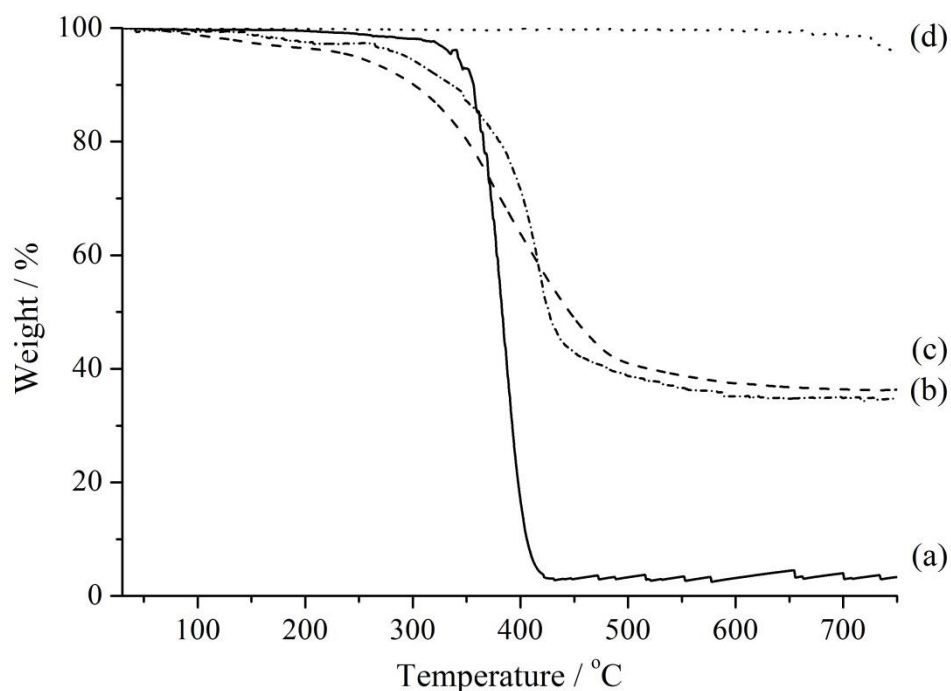


Figure 2-12. TGA curves of (a) *it*-PMMA ($M_n = 10500$, $M_w/M_n = 1.34$, $mm / mr / rr = 95 / 4 / 1$), (b) *st*-PF, (c) *it*-PF and (d) C₆₀ under N₂ atmosphere.

Figure 2-12 shows the TGA curves of *it*-PMMA ($M_n = 10500$, $M_w/M_n = 1.34$, $mm / mr / rr = 95 / 4 / 1$), C₆₀, *st*-PF, and *it*-PF under N₂ atmosphere. The weight

contents of C₆₀ moieties in ***st*-PF** and ***it*-PF** were estimated in a similar manner to the procedure as described in Chapter 1. The contents of C₆₀ moieties in ***st*-PF** (33.9 wt%) was lower than in ***it*-PF** (38.9 wt%), although the initial azide content was the same. The C₆₀ contents of ***st*-PF** and ***it*-PF** were lower than expected from the initial azide content (55 wt%), probably because the multi-addition of azide groups to C₆₀ moieties. Nevertheless, the obtained ***st*-PF** exhibited high solubility in common organic solvents such as CHCl₃, THF, and toluene, whereas ***it*-PF** was partially soluble in CHCl₃ and toluene. The high C₆₀ contents and good solubility of ***st*-PF** is promising as an electron acceptor for OPVs. The fundamental photoelectric properties and application to OPV devices are described in the next Chapter.

2.4 Conclusion

Syndiotactic-specific anionic copolymerization of MMA and CHMA was conducted with the binary initiator, Li-*i*PrIB / EtAl(ODBP)₂, while *isotactic*-specific polymerization was performed with Li-*i*PrIB / Me₃SiOLi. Although the 6-chlorohexyl chain of CHMA showed the prominent effect on the polymerization, controlled molecular weight and stereoregularity were achieved under the optimized conditions. The resulting copolymers were used as precursors for the synthesis of stereoregular C₆₀-containing polymethacrylates. The *isotactic* polymer afforded lower yield and broader molecular weight distribution than the *syndiotactic* polymer; branching of macromolecular chains, probably due to the addition of azide onto the several points of single C₆₀ moieties, were found in both cases. The *syndiotactic* polymer exhibited good solubility in common organic solvents, while the *isotactic* polymer was partly soluble in CHCl₃ and toluene. Thus, the *syndiotactic* polymer is a more promising material as an electron acceptor for OPVs.

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Chapter 3

Properties and application of stereoregular C₆₀-containing polymethacrylates to organic photovoltaics

3.1 Introduction

Fullerene (C₆₀)-containing polymers often exhibit very unique properties generated from the combination of the superior electronic properties of highly symmetrical fullerene moieties with the properties of the polymeric backbone.¹ The new properties that are important as materials for organic photovoltaic (OPV) applications are in terms of photoelectric properties and morphology in thin films. Characterization of photoelectric properties of fullerene C₆₀-containing polymers is a very important task before applying them as electron acceptors for OPVs. This is because the performance of a bulk-heterojunction OPV is dependent on the energy level difference between an electron-donor and an acceptor in an active layer.² In order to efficiently generate charge transfer, the lowest unoccupied molecular orbital (LUMO) level of a donor and an acceptor must be arranged properly so that suitable energetic driving force is enough to drift the electron from the LUMO level of an illuminated donor to the LUMO level of acceptor.³ Information about the highest occupied molecular orbital (HOMO)-LUMO levels of donor and acceptor materials will also allow us to carefully design the device structure and composition.²

Cyclic voltammetry (CV) is an effective and the most common method to

determine HOMO-LUMO energies of organic electronics materials.⁴ It is based on the measurement of oxidation and reduction potentials of materials. Oxidation corresponds to the removal of an electron from the HOMO energy level, while reduction corresponds to the electron addition to the LUMO level of the materials. Thus, the electrochemical bandgap can be calculated from the difference in the energy levels of HOMO and LUMO.

On the other hand, optical band gap of organic semiconductors is generally estimated from UV-Vis spectroscopy. As optical band gap represents the excitation energy of the material as a function of absorbed photon energy, the bandgap is generally determined from the cut-off of the absorption spectra. The bandgap can be evaluated more precisely from the correlation between the absorption coefficient and the photon energy.⁵ Besides, HOMO level of organic semiconductor can be determined by using spectroscopic method such as photoelectron spectroscopy in air (PESA).⁶ This is the plots of the number of electrons emitted against the irradiated light energy; the energy where the emission of electrons starts means the ionic potential, *i.e.* HOMO, of semiconductor. PESA provides the advantage on measurement condition because it allows direct measurement on the work function of a solid semiconductor under ambient condition, *i.e.*, the operating condition of OPV device. It should be noted that CV measurements cause the change of chemical structure during the oxidation process, while the spectral measurements do not. Thus, electrochemical HOMO-LUMO levels determined by CV and optical measurements should be discussed independently.

Various kinds of C₆₀-containing polymers have been reported to exhibit interesting morphology that is significantly affected by the structure of polymer backbone.⁷ For example, it is reported that a donor-acceptor block copolymer composed

of two segments containing poly(phenylenevinylene) (PPV) and C₆₀, respectively, formed regular honeycomb nanostructure.⁸ On the other hand, C₆₀-polynorbornene reported by Sivula *et al.* is an effective surfactant for a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) to afford nanoscale phase separation.⁹ More recently, Charvet *et al.* reported the formation of nanowires and nanosphere of C₆₀-polynorbornene by changing the solvent for drop casting.¹⁰ Nouridine *et al.* reported the surface morphology of P3HT blend with C₆₀-polystyrene can change drastically as the C₆₀ content on the polymer slightly increase.¹¹ In a similar way, nanophase separation can also be expected from the C₆₀-polymethacrylates system.

In Chapter 1, the author described the HOMO-LUMO level of *atactic* C₆₀-polymethacrylate prepared through radical polymerization. The HOMO level are found to be higher than those of C₆₀ and PCBM, while the difference between LUMO levels of C₆₀-polymethacrylates and P3HT is enough to provide energetic driving force for charge transfer. In this chapter, the author compares the photoelectric properties, *i.e.* HOMO-LUMO levels, band gap and fluorescence quenching in the blend with P3HT, between *atactic* and *syndiotactic* C₆₀-polymethacrylates prepared by radical and anionic polymerizations, respectively. The differences on surface morphology as well as OPV devices performances are also reported. The photoelectric properties of *isotactic* C₆₀-polymethacrylates are not discussed due to the low yield and low solubility of the polymer in CHCl₃.

3.2 Experiments

Materials

Fullerene C₆₀ (Aldrich, Purity $\geq 98\%$) and (PCBM, Aldrich, Purity $> 99\%$) were used as reference material for device characterization. P3HT (Aldrich, $M_n = 5.4 \times 10^3 - 7.5 \times 10^3$, $M_w / M_n \leq 2.5$) was used as an electron-donor material. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS; Heraeus CLEVIOS P VP Al 4083) was used as a hole extraction layer of solar cells. Indium–tin oxide (ITO) coated glass plates ($15 \Omega \text{ sq}^{-1}$) as a substrate was purchased from Asahi Glass. CHCl₃ and CH₃CN (anhydrous) from WAKO chemicals companies was used as received. *Atactic* and *syndiotactic* C₆₀-polymethacrylates, **at-PF** ($M_n = 10200$, $M_w/M_n = 2.77$, $mm / mr / rr = 10 / 32 / 58$, C₆₀ content = 41.4 wt%) and **st-PF** ($M_n = 11200$, $M_w/M_n = 1.94$, $mm / mr / rr = 3 / 10 / 87$, C₆₀ content = 39.9 wt%), prepared by radical and anionic polymerizations and the subsequent C₆₀ modification in similar manners as described in Chapter 1 and Chapter 2, respectively. All other reagents and solvents were used as received.

Instruments

Absorption spectra were recorded on a UV–vis spectrometer (Hitachi, U4100). The thicknesses of thin films were measured with a laser microscope (Keyence, VK9710).

Purification of C₆₀-containing polymethacrylates by preparative SEC

at-PF (90 mg) were purified by preparative size exclusion chromatography (SEC) equipped with a SEC column (NEXT JAIGEL-ODS-AP-50, Japan Analytical

Industry), using CHCl_3 as eluent at a flow rate 14 mL min^{-1} . The purified product was dried *in vacuo* and analyzed again by using SEC on a GPC-900 chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C ($300 \text{ mm} \times 7.5 \text{ mm}$), Polymer Laboratories], using tetrahydrofuran (THF) and CHCl_3 as an eluent (flow rate = 0.8 mL min^{-1}), and calibrated against standard poly(methyl methacrylate) (PMMA) samples (Shodex, MW: 1.25×10^6 , 6.59×10^5 , 1.95×10^5 , 4.96×10^4 , 2.06×10^4 , 6.82×10^3 , 2.00×10^3). The **st-PF** was also purified in similar manner to **at-PF**.

Cyclic voltammetry

Cyclic voltammetry (CV) measurements were carried out in a solution with a three-electrode cell configuration consisting of a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode at room temperature. Measurements were conducted using thin films of PCBM, **st-PF**, and **at-PF**, which had been loaded on glassy carbon by dip coating from their solutions in CHCl_3 with 0.1 M tetrabutylammonium tetrafluoroborate ($\text{Bu}_4\text{N}^+\text{BF}_4^-$) in CH_3CN as a supporting electrolyte. The potential was swept at a rate of 10 mV s^{-1} and reported against the potential of a ferrocene/ferrocenium (Fc/Fc^+) redox couple.

Photoelectron spectroscopy in air (PESA) analysis

ITO-coated substrates having area of $1.0 \text{ cm} \times 2.0 \text{ cm}$ (Asahi Glass, $15 \Omega \text{ sq}^{-1}$) were solvent-cleaned in an ultrasonic cleaner according to the following manner (each step was 5 minutes); rinsed in distilled water, detergent (2 vol%), flowing tap water, distilled water, acetone, and isopropanol. Subsequently, the substrates were dried and treated with UV- O_3 for 1200 s. P3HT, PCBM, **at-PF** and **st-PF** in CHCl_3 were spin coated on the pre-cleaned ITO substrate at 1200 rpm for 60 s, respectively. The films

were annealed at 120 °C *in vacuo* for 10 min and cooled to room temperature before analysis. PESA was recorded on an AC2 (Riken Keiki).

Measurement of fluorescence quenching

The films of P3HT and the blends of P3HT:PCBM, P3HT:**st-PF**, and P3HT:**at-PF** (P3HT : C₆₀ moieties = 1 / 1 in weight) were spin coated on glass substrates at 800 rpm for 30s from 1 wt% solution in chlorobenzene. All films were excited at a wavelength of 508 nm and fluorescence emission was recorded over 800-1100 nm on a Fluorolog fluorescence spectrometer (HORIBA).

AFM images

ITO-coated (24 mm × 24 mm, 9 Ω sq⁻¹) were cleaned in a similar manner to the previous procedure for PESA analysis. Mixtures of P3HT and **st-PF** or **at-PF** (P3HT : C₆₀ moieties = 1 / 1 in weight) dissolved in CH₃Cl (1.5 wt%) were spin-coated (1500 rpm, 60 s, slope 5 s) and wiped the edges by acetone-soaked cotton tip twice. The tapping mode AFM phase images were recorded on a SII SPA 400 (SII Nanotechnologies) equipped with a cantilever (non-coated Silicon Si DP401, spring constant = 33 N m⁻¹) under the ambient condition.

OPV device fabrication and evaluation of the performance

An ITO-coated substrates having 6 solar cell units with an active area 0.04 cm² were cleaned in a similar manner to the previous procedure for morphology analysis. A PEDOT:PSS solution was then spin-coated at 2000 rpm for 60 s (slope 5 s) on the pre-cleaned substrates. The edges of each substrate were wiped two times with a cotton

tip soaked with CHCl_3 . These films were then pre-annealed on a hot plate at 150 °C for 10 min in air. Subsequently, mixtures of P3HT and ***st*-PF**, ***at*-PF** or PCBM (P3HT : C_{60} moieties = 1 / 1 in weight) dissolved in CH_3Cl (1.5 wt%) were spin-coated (1500 rpm, 60 s, slope 5 s) and the edges were wiped again with a CHCl_3 -soaked cotton tip. The samples were loaded into a thermal evaporation chamber where LiF (5 nm, evaporation speed $0.3 - 0.5 \text{ \AA s}^{-1}$) and aluminum layers (100 nm, evaporation speed $1.8 - 2.5 \text{ \AA s}^{-1}$) were sequentially evaporated onto the samples under vacuum ($2 \times 10^{-4} \text{ Pa}$). After cooling to room temperature, the device was immediately sealed by glass in a glove box for protection from air exposure prior to analysis. Current–voltage (J - V) characteristics of the solar device were measured at room temperature in air with a photovoltaic measurement system (Bunkokeiki, CEP-015) under a simulated solar light (AM 1.5 G, 100 mW cm^{-2}).

3.3 Results and discussion.

3.3.1 Purification of C_{60} -containing polymethacrylates by preparative SEC

In order not only to achieve high performance of device but also to gain clear understanding on photoconversion processes over the whole components, high-purity OPV materials are required.¹² For polymeric materials, preparative SEC is known as a convenient and certain way for the purification.^{12, 13}

Atactic C_{60} -polymethacrylate (***at-PF***), prepared through the radical polymerization and the subsequent polymer modification described in Chapter 1, was purified by repeating reprecipitation in hexane and extraction with THF. The polymer was further purified on preparative SEC. **Figure 3-1** shows the chromatogram of ***at-PF*** recorded on the preparative SEC. The peak of polymeric product was observed at around 2100-2500 s (RI detector), while a single and small peak was observed around 6000 s. This small peak was assignable to unreacted C_{60} , indicating that the reprecipitation was not enough to remove C_{60} completely. In fact, the fraction of this peak colored light purple, characteristic to C_{60} solution. The former fraction with a peak tailing up to 3000 s was collected as a purified polymer with 71% recovery yield.

The purified polymer was analyzed again by analytical SEC as $CHCl_3$ solution by using UV detector (**Figure 3-2**). As described in Chapter 1, probably the broad and multi-modal peaks were not due to the presence of unreacted pristine C_{60} but to the intra- and inter-molecular aggregation of C_{60} moieties in the side groups in $CHCl_3$ solution. This consideration is also supported by the fact that the board peaks are still observed after the purification by preparative SEC. The *syndiotactic* polymer (***st-PF***) was also purified in a similar way.

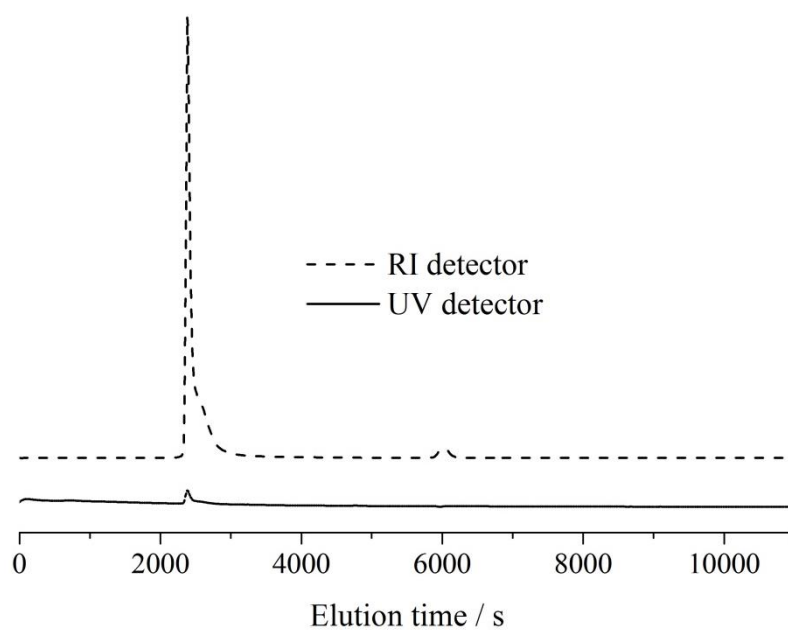


Figure 3-1. Preparative SEC charts of *at*-PF.

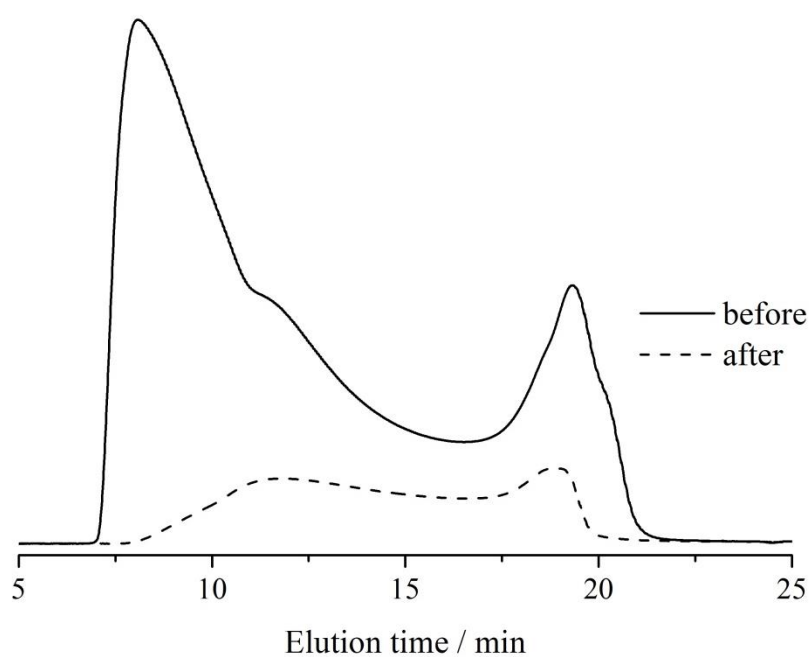


Figure 3-2. Analytical SEC charts of *at*-PF before and after purification by preparative SEC (40 °C, CHCl₃ PMMA standards, UV detector).

3.3.2 Photoelectric properties of C₆₀-containing polymethacrylates

HOMO-LUMO energy levels estimated by cyclic voltammetry

As mentioned previously in Chapter 1, **at-PF** did not afford clear peaks of oxidation potential $E_{\text{ox}1/2}$ and reduction potential $E_{\text{red}1/2}$ in the cyclic voltammogram. In contrast, **st-PF** and PCBM gave clear peaks on the reduction waves while the oxidation waves of **st-PF** and PCBM were irreversible (**Figure 3-3**). Thus the $E_{\text{ox}1/2}$ s could not be determined precisely. It is known that oxidized C₆₀ is chemically unstable, leading to irreversible oxidation wave.¹⁴ The same was also true of **st-PF** and PCBM.

In order to evaluate the LUMO level, the potential of Ag/AgCl reference electrode was calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc⁺), whose energy level is 4.98 eV below the vacuum level. From our experimental result, the oxidation potential ($E_{\text{ox}1/2}$) of ferrocene was found to be 0.2 V against Ag/Ag⁺. Thus, HOMO and LUMO levels can be determined according to the following equation:

$$\text{LUMO} = -[(E_{\text{red}1/2} - 0.2) + 4.98], \quad (1)$$

Where $E_{\text{red}1/2}$ is the onset of the first reduction and oxidation potentials of the material versus Ag/Ag⁺.

The $E_{\text{red}1/2}$ s of **st-PF** and PCBM were found to be -0.73 V and -0.76 (**Figure 3-3**), respectively. Thus the LUMO levels of PCBM and **st-PF** were found to be same at -4.0 eV, lower than those of C₆₀ (-4.5 eV). This indicates that LUMO level of **st-PF** was slightly affected by the modification of C₆₀ moieties. Haddon reported that functionalized C₆₀ usually shows higher negative reduction potential, which is proportional to LUMO as shown by equation (1), because of fewer π electrons and release of strain energy.¹⁵ The small increases of LUMO level of **st-PF** also can be explained by the similar reason.

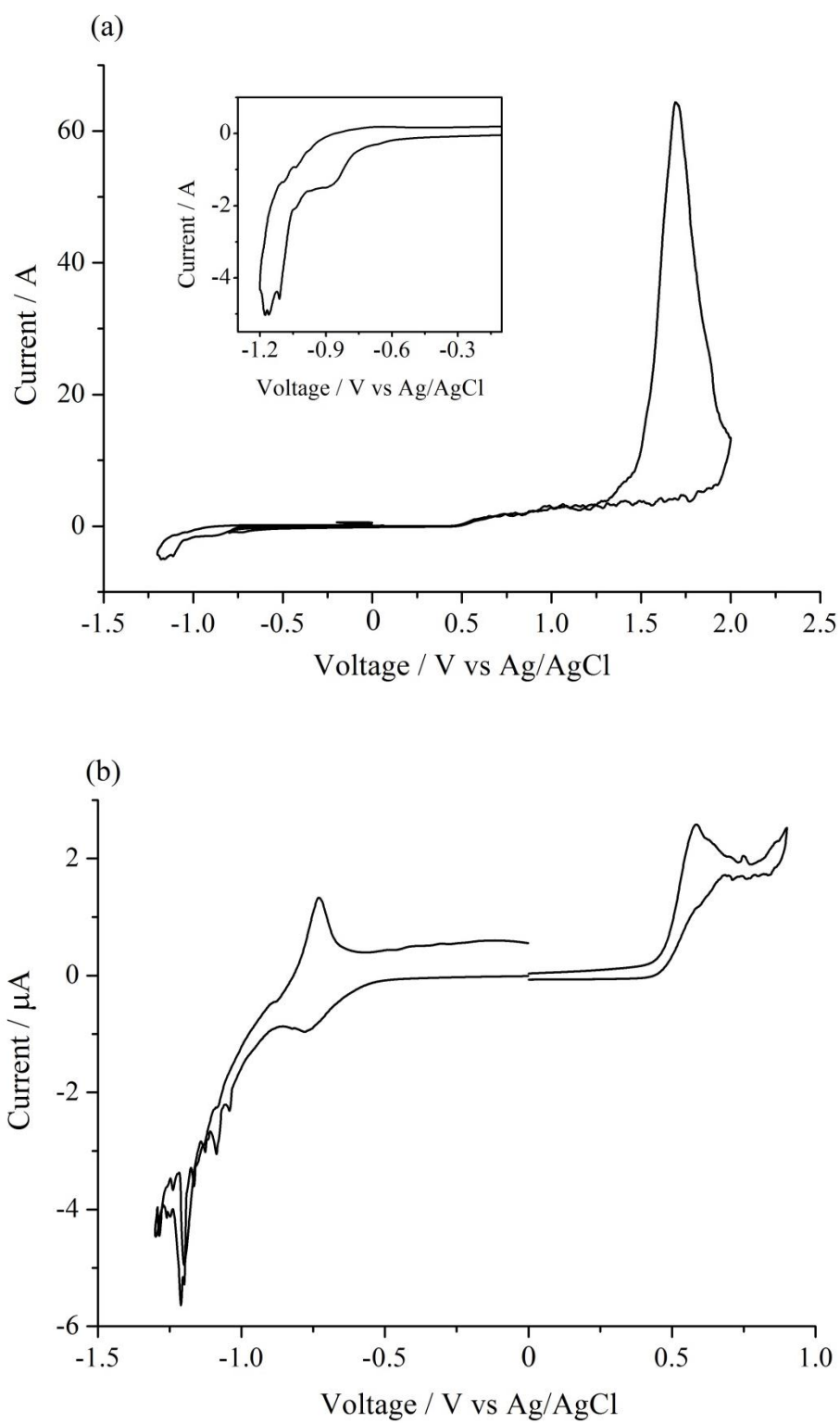


Figure 3-3. Cyclic voltammograms of (a) PCBM and (b) *st*-PF

HOMO-LUMO energy levels estimated by optical analysis

HOMO level of an organic semiconductor can also be evaluated by using spectroscopic methods such as PESA. **Figure 3-4** shows the results of PESA measurements for ***at*-PF**, ***st*-PF**, P3HT and PCBM; their HOMO levels were determined from photoemission threshold energies (intercepts) to be -5.5 eV, -5.5 eV, -4.7 eV and -5.7 eV, respectively. The HOMO level of ***st*-PF** was higher than that of PCBM. Apparently, HOMO level of ***st*-PF** is similar to that of ***at*-PF**. Thus, the difference in stereoregularity of both polymers does not affect the HOMO levels.

The UV-Vis of ***st*-PF**, ***at*-PF**, P3HT, PCBM and C₆₀ in CHCl₃ solutions and films are presented in **Figure 3-5**. UV-Vis of ***st*-PF** and ***at*-PF** in CHCl₃ exhibited a broad absorption band up to 800 nm both in films and solutions and displayed broad absorption peak at around 330 nm. According to Changduk's report,¹⁶ the impurity of unreacted C₆₀ in the polymeric product results in sharp absorption at 330 nm, whereas purified polymer exhibited not sharp but broad absorption at this region. Hence, the broad adsorption of ***st*-PF** and ***at*-PF** suggest the absence of unreacted C₆₀ in it.

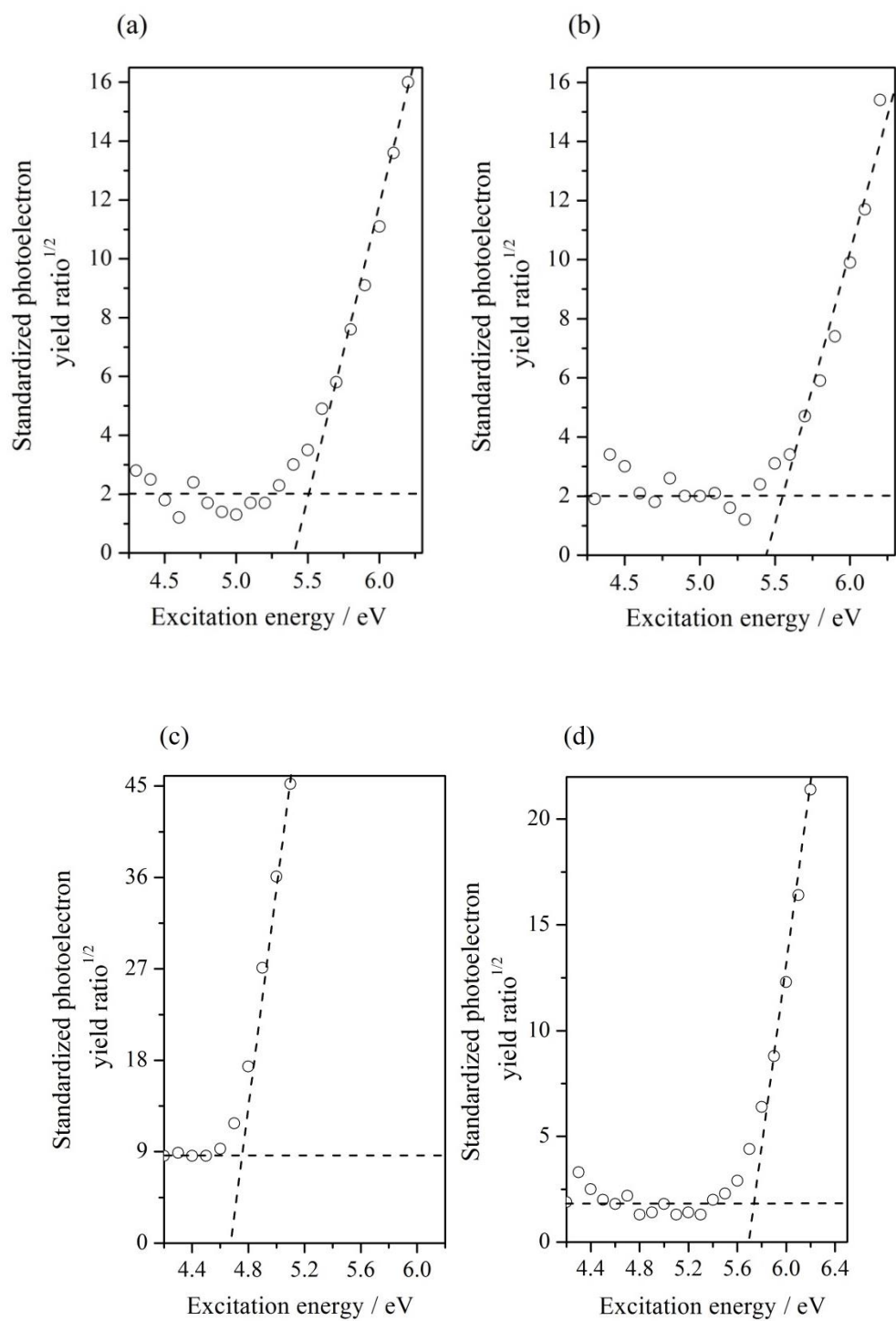


Figure 3-4. Photoelectron spectroscopy analyses in air of (a) *st*-PF (b) *at*-PF, (c) P3HT and (d) PCBM.

Gartner *et al.* have reported that the electronic band gap (E_g) of solid semiconductor can be estimated from the absorption coefficient (a) using the following equation:¹⁷

$$ah\nu = A(h\nu - E_g)^n \quad (2)$$

where A is a constant, h is Planck's constant, ν is wavelength, and n is a constant depending on the probability of transition; the n values are 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition gaps, respectively. The π - π^* transition in conjugated organic materials is categorized as direct allowed transition ($n = 1/2$). In order to determine the optical band gap of **st-P**, equation (2) was used to plot the correlation of absorption coefficients with photon energy. The UV-Vis spectra of P3HT, PCBM and C₆₀ as reference materials were also treated in similar manner. The results are presented in **Figure 3-6**. Band gap of **st-PF** was found to be around 1.6 eV. Furthermore, by substitution of the band gap and HOMO level to equation (3):

$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_g \quad (3)$$

LUMO level was calculated to be -3.9 eV. As described in Chapter 1, HOMO and LUMO levels of **at-PF** were determined in a similar manner to be -5.5 and -3.9 eV, respectively.

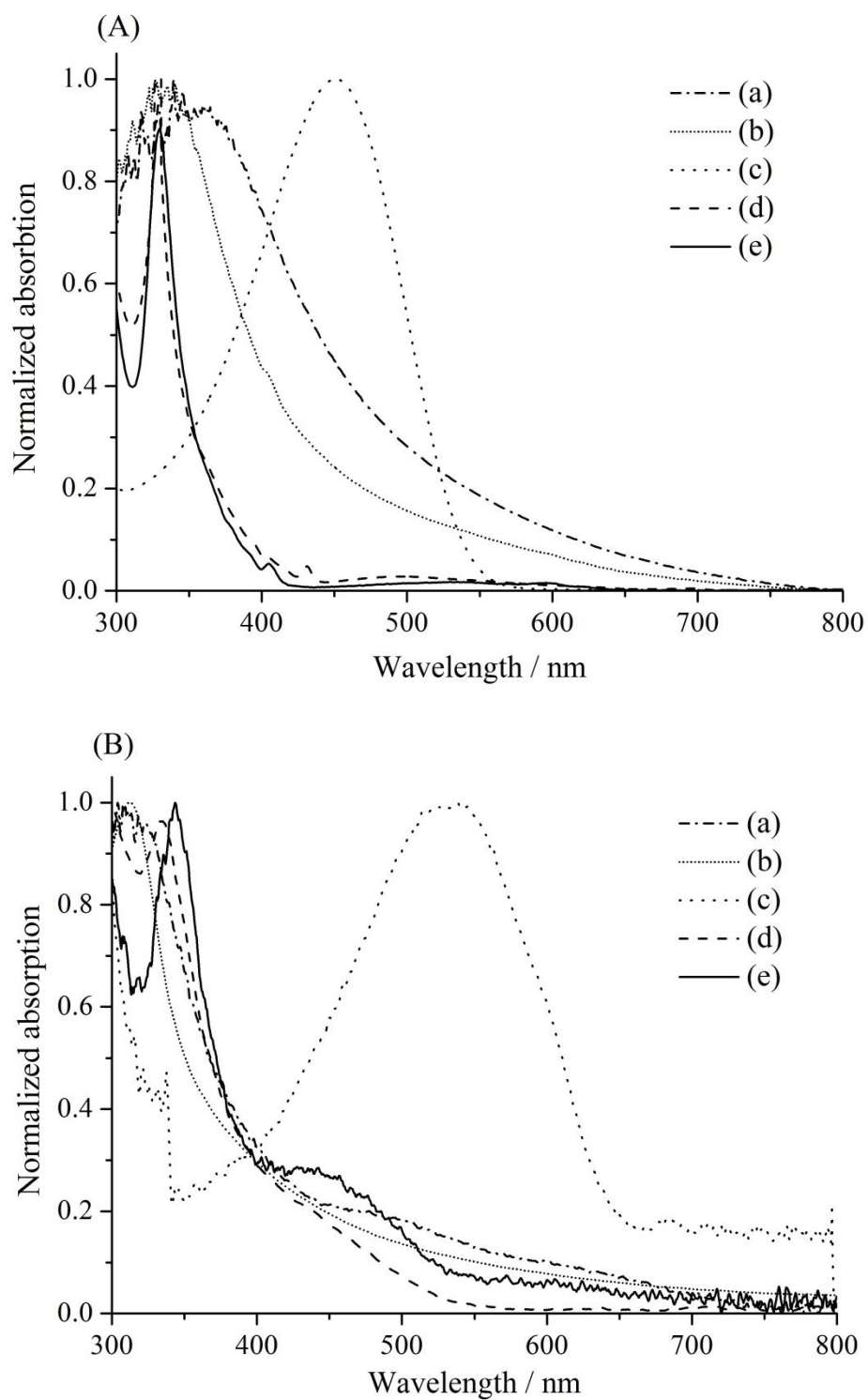


Figure 3-5. UV-Vis spectra of (a) *st*-PF, (b) *at*-PF, (c) P3HT, (d) PCBM, and (e) C₆₀ in (A) CHCl₃ and (B) thin films.

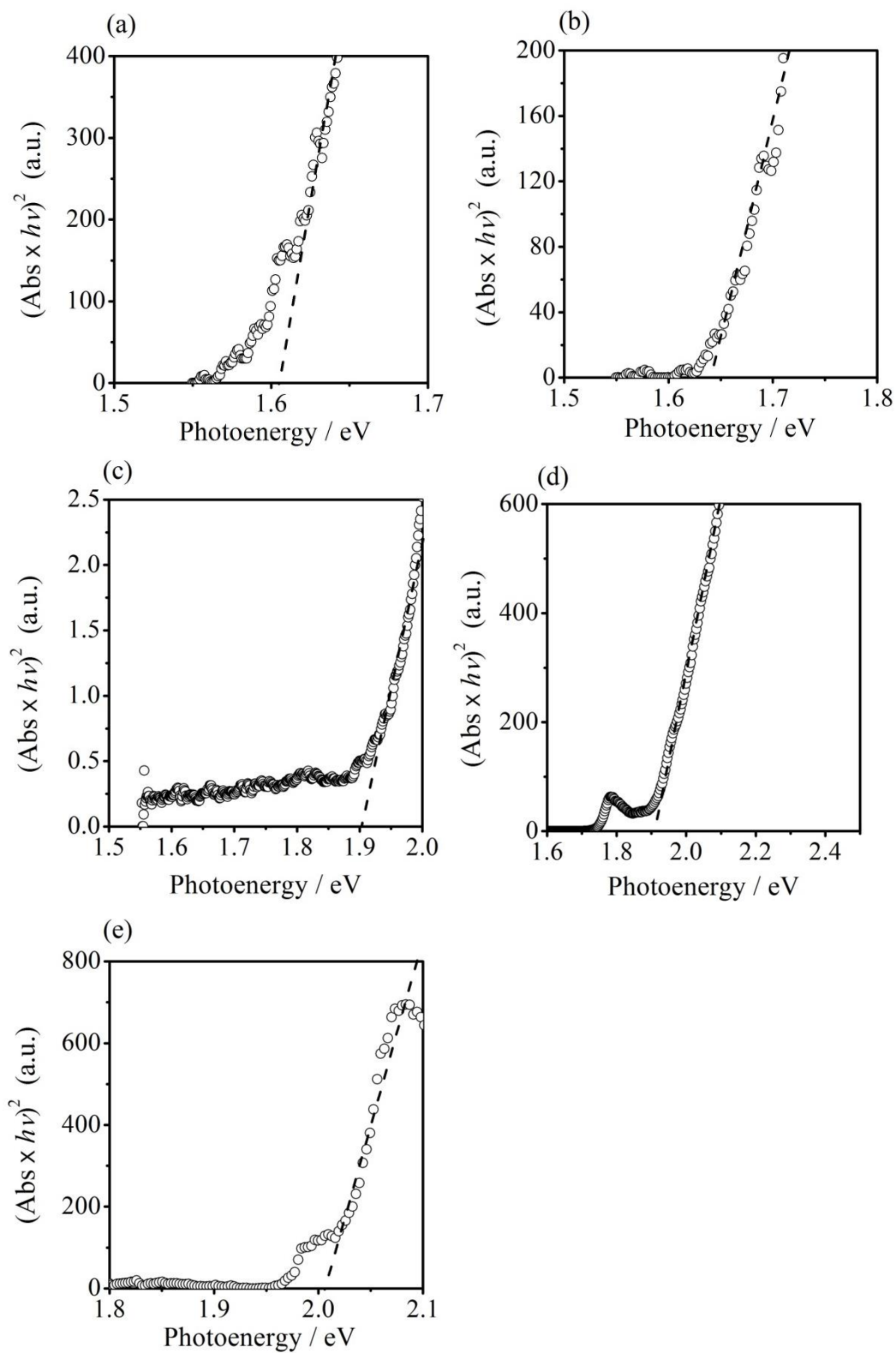


Figure 3-6. Plots according to equation (4) with $n = 1/2$. (a) **at-PF** and (b) **st-PF**, (c) P3HT, (d) PCBM, and (e) C₆₀.

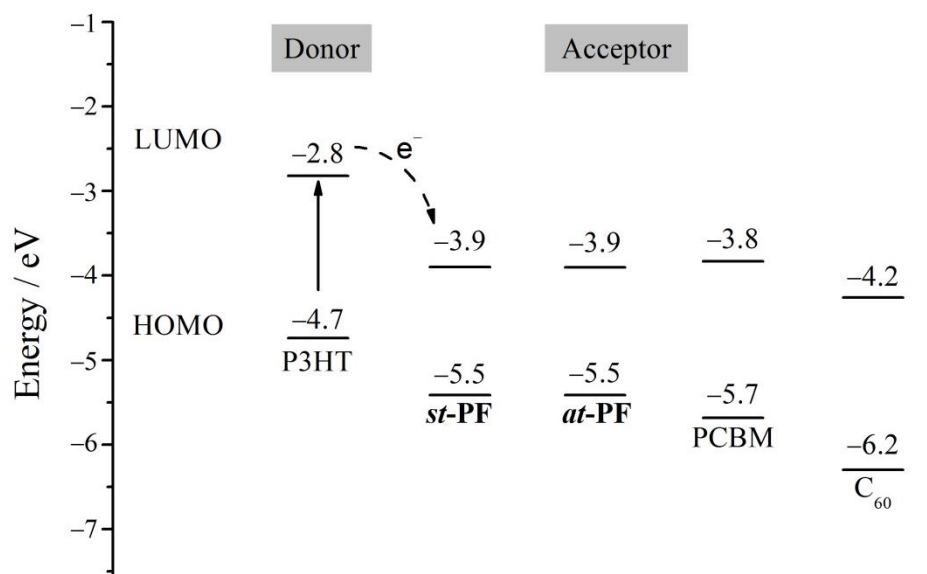


Figure 3-7. Schematic energy diagram of **at-PF** and **st-PF** compare to reference materials.

It is found that band gaps and LUMO levels are not affected by their precursor polymers which are their C₆₀ content is almost the same (**Figure 3-7**). The LUMO level of **st-PF** is similar to that of **at-PF** polymer. The carbonyl oxygen on polymethacrylates backbone do not have significant effect on the LUMO level as it is comparable to PCBM.¹⁸ The report gives an insight that stereoregularity of the polymethacrylate backbone does not influence the energy levels of C₆₀-polymethacrylates. In any event, LUMO levels of each polymer are in proportional position with that of P3HT for providing driving force of electron hole separation and injection to acceptor domain.^{3, 19}

Fluorescence quenching

Figure 3-8 shows the fluorescence quenching of P3HT blended with PCBM, **st-PF** and **at-PF** in thin film with the proportion of P3HT: C₆₀ moieties of 1:1 in mass. The quenching efficiency for the blend with **st-PF** was very high (97%), only 3% lower than the blend with PCBM (>99%). Interestingly, the quenching efficiency of **st-PF** was

higher than that of **at-PF** (94%), suggesting the large interfacial area of **st-PF** with P3HT. The results also imply that both **st-PF** and **at-PF** are suitable as a polymeric electron acceptor of enough compatibility with P3HT. The higher quenching of **st-PF** than **at-PF** will be discussed in the next subsection.

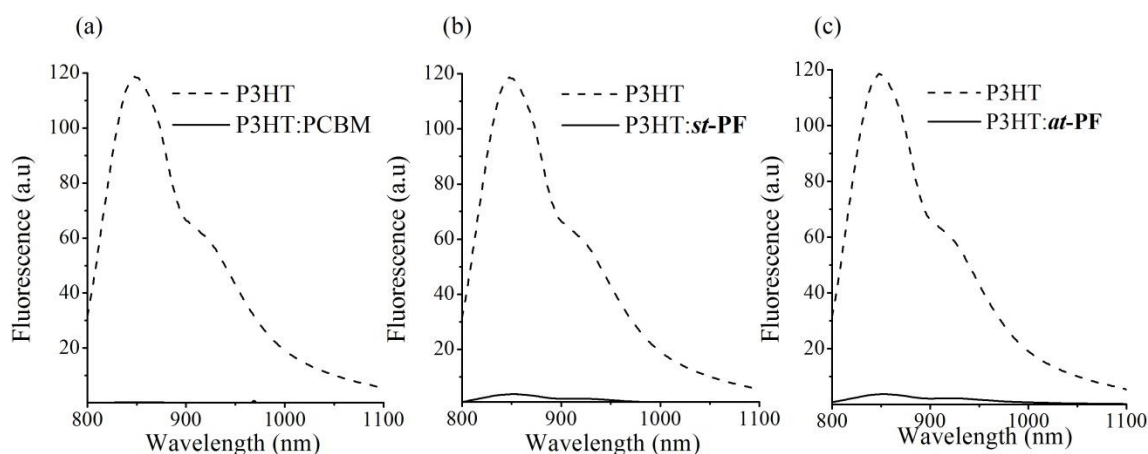


Figure 3-8. Fluorescence spectra of P3HT and its blends with (a) PCBM, (b) **st-PF** and (c) **at-PF** on films.

Surface morphology

Figure 3-9 displays the tapping-mode AFM phase images of **st-PF** and **at-PF** in the blends with P3HT. It is known that the increase in *meso* diad contents of poly(methyl methacrylate) (PMMA) decreases the interaction with other polymers in blends,²⁰⁻²² and thus *st*-PMMA has better miscibility with other polymers than *at*-PMMA. Obviously, the miscibility of C₆₀-polymethacrylates with P3HT exhibited significant differences; **at-PF** showed a coarse morphology in micrometer order, while **st-PF** showed a finer morphology. These results are consistent with the fluorescence quenching observation as shown on **Figure 3-8**; **st-PF** quenched the fluorescence of P3HT up to 97% in the blend, which was 3% higher than **at-PF**. Thus, **st-PF** has good

compatibility with P3HT and is a potential electron acceptor for OPVs.²³

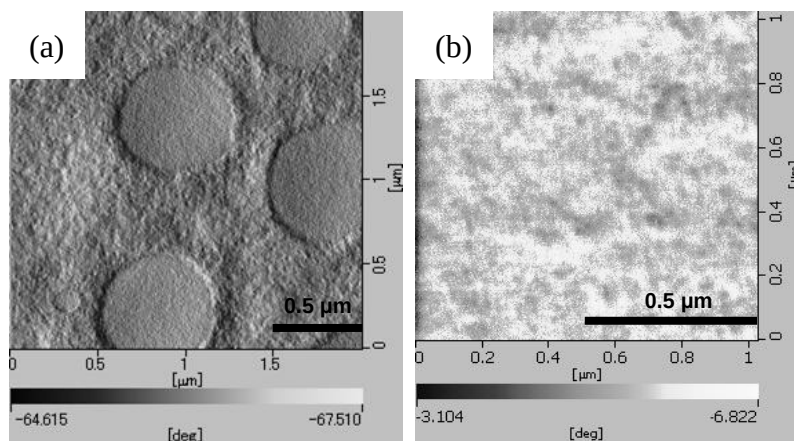


Figure 3-9. Phase images of thin films of P3HT blended with (a) *at*-PF and (b) *st*-PF on film.

3.3.3 Application to OPVs

The performance of bulk-heterojunction OPVs composed of P3HT as an electron donor and *at*-PF, *st*-PF, and PCBM as electron acceptors was investigated (**Table 3-1**). The current densities versus voltages (*J*–*V*) characteristics of solar cell device were taken under AM 1.5G irradiations from a calibrated solar simulator with an irradiation intensity of 100 mW cm^{–2}.

Table 3-1. OPV device performances of *st*-PF and *at*-PF in the blends with P3HT^a

Donor	Acceptor	J_{sc}	V_{oc}	FF	PCE	Thickness ^b
		mA cm ^{–2}	V		%	nm
P3HT	<i>st</i> -PF	0.043	0.89	0.26	0.011	92
	<i>at</i> -PF	0.011	0.73	0.34	0.0028	160
	PCBM	5.7	0.63	0.63	2.3	100

a) Measured under AM 1.5G irradiation (100 mW cm^{–2}).

b) Measured by laser microscope.

The P3HT:**st-PF** and P3HT:**at-PF** devices yielded poor current density (J_{sc}) and fill-factor (FF) which led to low power conversion efficiency (PCE) = 0.011 % (**st-PF**) and 0.0028 % (**at-PF**), while the P3HT:PCBM cell yielded PCE = 2.3%. Interestingly, however, open circuit voltage (V_{oc}) of the devices of **st-PF** and **at-PF** were 0.73 V, which were larger than that of the PCBM device. The increase in V_{oc} can be attributed to the higher LUMO levels of **st-PF** and **at-PF** than that of PCBM.

Since **st-PF** and **at-PF** devices have high fluorescence quenching and high V_{ocs} value, the fact that PCEs were low remains odd. As J_{sc} s were low, the author assumed that the charge transport might have been interrupted by the charge recombination before the reach to electrode. A similar result was observed by Yang *et al.*¹⁶ that reported C₆₀-containing polymers which form nanoscale domain.¹⁶ The authors assumed that it is due to the insulator effect of the polymeric backbone where C₆₀ attached. However, no experimental evidence was provided. Therefore, further investigation such as the measurement of electron hole mobility is necessary to elucidate the result.

3.4 Conclusion

Syndiotactic C₆₀-containing polymethacrylate, ***st*-PF**, purified by preparative SEC exhibited higher LUMO levels than ***at*-PF** as well as the better morphology in thin film of the blend with P3HT. Thus, ***st*-PF** is more suitable as an electron acceptor polymer for the combination with P3HT. In the application to OPVs devices, V_{oc} s of ***at*-F** and ***st*-F** are higher than that of PCBM, while the PCEs were very low. Although further analysis such as the measurement of electron-hole mobility is required to understand the electron transport properties of C₆₀-containing polymethacrylates, it can be concluded that stereoregularity is an important factor to affect the photoelectron properties and miscibility in the combination with P3HT.

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Chapter 4

Synthesis and reaction of block copolymer composed of independently clickable segments via monomer-selective living copolymerization

4.1 Introduction

In Chapter 3, the properties of C₆₀-containing polymethacrylates such as highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) level, fluorescence quenching, and device properties of the blend with poly(3-hexylthiophene) (P3HT) have been discussed. The results suggest that *syndiotactic* C₆₀-polymethacrylates has potentiality to be applied as electron acceptors in OPVS because the polymers exhibited larger open circuit voltage (V_{oc}) than the *atactic* polymer. However, the short-circuit current (J_{sc}) and fill factor (FF) were low so as to lead to poor power conversion efficiency (PCE) of the blend with P3HT. The low J_{sc} and FF can be ascribed due to the unoptimized morphology of the P3HT:C₆₀-polymethacrylates that deteriorates electron transport along the donor acceptor domains. As well known, optimum charge transports in a heterojunction organic photovoltaics (OPVs) requires an interpenetrating and bicontinuous percolation network of donor and acceptor phases in nanoscale order.^{1, 2, 3} Block copolymer bearing donor and acceptor moieties in side chains (**Figure 4-1**) is one promising approach to overcome this issue.

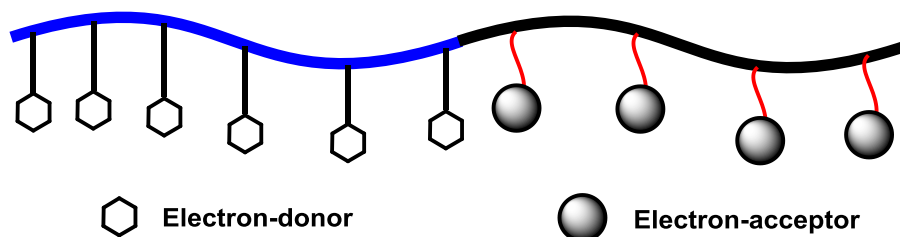


Figure 4-1. Block copolymer bearing donor and acceptor moieties on side chain.

Block copolymers can form microphase separation⁴ and nanoscale self-assembly⁵ in solid state, in melt and even in solution. Moreover, microphase separation in block copolymer not only forms random nanodomains but also arranges in regular alignment to establish a periodic structure (microlattice).^{4, 6} Therefore, a block copolymer containing donor and acceptor moieties in the side groups of each segment is expected to facilitate regular alignment of the donor and acceptor phases in OPVs device. In fact, Sivula *et al.* reported amphiphilic donor-acceptor block copolymer composed of two polynorbornene segments bearing oligothiophene and C₆₀ moieties, respectively.⁷ The block copolymer functioned as a compatibilizing agent and improved the surface morphology of the blend of P3HT:[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) to exhibit nanoscale domain size. Later, Charvet *et al.* prepared a similar block copolymer of polynorbornene where porphyrin and C₆₀ were introduced in the respective segments. Thin films of the copolymer exhibited nanowire structure where the nanowires consist of regularly alternating domain arranged perpendicular to their long axes. Photoinduced electron transfer at the interface of porphyrin domains to C₆₀ was observed with a fluorescence quenching efficiency up to 77%.⁸ In these literatures, the synthesis of block copolymer were carried out in sequential monomer addition by ring-opening metathesis polymerization.

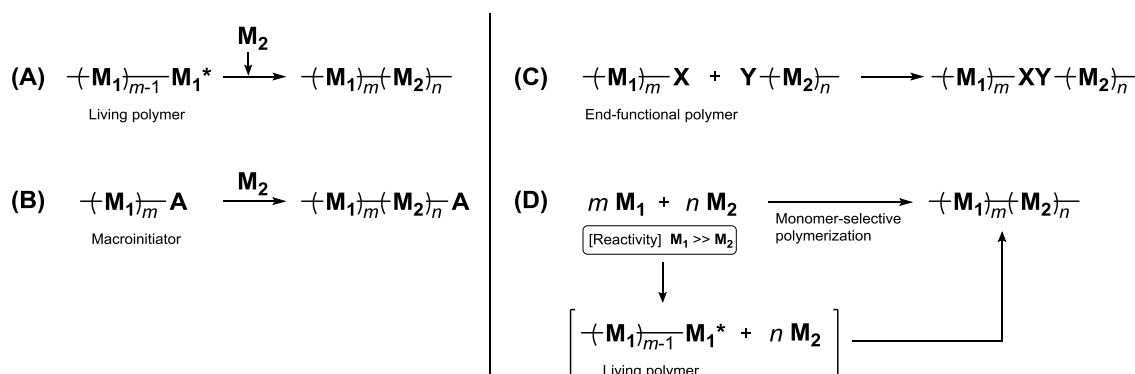
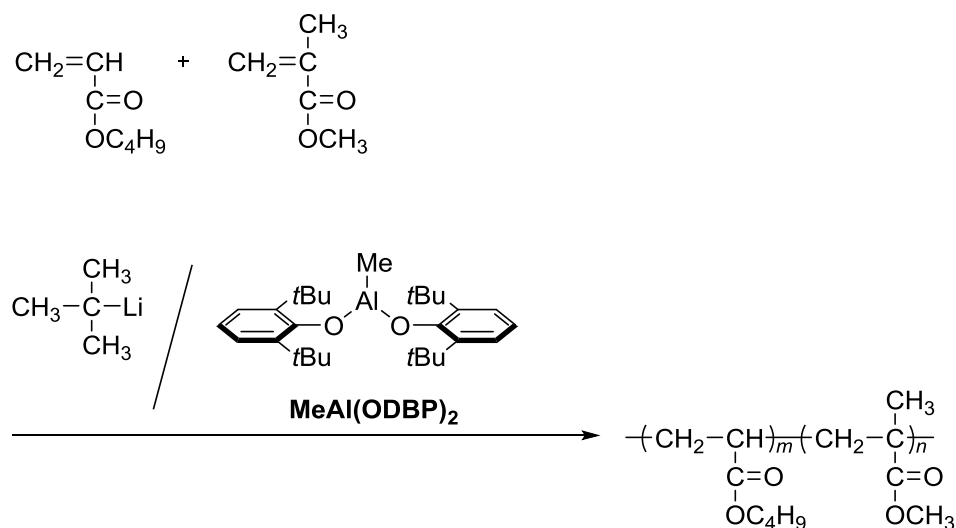


Figure 4-2. Synthetic methods of block copolymers.

The synthetic method of block copolymer can be roughly categorized as shown in **Figure 4-2**. Synthetic pathways (A) employ sequential addition of monomers to an active chain-end in living polymerizations.⁹⁻¹² Approach (B) is the polymerization of second monomer by the initiation with a macroinitiator, which can be prepared through homopolymerization with a bifunctional initiator or through the quenching of a homopolymerization with a functionalized chain terminator. Connecting two end-functional polymers at their chain-ends (C) is also possible approach.¹⁰⁻¹² Among them, pathway (A) is major approach. Furthermore, a more sophisticated method by monomer-selective polymerization (D), where the polymerization of second monomers follows the complete consumption of the first monomer, is possible in some specific combination of first and second monomers. For example, Tabuchi *et al.*¹³ reported the polymerization of alky acrylates initiated by a binary initiator of *t*-butyl lithium (*t*-BuLi) and ethylaluminum bis(2,6-di-*t*-butylphenoxide) [EtAl(ODBP)₂] proceeded in a living manner to afford *syndiotactic*-rich poly(acrylates). In this polymerization system, they also found that the anionic copolymerization of acrylate and methacrylate proceeds monomer-selective manner (**Scheme 4-1**); the polymerization of acrylate is dominant in

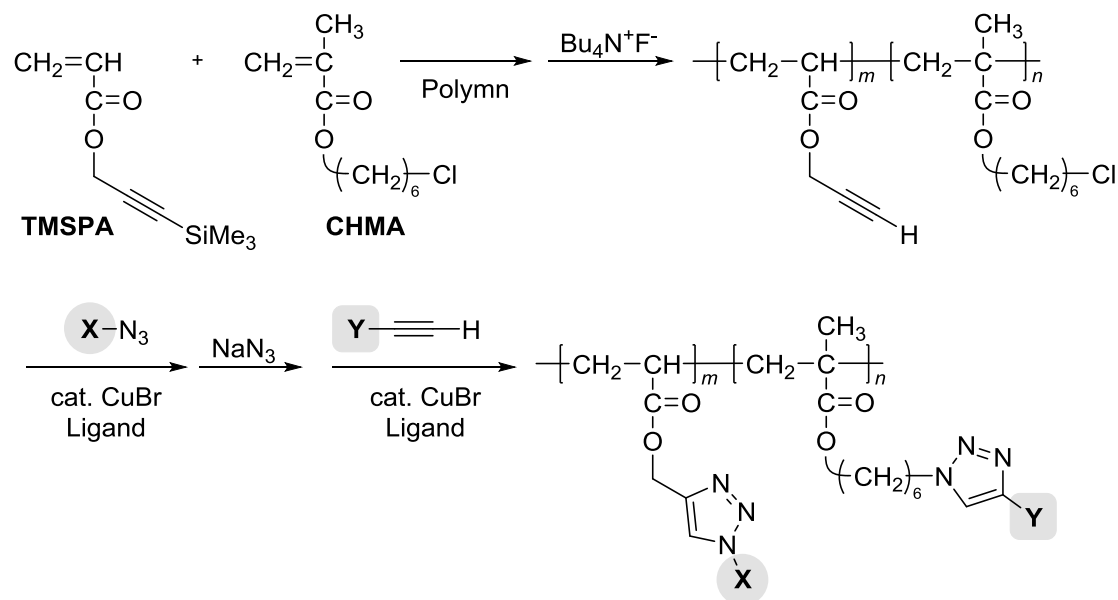
the first stage owing to the selective activation by EtAl(ODBP)_2 , and that of methacrylate was followed after the complete consumption of acrylate to yield a block copolymer with narrow molecular weight distribution.^{14, 15} Further analysis of ^{13}C NMR spectra revealed the high syndiotacticity of polymethacrylate block. This procedure is a very convenient way to prepare a block copolymer of acrylates and methacrylates with good control of molecular weight and stereoregularity.



Scheme 4-1. Block copolymer synthesis via monomer-selective polymerization.¹⁵

Cu(I) catalyzed azide-alkyne click (CuAAC) reaction facilitates the versatility of post-polymerization modification of a block copolymer on the side group,¹⁶ as it can be conducted with high efficiency, high yield, and tolerance against functional groups even at ambient condition.¹⁷ In the case of anionic polymerization of methacrylate, however, azide groups and acidic alkynyl protons may cause side reactions. Therefore, azide groups are usually incorporated after the polymerization via the azidation of chlorine atoms on the polymer side group, while an alkynyl group requires a protection

before polymerization.¹⁸



Scheme 4-2. Synthesis and modification block copolymer composed of independently clickable segments.

Inspired by these successes, the author designed a block copolymer, comprising of polyacrylate and polymethacrylate segments with independently clickable pendant groups, for the incorporation of donor and acceptor moieties (**Scheme 4-2**). The resulting block copolymer is expected to solve the problem for charge transport in an active layer of OPVSs. For this purpose, copolymerization of trimethylsilyl (TMS)-protected propargyl acrylate (TMS-PA) with 6-chlorohexyl methacrylate (CHMA) was examined to achieve monomer-selective living anionic copolymerization. Prior to the incorporation of donor and acceptor moieties, the synthesis and model double click reactions are described in this chapter. This is a unique process that combines the facile and effective one-shot block copolymerization with click chemistry.

4.2 Experiments

Materials

Toluene (Aldrich, anhydrous grade) was dehydrated with red colored adduct of butyllithium (*n*-BuLi, 1.64 M hexane solution, Kanto Chemical) and 1,1-diphenylethylene (Acros Organics), and distilled under high vacuum just before use. Ethylaluminum bis(2,6-di-*t*-butylphenoxide) [EtAl(ODBP)₂] and methylaluminum bis(2,6-di-*t*-butylphenoxide) [MeAl(ODBP)₂] were prepared according to the literature¹⁹ and stored as toluene solutions under nitrogen atmosphere. Isopropyl α -lithioisobutyrate (Li-*i*PrIB) was prepared and recrystallized in toluene according to the literature.^{20, 21} The initiator was treated as benzene solution (0.545 M) and stored under N₂ atmosphere at -20 °C in frozen state. CHMA was prepared according to the procedure written in Chapter 1 and dried over activated molecular sieves (MS) 4A beads (Aldrich). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), propargyl alcohol, and sodium azide were purchased from Aldrich. Chlorotrimethylsilane (TMSCl), tetrabutylammonium fluoride (TBAF) was purchased from Tokyo Chemical Industries. *N,N',N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA), benzyl azide, CHCl₃, CH₂Cl₂, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), triethylamine and hexane were purchased from Wako Pure Chemical Industry. Wakogel®-400 HG (Wako Pure Chemical Industry) was used silica gel flash column chromatography as an immobilized phase. NaHCO₃ and anhydrous MgSO₄ were purchased from Nacalai Tesque.

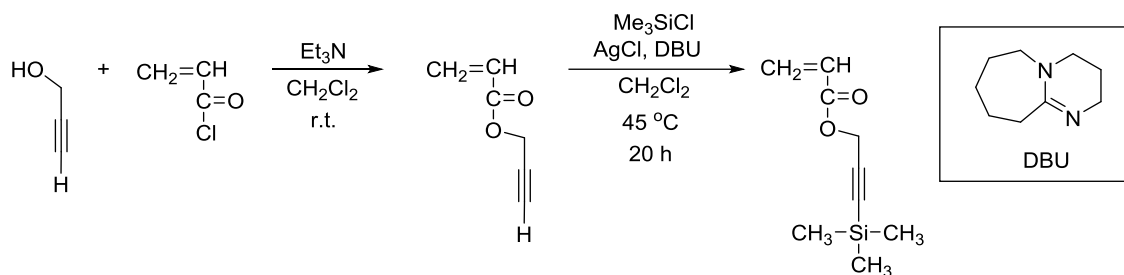
Instruments

¹H NMR spectra were recorded in CDCl₃ (Aldrich) on a JNM-ECS 400 (JEOL) spectrometer. Chemical shifts in ¹H NMR spectra were referred to the signal of

tetramethylsilane. Molecular weight and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on a GPC-900 chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm $\times$ 7.5 mm), Polymer Laboratories], using THF as an eluent (flow rate = 0.8 mL min⁻¹), and calibrated against standard poly(methyl methacrylate) (PMMA) samples (Shodex, MW: 1.25×10^6 , 6.59×10^5 , 1.95×10^5 , 4.96×10^4 , 2.06×10^4 , 6.82×10^3 , 2.00×10^3). IR spectra were recorded in KBr disc on an FT/IR-410 Fourier-transform infrared spectrophotometer (JASCO). Purities of monomers were evaluated by gas chromatography (GC) recorded on a GC-2014 (Shimadzu) equipped with an HP-5 capillary column (Hewlett-Packard).

Synthesis of propargyl acrylate (PA)^{22, 23}

To a 500 mL three-necked flask was added propargyl alcohol (11.5 mL, 0.192 mol) and triethylamine (111 mL, 0.792 mol) in CH₂Cl₂ (100 mL). The mixture was then cooled to 0 °C in an ice-water bath. Acryloyl chloride (22.5 mL, 0.283 mol) was added dropwise from a dropping funnel under N₂ atmosphere. The reaction mixture was stirred at room temperature for 30 min. Water (200 mL) was added to the reaction mixture, and the product was extracted with hexane (200 mL), washed twice with 0.5 M aqueous NaHCO₃ (200 mL) and water (200 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified on silica gel flash column chromatography [eluent: hexane-EtOAc (v / v = 1 / 2), R_f = 0.4] to afford propargyl acrylate (PA) (8.91 g) as colorless liquid (yield 42.1%, purity 100%). PA: ¹H NMR (400 MHz, 30 °C, CDCl₃) δ /ppm 6.47 (dd, J_1 = 17.4 Hz, J_2 = 1.4 Hz, 1H, CHH), 6.16 (dd, J_1 = 17.4 Hz, J_2 = 10.5 Hz, 1H, CHH), 5.89 (dd, J_1 = 10.5 Hz, J_2 = 1.4 Hz, 1H, =CH), 4.76 (d, J = 2.8 Hz, 2H, OCH₂), 2.49 (t, J = 2.6 Hz, 1H, C $\equiv$ CH).



Scheme 4-3. Synthesis and protection of PA.

Protection of propargyl acrylate²²

In a 500 mL three-necked flask equipped with two dropping funnels, AgCl (5.6 g, 39 mmol) was suspended in anhydrous CH₂Cl₂ (335 mL) and stirred for 15 min under dark. DBU (50.3 mL, 337 mmol) and PA (28.5 g, 259 mmol) were added dropwise through the dropping funnel. The reaction mixture was refluxed, and chlorotrimethylsilane (45.0 mL, 3.35 mmol) was added dropwise through another dropping funnel under N₂ atmosphere over 10 min. The reaction mixture was stirred for 20 h at 45 °C under dark and cooled to room temperature. Hexane (200 mL) was added, and the mixture was washed twice with *sat.* aq NaHCO₃ (200 mL), water (200 mL), and 1 M aq HCl (200 mL). The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The product was then purified on a silica gel flash column chromatography [eluent: hexane-Et₂O (v / v = 25 / 1)] to yield TMS-PA (23.1 g) as colorless liquid (yield 48.9%, purity 100%). The product was dried over CaH₂ and distilled under reduced pressure (bp 40 - 42 °C / 0.5 mm Hg) just before the polymerization. TMS-PA: ¹H NMR (400 MHz, 30 °C, CDCl₃) δ/ppm 6.46 (dd, *J*₁= 17.3 Hz, *J*₂ = 1.4 Hz, 1H, *CHH*), 6.15 (dd, *J*₁ = 17.3 Hz, *J*₂ = 10.2 Hz, 1H, *CHH*), 5.87 (dd, *J*₁ = 10.2 Hz, *J*₂ = 1.4 Hz, 1H, C=CH), 4.77 (s, 2H, OCH₂), 0.18 [s, 9H, Si(CH₃)₃]; density = 0.936 g mL⁻¹

Polymerization of TMS-PA and CHMA

[Method A: sequential monomer addition]

A typical procedure (**Table 4-2**, Run 3): All the polymerization reactions were carried out under dried nitrogen atmosphere in glass ampoules fitted with three-way stopcocks and the solvents and reagents were transferred via hypodermic syringes. To a glass ampoule filled in dried N₂ passed through MS4A at –78 °C, toluene (5.0 mL), Li-*i*PrIB (0.05 mmol) and EtAl(ODBP)₂ (0.25 mmol) were added at room temperature. The reaction mixture was cooled at –60 °C for 30 min, and TMS-PA (5.0 mmol) was injected. After 30 min, CHMA (4.0 mmol) was added. The reaction was quenched after 24 h by adding 1 M HCl water-methanol solution. The reaction mixture was then concentrated under reduced pressure, and the residue was diluted with CHCl₃ and washed with 1 M aq HCl and water. The organic layer was dried *in vacuo* at 40 °C for 12 h to afford a polymeric product (1.6 g, yield 94.1%).

[Method B: one-shot monomer addition]

A typical procedure (**Table 4-2**, Run 4): To a glass ampoule filled in dried N₂ passed through MS4A at –78 °C, toluene (5.0 mL), Li-*i*PrIB (0.05 mmol) and EtAl(ODBP)₂ (0.25 mmol) were added at room temperature. The reaction mixture was cooled at –60 °C for 30 min, and a mixture of TMS-PA (5.4 mmol) and CHMA (2.1 mmol) was added. After 24 h, the reaction was quenched by adding 1 M HCl water-methanol solution. The reaction mixture was then concentrated under reduced pressure, and the residue was diluted with CHCl₃ and washed with aq 1 M HCl and water. The organic layer was dried *in vacuo* at 40 °C for 12 h to afford a polymeric product (2.1 g, yield 100%).

Deprotection of the block copolymer

To a solution of block copolymer (**Table 4-2**, Run 4, 100 mg, 0.258 mmol per TMS-PA unit) in THF (2.6 mL) was added acetic acid (22 μ L, 0.39 mmol) via syringe. The reaction mixture was purged with N₂ bubble for 10 min and cooled to 0 °C. A solution of TBAF (0.387 mmol) in THF (1 mL) was added dropwise at 0 °C over 30 min, and the reaction mixture was warmed to room temperature. After 4 h, the reaction mixture was concentrated under reduced pressure, and the residue was passed through silica gel short column (5 g of silica gel) with THF as eluent in order to remove the unreacted TBAF and other polar bi-product. The collected polymer was dissolved in THF, reprecipitated to hexane (50 mL) twice, and dried *in vacuo* for 4 h to afford the deprotected block copolymer as a white powder (58 mg, yield 71.6%)

First Click reaction

To a solution of the deprotected polymer (**Table 4-2**, Run 4, 20 mg, 64 μ mol per PA unit) in THF (0.64 mL) in a 10 mL sample vial were added PMDETA (1 μ L, 6 μ mol), benzyl azide (9 μ L, 80 μ mol), and CuBr (0.9 mg, 6 μ mol). The reaction mixture was stirred at room temperature for 24 h, diluted with CH₃Cl (4 mL), and washed with 0.6 M aq disodium dihydrogen ethylenediaminetetraacetate (EDTA·2Na) (10 mL, 5 times) until the blue color of copper (II) ion faded. The organic layer was then passed through phase separator (Biotage, Isolute®) and reprecipitated in hexane (50 mL) and dried *in vacuo* overnight to afford a polymeric product (26 mg, yield 91.2%) as light-yellow powder.

Azidation of the block copolymer

A typical procedure for azidation: To a solution of block copolymer (8 mg, 20 μmol per CHMA unit) in DMF (0.2 mL) was added NaN_3 (5 mg, 70 μmol). The reaction mixture was stirred at 60 °C for 24 h and poured into water-methanol co-solvent (15 mL / 35 mL). The precipitates were collected by centrifugation, washed with water and methanol, and dried *in vacuo* at room temperature for 4 h to afford the azidated block copolymer (4 mg, yield 50%).

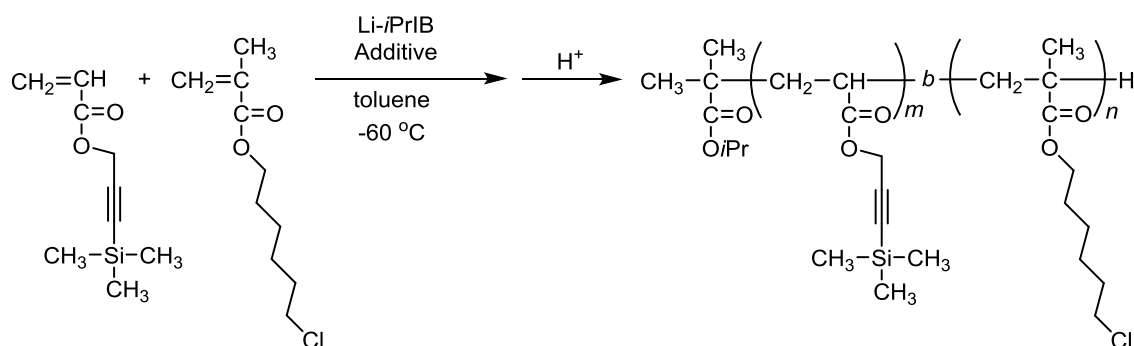
Second Click reaction

To a mixture of the PMDETA (2.3 μL , 11 μmol), phenyl acetylene (14.5 μL , 132 μmol), and CuBr (1.6 mg, 11 μmol) in CH_2Cl_2 (0.5 mL) in a 10 mL sample vial was added a solution the azidated polymer (50 mg, 110 μmol per PA unit) in CH_2Cl_2 (0.6 mL). The reaction mixture was stirred at room temperature for 24 h, and washed with 0.6 M aq disodium dihydrogen ethylenediaminetetraacetate ($\text{EDTA} \cdot 2\text{Na}$) (10 mL, 5 times) until the blue color of copper (II) ion faded. The organic layer was then transferred to a 50 mL sample vial and dried *in vacuo* overnight to afford a polymeric product (56 mg, yield 91.5%) as yellow powder.

4.3. Results and discussion

4.3.1 Block copolymerization of TMS-PA and CHMA

As described in the previous reports,^{13, 15} living polymerization of tertiary alkyl acrylates was achieved by a combined initiator, *t*-BuLi / MeAl(ODBP)₂, while the polymerization of primary alkyl acrylates with controlled molecular weight only proceeded smoothly with the aid of EtAl(ODBP)₂ but not with MeAl(ODBP)₂. To examine the effect of organoaluminum additives on the polymerization of TMS-PA and CHMA, the copolymerizations were carried out in toluene at -60 °C together with the homopolymerization of TMS-PA (**Scheme 4-3**). Li-*i*PrIB was used as an effective initiator for living anionic polymerization of (meth)acrylates. The results are summarized in **Table 4-1**.



Scheme 4-3. Anionic copolymerization of TMS-PA and CHMA .

Table 4-1. Copolymerization of TMS-PA and CHMA initiated by Li-*i*PrIB in toluene at –60 °C with different additives for 24 h.^a

Run	Additives	Monomer / mmol		Conversion/ % ^c		Yield	$M_n / 10^3$		M_w^d
		TMS-PA	CHMA	TMS-PA	CHMA	%	SEC ^d	Calcd	M_n
1 ^b	MeAl(ODBP) ₂	5.0	—	72.5	—	79	23.7	13.2	1.42
2		5.0	2.1	98.8	5.30	90	40.8	18.6	1.77
3 ^b	EtAl(ODBP) ₂	5.0	—	72.8	—	71	22.6	13.2	1.37
4		5.0	2.1	100	100	96	61.8	26.9	1.39

a) Li-*i*PrIB 0.05 mmol, additive 0.25 mmol, toluene 5 mL.

b) Polymerization time 30 min.

c) Determined by ¹H NMR spectra of the sampled reaction mixture (400 MHz, CDCl₃, 30 °C).

d) Determined by SEC at 40 °C in THF calibrated against PMMA standards.

Polymerization of TMS-PA in the presence of MeAl(ODBP)₂ (**Table 4-1**, Run 1) did not proceed completely within 30 min. By one-shot copolymerization with CHMA (Run 2), the conversion of TMS-PA reach to 98.8% while only 5.3%, CHMA was consumed after 24 h. As TMS-PA polymerized preferentially within the early stage (Run 1), this result indicates the reinitiation from from poly(TMS-PA) living anion to CHMA did not proceed smoothly. The molecular weight distributions for both polymerizations were broad as depicted in the SEC charts (**Figure 4-2**). In contrast, the polymerization with EtAl(ODBP)₂ (Runs 3 and 4) attained unimodal and narrower molecular weight distribution than that with MeAl(ODBP)₂, and the complete consumption of both monomer was achieved. The results suggest that EtAl(ODBP)₂ is more effective to control the polymerization of TMS-PA and block copolymerization with CHMA.

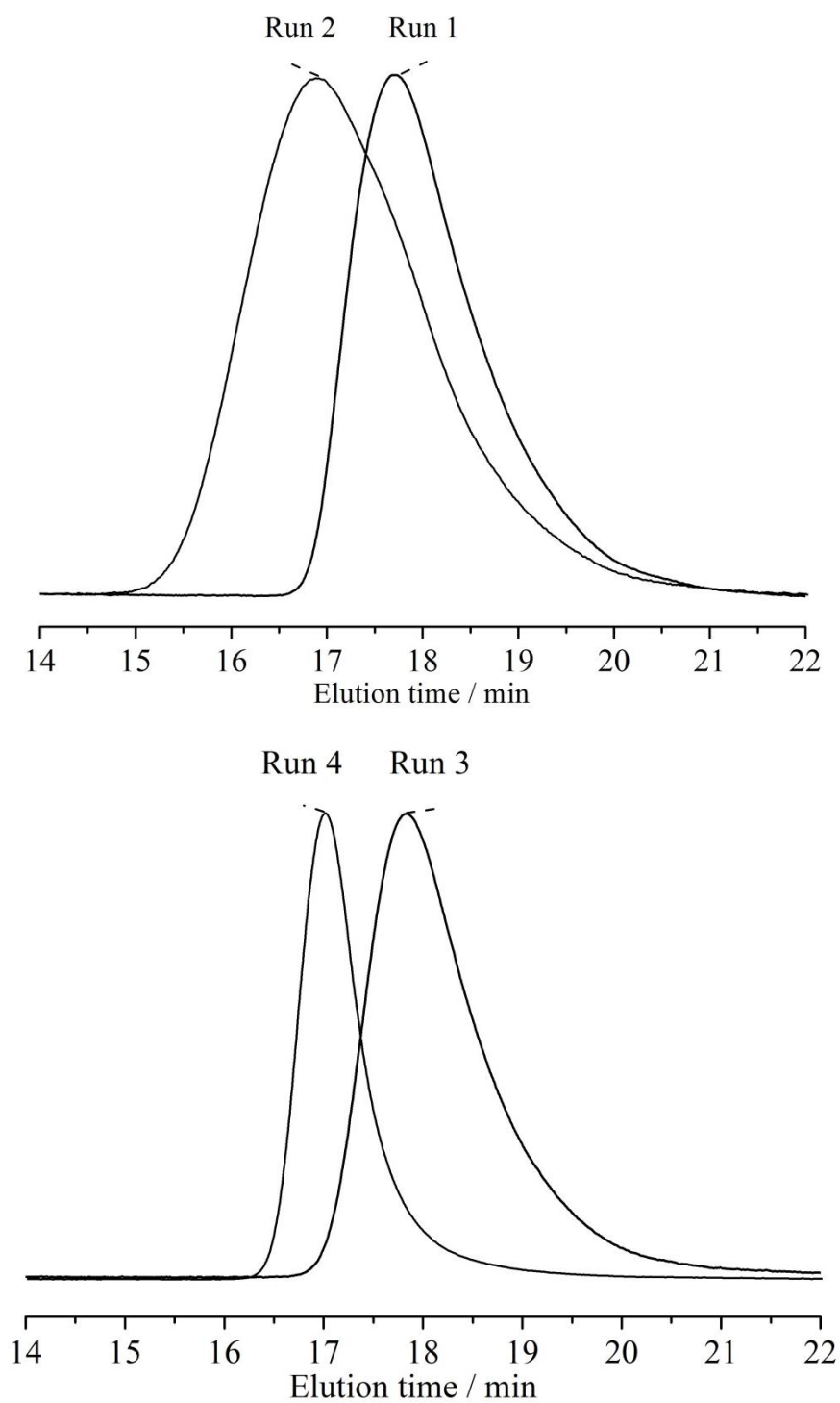


Figure 4-2. SEC charts of the polymers obtained from (co)polymerizations of TMS-PA and CHMA initiated by Li-*i*PrIB in toluene at $-60\text{ }^{\circ}\text{C}$ with different additives for 24 h (THF, $40\text{ }^{\circ}\text{C}$, PMMA standards).

Table 4-2. Sequential and one-shot addition copolymerizations of TMS-PA and CHMA initiated by Li-*i*PrIB in toluene at -60 °C for 24 h.^a

Run	Monomer / mmol		Conversion/ % ^b		Yield %	$M_n / 10^3$		M_w^c M_n	Tacticity/ % ^d		
	TMS-PA	CHMA	TMS-PA	CHMA		SEC ^d	Calcd.		<i>mm</i>	<i>mr</i>	<i>rr</i>
1 ^e	5.0	–	100	–	72	17.0	9.10	1.17	–	–	–
2	–	5.0	–	100	100	23.5	20.5	1.12	1	6	93
3 ^f	5.4	4.0	100	100	91	30.4	36.2	2.77	1	6	92
4	5.4	5.4	100	100	100	45.1	21.0	1.16	1	7	93

a) Li-*i*PrIB 0.05 mmol, EtAl(ODBP)₂ 0.25 mmol, toluene 5 mL.

b) Determined by ¹H NMR spectra of the sampled reaction mixture (400 MHz, CDCl₃, 30 °C).

c) Determined by SEC at 40 °C in THF calibrated against PMMA standards.

d) Tacticity of poly(CHMA) segments determined by ¹H NMR spectra (400 MHz, CDCl₃, 55 °C).

e) Polymerization time: 30 min.

f) Sequential monomer addition.

As described in the introduction, there are two way to prepare the block copolymer of the pair of acrylates and methacrylates: Sequential and one-shot additions of the monomers. In order to investigate the copolymerization behaviors in each method, sequential and one-shot block copolymerizations were carried out together with the homopolymerizations (**Table 4-2**).

The SEC charts of the resulting polymers are shown in **Figure 4-3**. TMS-PA was completely consumed within 30 min (Run 1). Although the molecular weight did not agree well with the aimed one, the molecular weight distribution was narrow. In the polymerization of CHMA, the aimed molecular weight and narrow molecular weight distribution were achieved. However, block copolymerization by the sequential monomer addition resulted in a broad molecular weight distribution (Run 3). On the contrary, one-shot addition procedure (Run 4) gave the copolymer with narrow molecular weight distribution as seen in **Figure 4-3**. This observation confirmed the advantages of the one-shot block copolymerization; in sequential block

copolymerization, CHMA monomer injected should be in higher temperature than the polymerization temperature of $-60\text{ }^{\circ}\text{C}$, which might cause fast reinitiation and deactivation of the living polymer anions. In contrast, one-shot addition proceeded in a homogeneous system, and the reinitiation from poly(TMS-PA) anions to the existing CHMA monomer can proceed smoothly at the same temperature.

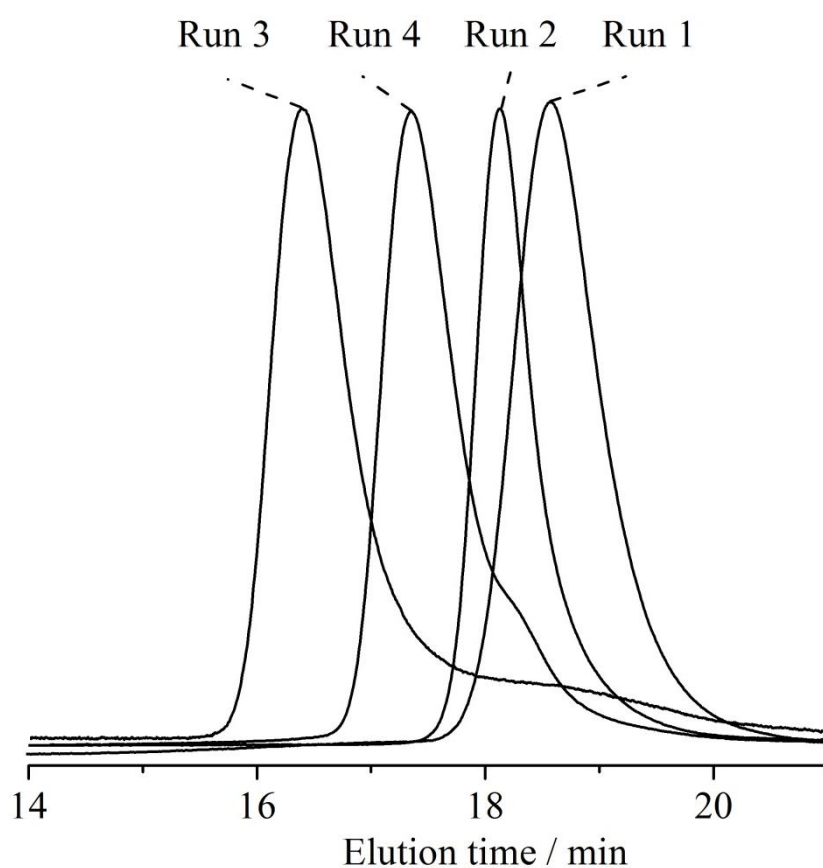


Figure 4-3. SEC charts of polymers obtained from one-shot and sequential block copolymerizations of TMS-PA and CHMA initiated by Li-*i*PrIB in toluene at $-60\text{ }^{\circ}\text{C}$ (THF, $40\text{ }^{\circ}\text{C}$).

^1H NMR spectra of the obtained polymers are shown in **Figure 4-4**. All NMR signals of the block copolymers both by sequential and one-shot monomer addition are superposition of their respective homopolymers as assigned, indicating the polymerization afforded block-like structure. The high stereoregularity of poly(CHMA) block with respect to the control of monomer addition by EtAl(ODBP)_2 was determined from α -methyl protons of the corresponding polymers. Based on ^1H NMR analysis, Run 3 has *rr* triad content up to 92%, agreed well with the homopolymer of CHMA (93%). The high syndiotacticity was also observed on Run 4 (93%).

In order to confirm the monomer-selective propagation by one-shot addition procedure, copolymerizations of TMS-PA and CHMA were carried out in four sets of time at $-60\text{ }^\circ\text{C}$. The results are summarized on **Table 4-3**. It is clearly shown that TMS-PA polymerized much faster than CHMA (**Figure 4-5**); 99% of TMS-PA was consumed within 15 min, while only 1% of CHMA was converted to polymer. After the complete consumption of TMS-PA, CHMA polymerized slowly, indicating that the copolymerization of TMS-PA and CHMA proceeded in a monomer selective manner to give the copolymer with a blocky structure.

Table 4-3. Time course polymerization of TMS-PA and CHMA in toluene initiated by Li-*i*PrIB / EtAl(ODBP)₂ at -60 °C^a.

Run	Polymerization time	Conversion / % ^b		$M_n / 10^3$			M_w^c
	min	TMS-PA	CHMA	SEC ^c	NMR ^d	Calcd	M_n
1	15	99	1.0	11.5	12.2	6.1	1.09
2	30	100	6.5	21.3	15.1	6.6	1.11
3	60	100	31	28.2	19.6	9.1	1.14
4	180	100	100	37.5	33.4	17.1	1.17

a) TMS-PA 3.3 mmol, CHMA 4.9 mmol, Li-*i*PrIB 0.10 mmol, EtAl(ODBP)₂ 0.50 mmol, toluene 5 mL.

b) Determined by ¹H NMR spectra of the sampled reaction mixtures (400 MHz, CDCl₃, 30 °C).

c) Determined by SEC at 40 °C in THF calibrated against PMMA standards.

d) Determined by ¹H NMR spectra (400 MHz, CDCl₃, 55 °C)

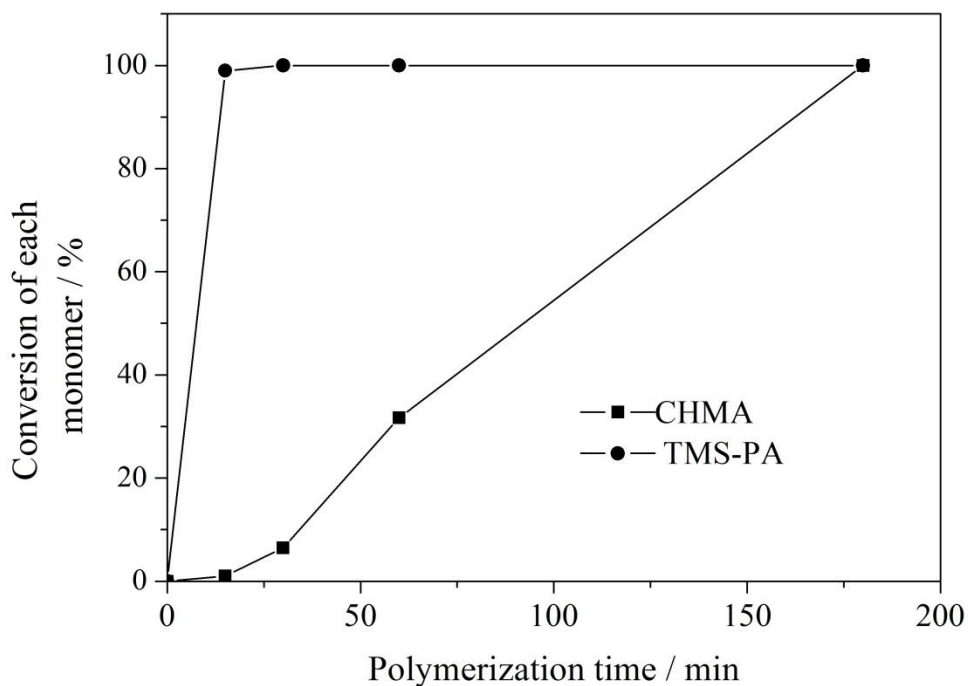


Figure 4-5. Time vs conversion plots in the copolymerizations of TMS-PA and CHMA in toluene initiated by Li-*i*PrIB / EtAl(ODBP)₂ at -60 °C.

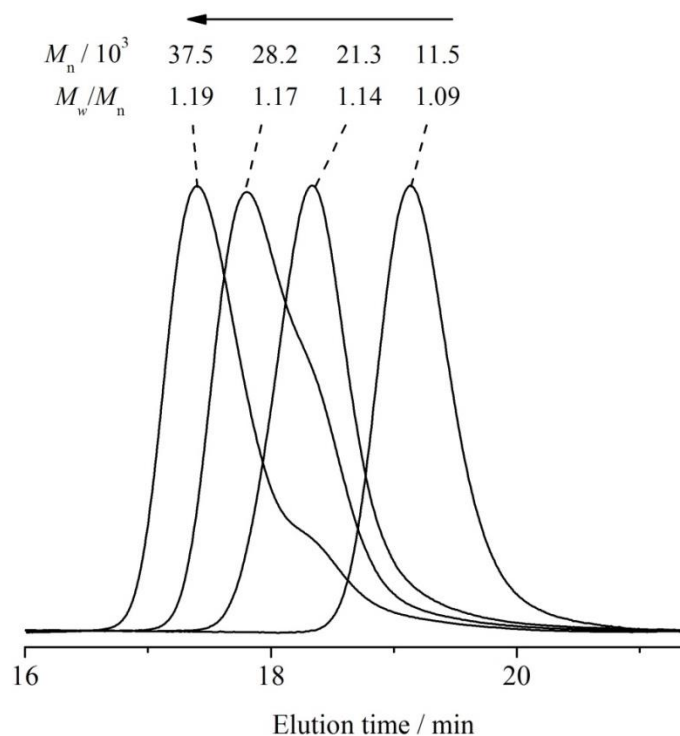


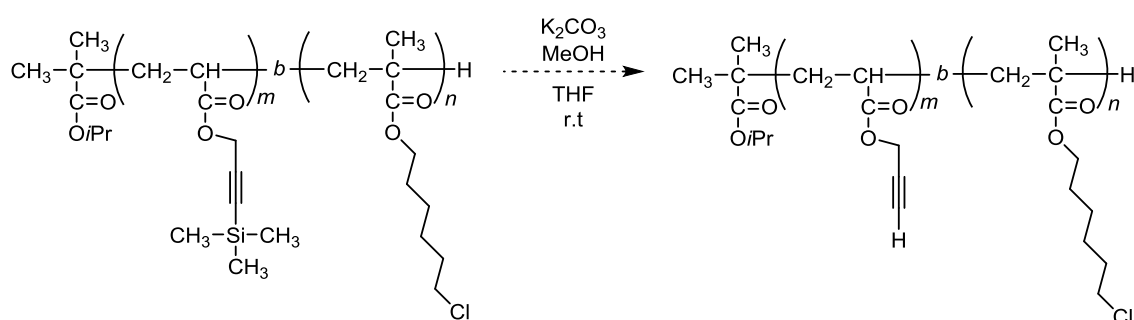
Figure 4-6. SEC charts of the polymers formed in time-course copolymerizations of TMS-PA and CHMA in toluene initiated by Li-*i*PrIB / EtAl(ODBP)₂ at -60 °C (THF, 40 °C, PMMA standards). From right to left: polymerization time 15, 30, 60, and 180 min.

Some small shoulders were observed on SEC charts of the products polymerized for 60 min and more (**Figure 4-6**). The products by the polymerization for 30 min mostly consisted of TMS-PA and the polymerization of CHMA mainly proceeded by the poly(TMS-PA) anions thereafter. Thus, a small portion of the living polymer anions probably failed to add CHMA and remained as a lower molecular weight product. In fact, the peak top molecular weight of the polymer formed at 30 min is close to that of the shoulders seen in the SEC traces of the product at 60 and 180 min. Nevertheless, all SEC charts showed narrow molecular weight distribution displaying the remarkable activity of Li-*i*PrIB / EtAl(ODBP)₂ for the one-shot block copolymerization of TMS-PA and CHMA.

4.3.2 Modification of block copolymer by double click reactions

Deprotection

The deprotection of TMS-PA units in the copolymers was performed prior to click reaction. Kitaura *et al.* reported that K_2CO_3 / MeOH is a very convenient way for the deprotection of TMS-protected propargyl methacrylate polymer at room temperature.²⁴ Thus, the deprotection of the block copolymer was first conducted under the similar conditions (**Scheme 4-4**).



Scheme 4-4. Deprotection of the block copolymer with K_2CO_3 / MeOH.

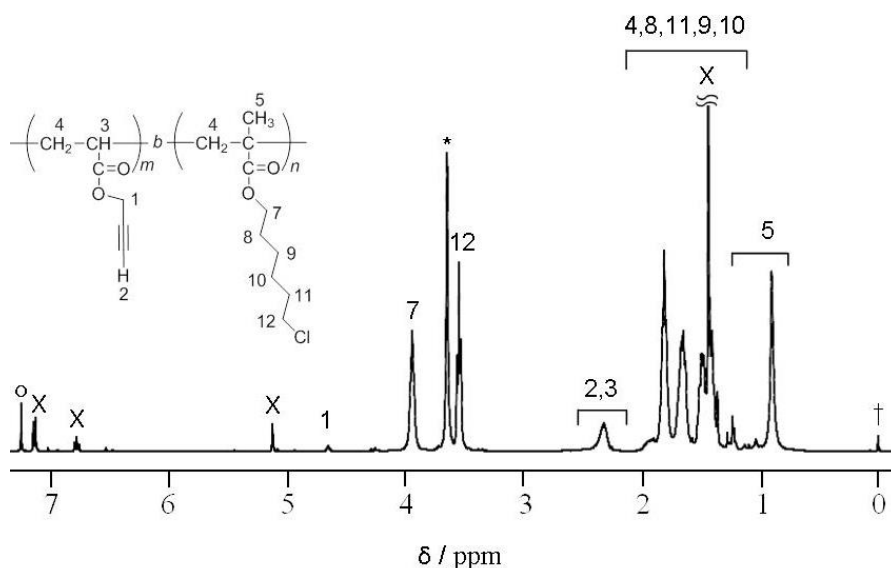
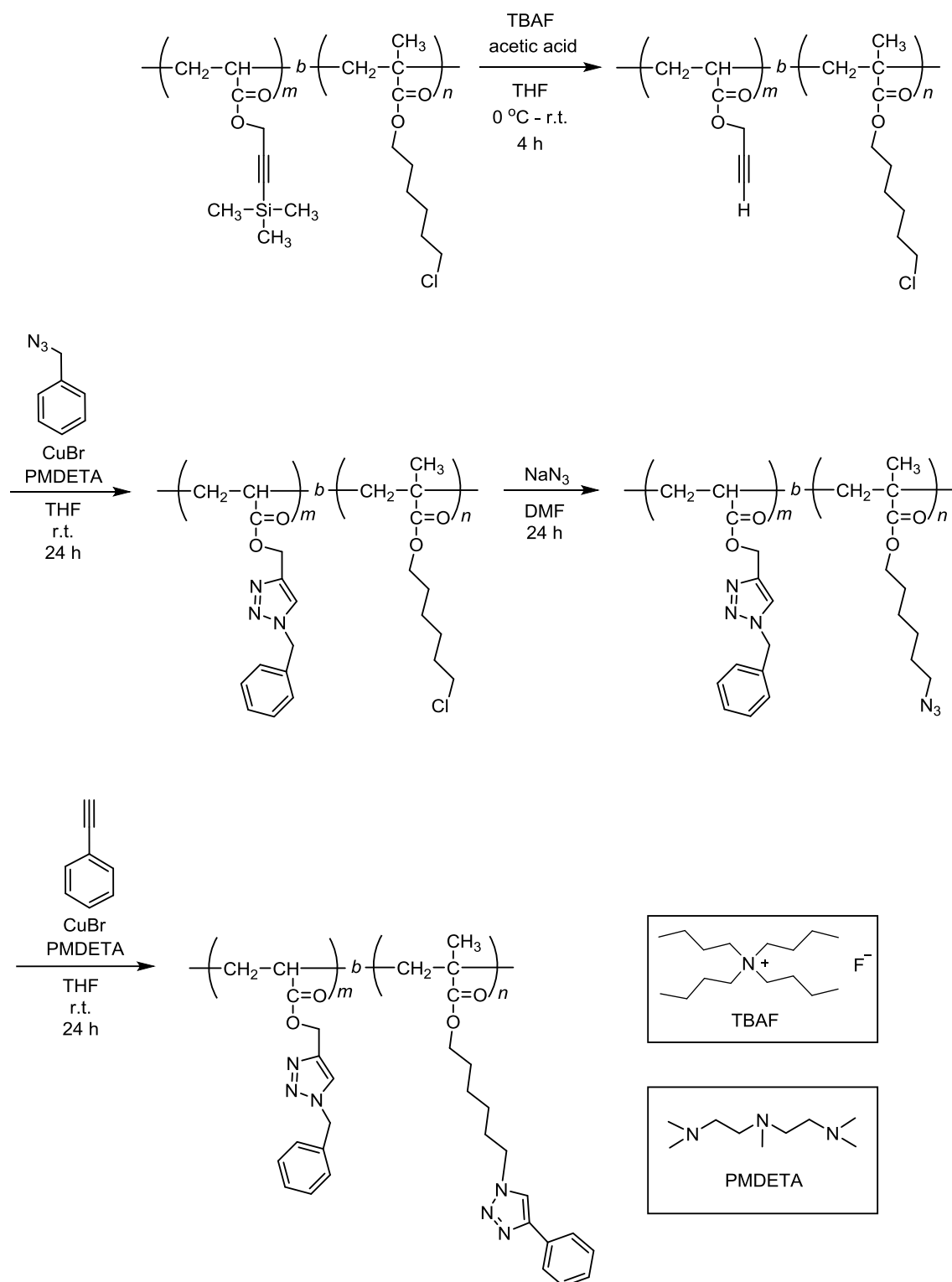


Figure 4-7. ^1H NMR spectrum of the block copolymer of TMS-PA and CHMA (Run 4, Table 4-3) after deprotection with K_2CO_3 / MeOH (400 MHz, $CDCl_3$, 55 °C).

*: methanol, X : 2,6-Di-*t*-butylphenol, o: $CHCl_3$ and †: tetramethylsilane.

Figure 4-7 shows the ^1H NMR spectrum of the resulting polymer. The signal of the TMS group at 0.18 ppm completely disappeared, apparently indicating the deprotection of the alkyne group successful. However, it was found that the OCH_2 proton signal (4.75 ppm) became broader and its intensity was lower than those of $\alpha\text{-CH}$ proton in the main-chain of the polyacrylate backbone (2.32 ppm). Thus, some ester decomposition might occur on the polyacrylate block. Consequently, the deprotection by K_2CO_3 / MeOH is not effective and an alternative deprotection reaction must be conducted.

Recently, Geng *et al.* reported that the deprotection of a poly(TMS-PA) with tetrabutylammonium fluoride (TBAF) / acetic acid in THF proceeded quantitatively.²⁵ The deprotection of the block copolymer was then undertaken in a similar manner (**Scheme 4-5**), and the product was analyzed by ^1H NMR spectroscopy. The spectrum of the block copolymer after deprotection is presented in **Figure 4-8a**. The peak assignable to TMS proton at 0.18 ppm completely disappeared after deprotection. A new peak (2) assignable to alkyne proton is observed at 2.4 ppm, though it is overlapped with $\alpha\text{-CH}$ proton of acrylate unit. The other peaks remain clear, and the intensity ratios of each proton agreed well to those expected. Thus, TBAF / acetic acid is effective to deprotect the block copolymer possessing TMS groups prior to click reaction.



Scheme 4-5. Stepwise click reactions on the pendant groups of the block copolymer (Run 4, Table 4-4).

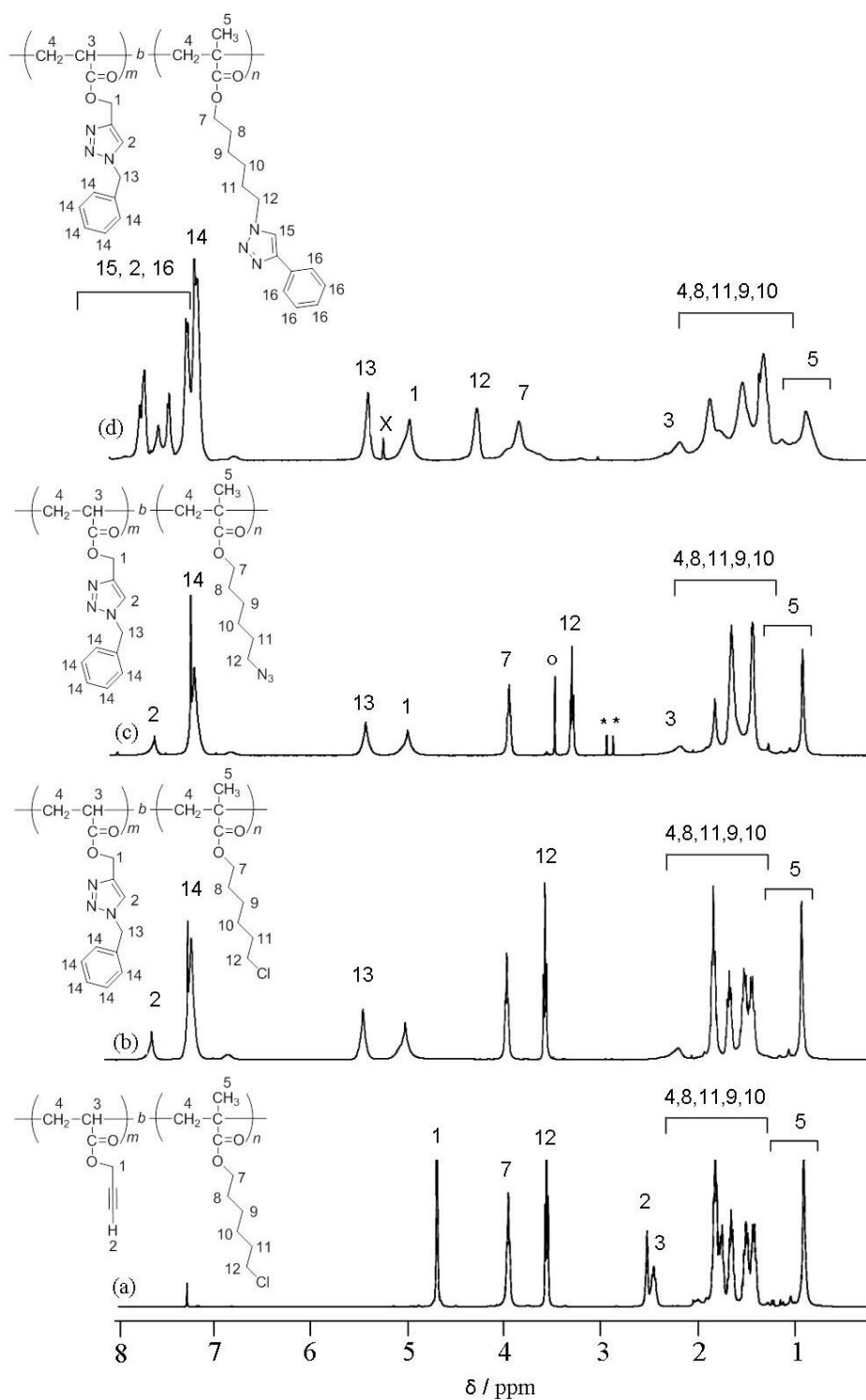


Figure 4-8. ^1H NMR spectra of the block copolymers (Run 4, **Table 4-4**) on the stepwise modifications after (a) deprotection, (b) first click reaction, (c) azidation, and (d) second click reaction (400 MHz, CDCl_3 , 55 $^\circ\text{C}$).

*: *N,N*-Dimethylformamide (DMF), $\circ$: Methanol, $\times$: CH_2Cl_2

First click reaction

Click reaction on the poly(PA) block was carried out with benzyl azide catalyzed by CuBr / PMDETA in THF at room temperature for 24 h (**Scheme 4-5**). ^1H NMR spectrum (**Figure 4-8b**) of the product clearly confirmed that the CuAAC reaction successfully proceeded on the block copolymer. A new peak due to triazole proton at 7.6 ppm (2) was observed with the same intensity to α -CH proton of acrylate (3). The benzylic protons (13) were detected at 5.5 ppm, while phenyl protons (14) were overlapped with the signal of CHCl_3 around 7.25 ppm. The signal assignable to OCH_2 slightly shifted to 5.0 ppm (1) due to the formation of triazole group. Thus, the whole alkyne group was converted to triazole after 24 h without any side reaction.

Azidation

In order to access the second click reaction on the poly(CHMA) block, the chlorine atoms of the poly(CHMA) block in the “clicked” block copolymer was converted to azide groups by the reaction with NaN_3 in DMF at 60 °C for 48 h (**Scheme 4-5**), as practiced in the homopolymers of CHMA (see Chapters 1 and 2). Long reaction time was needed probably due to the decreasing solubility of the sample in DMF after the click reaction with benzyl azide on the side groups. Nevertheless, the shift of peak (12) from 3.5 ppm to 3.3 ppm with same integral ratio to OCH_2 peak at 3.9 ppm (7) indicates the complete substitution of the chlorine atoms to the azide groups (**Figure 4-8c**). The block copolymer was then accessible to the second click reaction.

Second click reaction

Click reaction of the azidated poly(CHMA) block was performed with phenylacetylene catalyzed by CuBr / PMDETA in CH_2Cl_2 at room temperature for 24 h

(**Scheme 4-5**). ^1H NMR spectrum (**Figure 4-8d**) of the product clearly confirmed that the CuAAC reaction successfully proceeded on the block copolymer. The peak (12) shifted from 3.3 ppm to 4.3 ppm due to the formation of triazole group. A new peak due to triazole proton at 7.5 ppm (15), while phenyl protons (17) were at 7.3-7.7 ppm. This observation confirmed that the whole azide groups were converted to triazole within 24 h.

4.4. Conclusion

Anionic polymerization of TMS-PA and CHMA initiated by Li-*i*PrIB/EtAl(ODBP)₂ at -60 °C by one-shot monomer injection proceeded in a monomer-selective fashion to afford block copolymer structure. The resulting block copolymer exhibited unimodal SEC charts and narrow molecular weight distribution with high syndiotacticity of the poly(CHMA) block. In contrast, sequential monomer injection gave block copolymer with broad molecular weight distribution probably due to fast reinitiation [(polymerization of CHMA by poly(TMS-PA) anions)] as well as some deactivations of poly(TMS-PA) anions. This implies the advantage of one-shot block copolymerization over the typical block copolymerization by the sequential monomer addition, as the second monomer, CHMA, was pre-mixed with the poly(TMS-PA) anions at the same temperature, allowing smooth re-initiation process.

Deprotection and CuAAC click reaction on the poly(PA) catalyzed by CuBr / PMDETA was performed to introduce organic azide moieties. Subsequently, azidation and CuAAC click reaction on poly(CHMA) block was conducted to introduce alkyne moieties. The success of both click reactions realizes the formation of the reactive block copolymer double-clickable with azides and alkynes. As demonstrated in the previous chapters, the azidated poly(CHMA) block is readily reacted with C₆₀ and thus potentially converted to acceptor block. Azide compounds as candidates for donor moiety can be obtained from the respective halides of terthiophene. Thus, the results demonstrated in this chapter will provide a facile method for the preparation of block copolymer bearing functional moieties such as donor and acceptor electrons for OPVS application.

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and induction of immunological function. *Journal of the American Chemical Society* 129, 15156-15163 (2007).

List of Publications

[Original Paper]

Chapter 1

V. Ladelta, Y. Kohsaka, T. Ohnishi, M. Matsumura, T. Kitayama

Polymer Bulletin, *accepted*.

“C₆₀-containing polymethacrylates: Synthesis, properties, and potential application as n-type semiconductor for organic solar cell”

Chapter 2&3

V. Ladelta, Y. Kohsaka, T. Ohnishi, M. Matsumura, T. Kitayama, *submitted to Journal of Polymer Science Part A: Polymer Chemistry*.

“Synthesis and properties of stereoregular C₆₀-containing polymethacrylates for organic photovoltaic application”

Chapter 4

V. Ladelta, Y. Kohsaka, T. Kitayama, *to be submitted*.

“Synthesis of block copolymer composed of independently clickable segments via monomer-selective living copolymerization”

[International Conference]

1. V. Ladelta, Y. Kohsaka, T. Kitayama
“Synthesis and properties of polymethacrylate with high content of C₆₀ moieties”
IUPAC International Symposium on Ionic Polymerization 2013 (IP2013), Pa59,
September 23rd-28th, 2013, Awaji, Japan.
2. V. Ladelta, Y. Kohsaka, T. Ohnishi, T. Kitayama
“Synthesis of stereoregular C₆₀-polymethacrylates and their potential application as electron acceptor for organic solar cell”
2014 Material Research Society (MRS) fall meeting & exhibit, November 30th -
December 5th, 2014, Boston, USA.

[Domestic Conference]

1. V. Ladelta, Y. Kohsaka, T. Ohnishi, T. Kitayama
“Fullerene -containing polymethacrylates: A potential electron acceptor for polymer

solar cell”, 63rd Society of Polymer Science, Japan (SPSJ) Annual Meeting, 2M05, May 28th-30th, Nagoya, Japan.

2. V. Ladelta, Y. Kohsaka, T. Ohnishi, T. Kitayama,
“Synthesis and properties of soluble poly(methacrylates) possessing fullerene moieties”, 62nd Society of Polymer Science, Japan (SPSJ) Annual Meeting, 3Pb002, May 29th-31th, Kyoto, Japan.

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