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STUDIES ON PHYSICAL PROPERTIES OF POLYOLEFIN GELS AND THE APPLICATIONS

1990

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PREFACE

This thesis has been organized under the supervision of Professor Kiichi Takemoto of Osaka University.

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LIST OF PUBLICATIONS

The contents of this thesis are composed of the following papers.

1. Thermochromism of Polypropylene Gels.
   Hitoshi Fujimatsu and Shigetaka Kuroiwa,
   Colloid & Polymer Sci., 265, 938 (1987).

2. Adhesion of a Pair of Polyethylene Moldings by Polyethylene Gels.
   Hitoshi Fujimatsu and Shigetaka Kuroiwa,
   Colloid & Polymer Sci., 265, 747 (1987).

3. Adhesion of Molded Polypropylene Using Polypropylene Gels.
   Hitoshi Fujimatsu and Shigetaka Kuroiwa,
   J. Colloid Interface Sci., 123, 309 (1988).

4. Thermochromism of Poly-1-butene Gels.
   Hitoshi Fujimatsu, Shinji Ogasawara, Hiroyuki Ihara, Terutomo Takashima, and Shigetaka Kuroiwa,
   Colloid & Polymer Sci., 266, 688(1988).

5. Adhesive Effect of High Density Polyethylene Gels on Polyethylene Moldings.
   Hitoshi Fujimatsu, Shinji Ogasawara, Nobuya Satoh, Kazuhiro Komori, and Shigetaka Kuroiwa,
   Colloid & Polymer Sci., 267, 500(1989).

6. Adhesive Effect of Low-Density Polyethylene Gels on Polyethylene Moldings.
   Hitoshi Fujimatsu, Shinji Ogasawara, Nobuya Satoh,

Kazuhiro Komori, Yoshihito Matsunaga, and Shigetaka Kuroiwa,
Colloid & Polymer Sci., 268, 143(1990).

7. Adhesion of Molded Polyethylene Using Polyethylene Gels by Microwave Heating.
Hitoshi Fujimatsu, Shinji Ogasawara, and Shigetaka Kuroiwa,
Colloid & Polymer Sci., 268, 28(1990).

8. Swollen Polyethylene Films as Adhesives to Bond Polyethylene Moldings.
Hitoshi Fujimatsu, Shinji Ogasawara, and Shigetaka Kuroiwa,
J. Adhesion Sci. Tech., 4, 35(1990).

The other results reported by the author, with the exception of the investigation presented in this thesis, have already been published in the following papers.

1. Structures and Properties of Liquid Crystals Formed in the Highly Concentrated Aqueous Solutions of Nonionic Surface Active Agents.
Shigetaka Kuroiwa, Hideomi Matsuda, Hitoshi Fujimatsu, and Akira Miyazawa,
Nippon Kagaku kaishi, (7), 1040(1976).

2. Temperature Dependence of Solution Properties of Nonionic Surface Active Agent.
Shigetaka Kuroiwa, Hideomi Matsuda, and Hitoshi Fujimatsu,
Nippon Kagaku Kaishi, (3), 362(1980).

3. Dissolution of Disperse Dyes in the Aqueous Solution of Polyoxyethylene Glycol.
   Shigetaka Kuroiwa, Hitoshi Fujimatsu, and Yoshinori Uegaki,
   Sen-i Gakkaishi, 37(1), T-48(1981).

4. Studies on the Solution Properties of Nonionic Surfactants, Alkanamide Poly(oxyethylene) Sulfates I, Viscosities of Surfactant/Thickener/Water Systems.
   Shigetaka Kuroiwa, Hitoshi Fujimatsu, Kazuyuki Takagi, and Shigemi Mukai,
   Yukagaku, 30(4), 244(1981).

5. Sol-Gel Transition of Fractionated Low Density Polyethylene in Cyclohexane-Carbondisulfide Mixed Solvent.
   Hideomi Matsuda, Kazuhiro Araki, Hitoshi Fujimatsu, and Shigetaka Kuroiwa,
   Polymer J., 13, 587(1981).

6. Sol-Gel Transition of Low-Density Polyethylene in Decalin, Tetralin and *o*-Xylene.
   Hideomi Matsuda, Hitoshi Fujimatsu, Mitsuhiro Imaizumi, and Shigetaka Kuroiwa,
   Polymer J., 13, 807(1981).

7. Sol-Gel Transition of Polypropylene in Decalin and Tetralin.
   Hideomi Matsuda, Mitsuhiro Imaizumi, Hitoshi Fujimatsu, and Shigetaka Kuroiwa,
   Rept. Progr. Polym. Phys. Japan, 24, 41(1981).

8. Sol-Gel Transition of Linear Low Density Polyethylene in Organic Solvents.
Hideomi Matsuda, Mitsuhiro Imaizumi, Munetoshi Isayama, Hitoshi Fujimatsu, and Shigetaka Kuroiwa,
Rept. Progr. Polym. Phys. Japan, 25, 87(1982).

9. Studies on the Solution Properties of Nonionic Surfactants, Alkanamide Poly(oxyethylene) Sulfates II, Surface Viscosities of Surfactant/Thickener/ Water Systems.
Shigetaka Kuroiwa, Hitoshi Fujimatsu, Tsuyoshi Komiyama, and Masashi Nagasawa,
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Hitoshi Fujimatsu, Kazuyuki Takagi, Hideomi Matsuda, and Shigetaka Kuroiwa,
J. Colloid Interface Sci., 94, 237(1983).

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Hideomi Matsuda, Mitsuhiro Imaizumi, Hitoshi Fujimatsu, Shigetaka Kuroiwa, and Masaru Okabe,
Polymer J., 16, 151(1984).

12. Lower Critical Solution of Nonionic Surface Active Agents of Various Polyoxyethylene Chain Lengths.
Hitoshi Fujimatsu, Shinji Ogasawara, and Shigetaka Kuroiwa,
Colloid & Polymer Sci., 266(7), 594(1988).

CONTENTS

GENERAL INTRODUCTION

Gels of gelatin and agarose are well known from of old, and are attached in daily life. Our predecessors have used gels by utilizing their characteristics. The liquid prevents the polymer network from collapsing into a compact mass; the network prevents the liquid from flowing away. Depending on chemical composition and other factors, gels vary in consistency from viscous fluids to fairly rigid solids, but typically they are soft and resilient or, in a word, jellylike.

Gels have attracted the attention of numerous investigators for a long time [1]. The physical chemistry of various gels has been studied intensively since the 1940's; early contributions of notable importance were made by Paul J Flory [2] of Stanford University. Flory's theory has been reduced to problem in Bethe's lattice, and has been succeeded by Gordon et al [3]. On the other hand, de Gennes [4] and Cloijeaux [5] have been found that phase transition phenomenon of polymer are analogous to that of magnetic material in statistics. In this connection, since phase transition phenomenon and critical phenomenon of polymer gels have been recently found by Tanaka of Massachusetts Institute of Technology [6-12], possibility that gel can be understood consistently from both sides of physics and chemistry occurred, and recently the study of gel has developed and its achievements have become a center of attraction.

According to Tanaka's theory [13], properties of polymer gels depend upon the osmotic pressure defined as the sum of three forces: the rubber elasticity, the polymer-polymer affinity and the hydrogen-ion pressure.

The theory has been improved to be applied hydrogel of polyacrylamide. Phase transitions and critical points are found in a great diversity of physical systems besides gels. The most familiar examples are the solid-to-liquid and liquid-to-vapor transitions that almost all substances undergo when the temperature and pressure are varied. A ferromagnetic material exhibits a phase transition of a somewhat different kind: at high temperature the magnetic moments of the atoms are randomly oriented and the material is unmagnetized, but when the temperature falls to a particular value, the atomic moments begin to line up and the material develops a magnetization. The critical phenomena can be encompassed by the same mathematical description. In particular, as micro-characters and -dispositions of polymer be vividly reflected in phase transition phenomena of gels, investigations on macro-properties of gel are expected to be available for understanding of polymer itself. According to finding of phase transition of gel, the application of gel technology to switches, sensors, memories, display units, and mechanochemical transducers and functional membranes is anticipated.

Gelation as a consequence of the crystallization of copolymers from dilute and moderately dilute solutions is a well-known phenomenon [14-17] which has been receiving renewed attention [18-20]. The presence of noncrystallizing chain units in the chain, randomly distributed in some cases, has led to the concept that crystallization-gelation is micellar, as compared with the more conventional lamellarlike crystallites formed from solution [14,19,20,22]. The perception of a fringed micelle crystallite habit for such gels is at present a deductive one. Despite the apparent logic of the arguments leading to the fringed micelle concept [14,19,20,22], there is in fact as yet no direct evidence for the existence of such structures.

Polyethylene gel also have been found through studies on crystallization of polyethylene from solution. The gelation of polyethylene by crystallization from solution has been mentioned cursorily in earlier literature and tacitly ignored [23,24]. Recently, following the important original observation by Pennings and co-workers [25,26] that gelation occurs during the crystallization from stirred solutions, has been further developed in this phenomenon [27-29]. Matsuda and his co-workers [30,31] have reported that under quiescent conditions the gelation took place through the crystallization of polyethylene from a solution with cooling. From that time on, a new impetus was given to the subject by a novel sample preparation method developed by Zwijnenburg and Pennings and termed the "surface growth technique". Continuous filaments can be grown by this method at temperatures as high as 123° C [32]. Fibers grown at the highest temperatures are reported to be overgrowth free and show a very high tensile modulus. Smith and Lemstra of DSM Co. [33] have found that gel filament of polyethylene which are produced by solution spinning and subsequently drown in a hot-air oven at 120° C, and shows a high-strength and high-modulus feature. Their experimental results have increased expectation for the presence of high-strength and high modulus fibre, and advanced appearance of gel-spinning method [34] and hot-drowing method [35].

High-strength fibres of polyethylene made of gel-spinning method are already made by the pilot production. Dineema Co. and Allied Chemical Co. are providing super-fibre samples in the name of Dineema and Spectra,respectively. Mitsui Petro Chemical Co. is providing Techmilon fibre made by wax-blend method which has been developed from gel-spinning method.

The appearance of high-strength and high-modulus fibres of polyethylene stimulates other polymers to realize high-strength and high-modulus ones. For polypropylene [36] and polyvinylalcohol [37], higher strength and modulus fibres than that obtained by other method have been obtained by gel-spinning method.

Investigations on structure and molphology of polyethylene contributed to the appearance of high-strength and modulus fibres as mentioned above. However, unknown points concerning properties of polyethylene gels still remain, and their applied investigations are rarely carried out.

In this paper, thermochromic phenomenon of polyolefin gels, that the author for the first time have found, has been investigated in detail, furthermore, as an applied investigation of polyolefin gels, the adhesive effect and manner of polyolefin gels on polyolefin moldings have been investigated in detail though it is well known that an adhesion of polyolefin, particularly polyethylene, is difficult.

In chapter 1, the characteristics of the thermochromism of polyolefin gels are clarified, especially with regard to the polypropylene gels. In chapter 2, the characteristics of the thermochromism of the gels of poly-1-butene and polymethylpentene are clarified. In chapter 3, the adhesive effects of high density polyethylene gels on polyethylene and polypropylene moldings are clarified. In chapter 4, the adhesive effect of low density polyethylene gels on polyethylene moldings are examined. In chapter 5, the adhesive effect of polypropylene gels on polypropylene moldings are examined. In chapter 6, the study on adhesion of molded polyethylene using polyethylene gels by microwave heating is described. And the adhesive effects of swollen polyethylene films on polyethylene moldings are discussed in chapter 7.

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CHAPTER I

THERMOCHROMISM OF SWOLLEN AND GELLED POLYPROPYLENE

I -1 Introduction

Since shearing flow-induced crystallization of high density polyethylene from xylene solution was initiated by Pennings and Kiel [1] in 1965, a number of works in connection with it have been reported by Pennings and associates [2-10], Kobayashi [11], Manley [12,13], and Keller [14-20]. However, all these investigations have been carried using dilute and quasi-concentrated solutions.

Matsuda and co-workers reported on the gelation of the concentrated solutions of polyethylene in cyclohexane and carbondisulfide mixed solvent [21-23]. Successively, Matsuda, the author, and co-workers reported on the gelation of the concentrated solutions of polyethylene [24,25] and polypropylene [26] also in a single organic solvent such as benzene, toluene, xylene, decalin, and tetralin. In preparing the gels, these solvents were added to polypropylene or polyethylene contained in glass tubes. The glass tubes were then sealed and the temperature raised up to near boiling point of the solvent. The polymer solutions were then cooled with running water until the gels were formed.

The author found that when powdery isotactic polypropylene, prepared from xylene solution by addition of methanol, were swelled with benzene-derivative solvents prior to heating, the powder was faintly coloured. A subsequent change of the temperature of these swelled powdery polymer resulted in the colour change. The yellowish colour at higher temperatures changed to a bluish colour at lower temperatures.

The author found that the gels prepared with these powdery polymer and the benzene-derivative solvents mentioned above also showed a faint colouring.

In the present chapter, thermochromic properties of polypropylene swelled and gelled in organic solvents were investigated by measurements of scattered- and transmitted-light spectra in the visible and near-ultraviolet region, X-ray diffraction, and electron microscopic observation.

I -2 Experimental

Materials

Seven samples of unfractionated polypropylene (PP) supplied by Showa Denko Co. and Mitsubishi Rayon Co. were used. The physical properties of samples are tabulated in Table 1. These weight-average molecular weights determined by GPC are in the range of about 10×10^4 to 50×10^4.

Purification of the samples was carried out as follows: Pellets of the sample were dissolved completely in xylene at its boiling point under a reflux condenser and then precipitated into an excess of cooled methanol with stirring. After washing with methanol, it was then dried under reduced pressure until a constant weight was attained.

The solvents used in present experiments were Wako reagent grade of benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, decalin, tetralin, cyclohexane, tetrachloroethylene, *o*-dichlorobenzene, 1,1,2,2-tetrachloroethane, chlorobenzene, carbontetrachloride, and methyl alcohol, ethyl alcohol, propyl alcohol, buthyl alcohol, and hexyl alcohol. The solvents (benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene) were purified by the following procedure. Each solvent was mixed with concentrated sulphuric acid in the proportion of 10%. The solvent layer was washed with water and then with a sodium hydrate solution. It was then dehydrated with calcium chloride and finally distilled. The other solvents were distilled before use.

Table 1. Physical properties of polypropylenes

Sample	Density (g/cm^3)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	T_m (°C)	α (%)
PP-1	0.8997	50.1	8.75	5.7	157.3	26.6
PP-2	0.9002	38.6	6.88	5.6	157.8	34.2
PP-3	0.9001	31.8	5.10	6.2	158.3	35.3
PP-4	0.9008	28.0	4.81	5.8	157.9	35.6
PP-5	0.9020	19.8	2.70	7.3	157.9	36.3
PP-6	0.9002	11.0				
PP-7	0.9000	30.0			161.2	34.0

Powdery PP were prepared as follows: 1.5 g of purified PP of were dissolved in 250 ml of xylene at its boiling points under a reflux condenser. After samples were dissolved completely, 100 ml of a series of alcohols such as methyl, ethyl, n-propyl, n-buthyl, and n-hexyl alcohol were added to the solutions. The precipitated PP were filtered through a sintered glass disk, then dried under reduced pressure at 60℃ until a constant weight was attained.

PP gels were prepared in glass tubes as follows: A definite weight of the PP and a definite volume of the solvent were placed in a glass tube. It was then sealed. After the PP was dissolved completely at 150℃, the solution was quenched in a thermobath kept at 0°, -44°, -195℃. The PP concentration in gels was 3 g/100cm^3 in all systems.

Methods

The wavelength-dependent transmittance of swollen and gelled PP was measured using a Shimadzu MPS-2000 spectrophotometer with a quartz cell of 10 mm in optical path length. The temperature was controlled by circulating water through the cell jacket in the range of about 10° to 80℃.

The light scattered spectrum of swollen and gelled PP in the direction perpendicular to the incident light was recorded by the same spectrometer which had an attachment of a double beam fluorescence apparatus. The sample temperature was controlled by the electric heater buried into the cell jacket in the range of about 30° to 80℃.

Observation of PP crystallites was carried out using an Akashi Model ALPHA-10A scanning electron microscope (SEM). The specimen for SEM measurement was prepared as follows: After a gel was lyophilized, it was coated with a thin layer of gold by the vacuum evaporation technique. The specimen of powdery PP was also prepared in the same method.

X-ray diffraction of a gelled and lyophilized PP was performed on a Rigaku Geigerflex 2028 diffractometer equipped with a scintillation counter and a pulse height analyzer, using CuKα radiation.

I -3 Results and Discussion

Themochromism of swollen PP

Powdery PP obtained by precipitating from xylene solution of PP on addition of methyl alcohol was swollen by benzene in a glass tube. When natural light was radiated from behind the glass tube, colouring phenomenon in the visible region was easily detected with the naked eye. Furthermore, as the temperature increased, the colour changed in the order of blue, violet, red, orange and yellow. It is striking experimental fact that the PP swollen in benzene shows a thermochromic phenomenon although polypropylene itself is colourless and has no asymmetric carbons in the molecules.

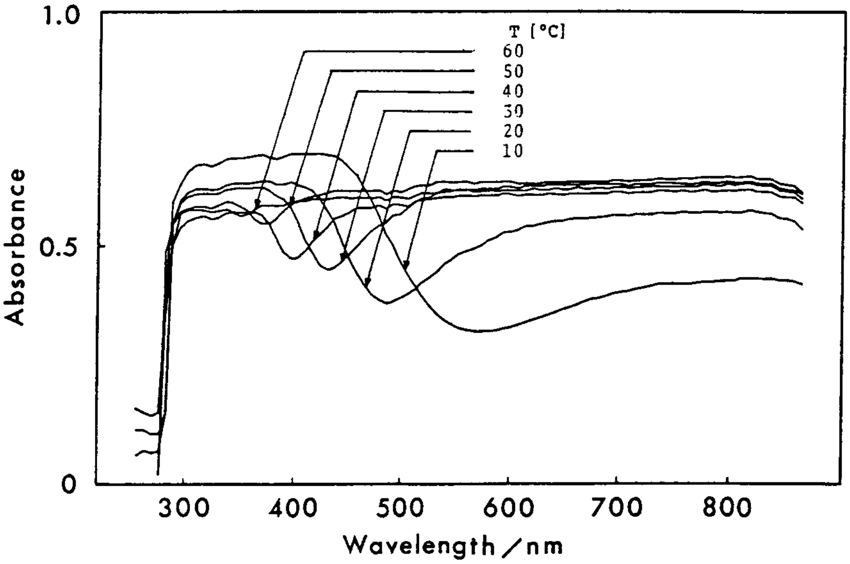


Fig. 1. Transmitted-light spectra of PP swollen in benzene, using PP-7 sample precipitated by the addition of methyl alcohol.

In order to make this more quantitative, the transmitted-light spectra of the PP swollen in benzene were measured at various temperatures. These are shown in Fig.1. The spectrum at 10℃ has a broad peak in the wavelength range of 300 to 430 nm and a trailing edge in the wavelength range of 430 to 550 nm. In this case, the sample is bluish with the naked eye. As the temperature is raised, the absorbance of the transmitted-light diminishes, on the other hand the absorbance of a broad band with a maximum near 800 nm increases and the valley of the spectrum shifts to shorter wavelengths together with its recovery. Comparing the change of these spectra with it in colour observed by eye as the temperature is raised, the light in the wavelength bands of the larger absorbance is found to be observed with

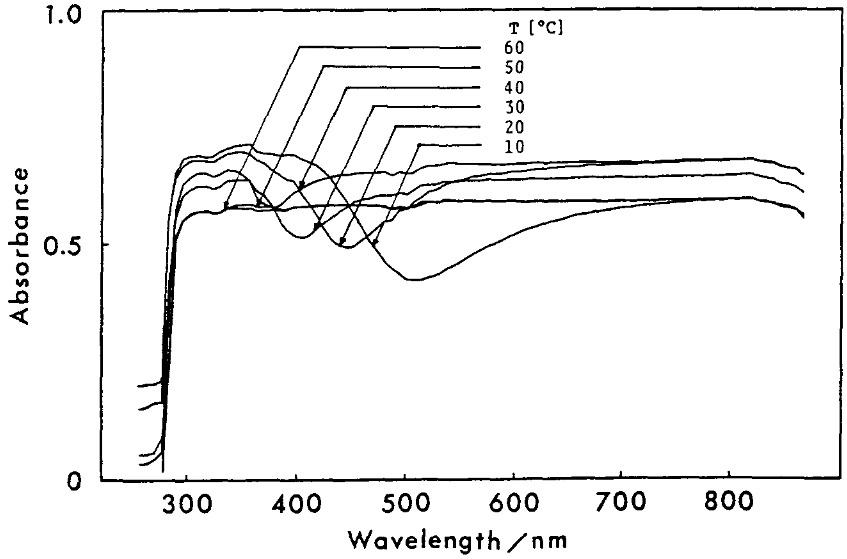


Fig. 2. Transmitted-light spectra of PP swollen in benzene, using PP-7 sample precipitated by the addition of ethyl alcohol.

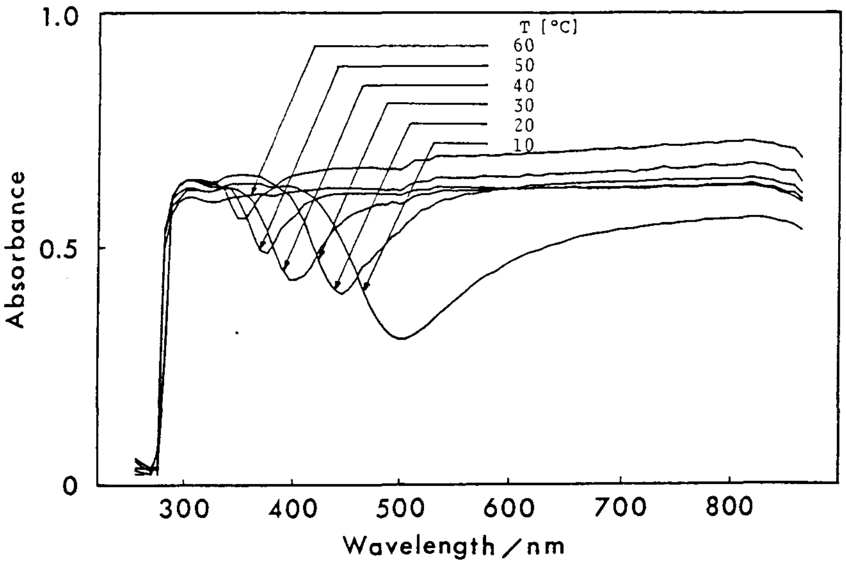


Fig. 3. Transmitted-light spectra of PP swollen in benzene, using PP-7 sample precipitated by the addition of propyl alcohol.

naked eye. Accordingly, this suggests that the colouring phenomenon is due to selective scattering, but not to optical absorption.

Further, in order to examine the effect of solvent added for the precipitation from PP solution in xylene, a series of unsaturated alcohols as precipitant were used. Powdery PP obtained on addition of ethyl-, propyl-, buthyl-, and hexyl alcohol was swollen in benzene. The transmitted-light spectra are showed in Figs.2,3,4, and 5, respectively. The shape, intensity and the temperature change of these spectra are different in each system. In the case of PP on addition of ethyl alcohol, Fig.2, a broad peak over the wide visible region is observed even at 10℃ , and a valley is rarely found beyond 50℃ . Such tendency is remarkable as alkyl chain of alcohol used as a precipitant is longer. This

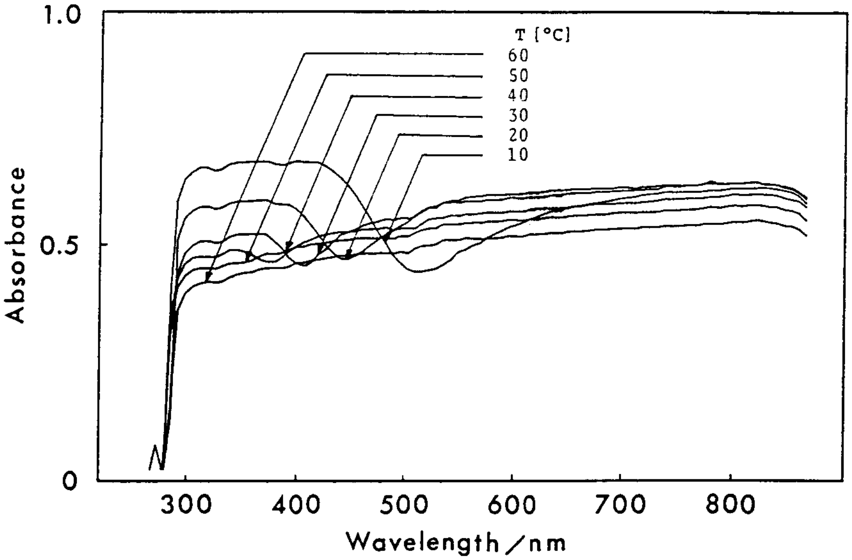


Fig. 4. Transmitted-light spectra of PP swollen in benzene, using PP-7 sample precipitated by the addition of buthyl alcohol.

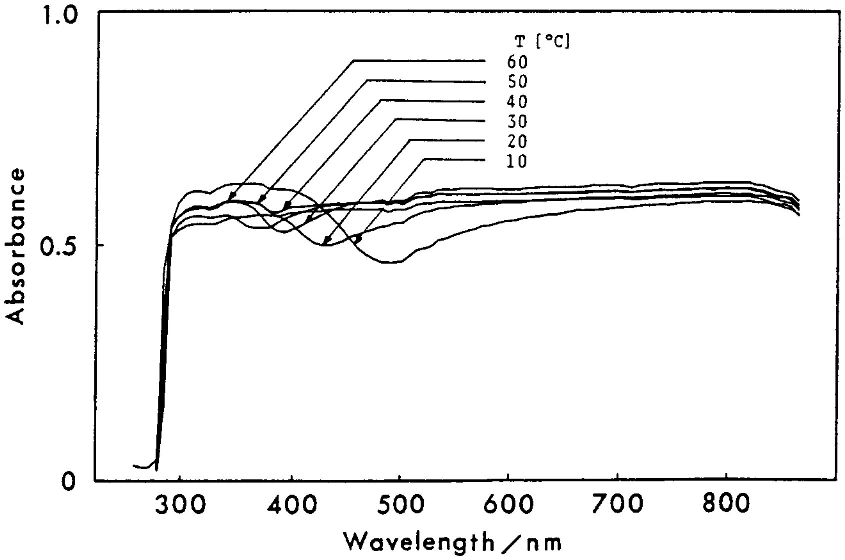


Fig. 5. Transmitted-light spectra of PP swollen in benzene, using PP-7 sample precipitated by the addition of hexyl alcohol.

Table 2. SP values of solvents

Solvent	SP value $(cal/cm^3)^{1/2}$
Xylene	8.8
Methyl alcohol	14.5
Ethyl alcohol	12.9
n-Propyl alcohol	11.9
n-Buthyl alcohol	11.3
n-Hexyl alcohol	10.5

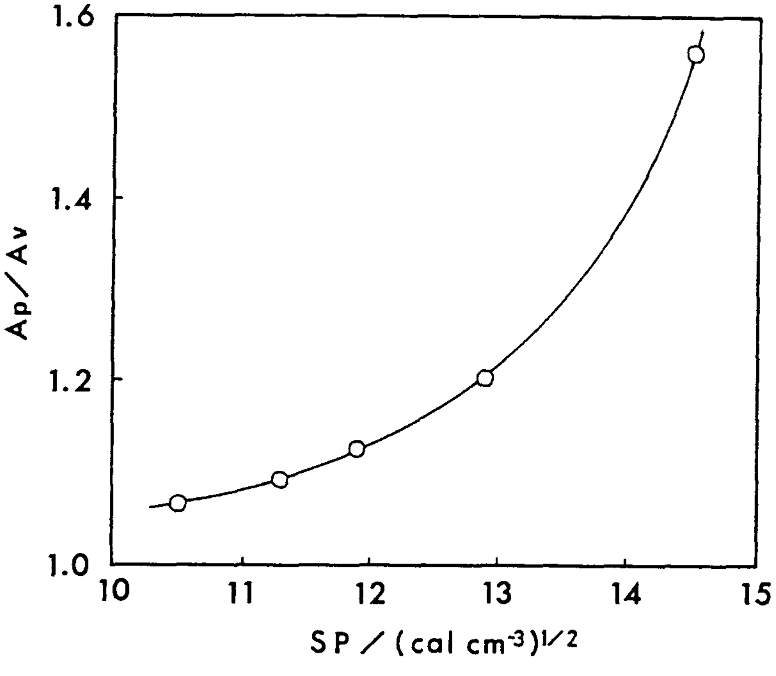


Fig. 6. Plots of A_p/A_v against SP values of the solvents.

may be due to the different solubility of alcohols on PP. In order to examine quantitatively the results, the degree of colouring was evaluated using the ratio of the absorbance of a peak in near-ultraviolet region against that in visible region, R. The ratios at 10℃ and the solubility parameters (SP) of alcohols are tabulated in Table 2. The ratios against the SP of alcohol were plotted in Fig.6. The correlation is recognized between both terms. The swollen PP precipitated by alcohol having larger SP shows larger R, that is, in the case of methyl alcohol R indicates the largest value. This suggest that the crystalline state according to the alcohol used is different, this influences the colouring.

Thermochromism of PP gels

It became apparent that PP swollen in benzene inhibits thermochromic phenomenon in the preceding section. However, as the system is the heterogeneity, it is difficult to examine quantitatively the thermochromic phenomenon. Fortunately, PP gels in various solvents. The author examined whether PP gel shows a colouring or not. PP gels in benzene-derivative solvents also showed a faint colouring. Moreover, it was found that on cooling the gels, the colour changes although the change is not as clear as that of the swollen PP. These gels were formed by gradual cooling of the PP solution with running water. The author therefore thought that the method of cooling might affect the thermochromic characteristics of the gels. In order to determine this, the PP solutions were rapidly cooled to about 0℃ . Some of the solutions were frozen and others were not, but gels were formed anyway. Thus formed gels

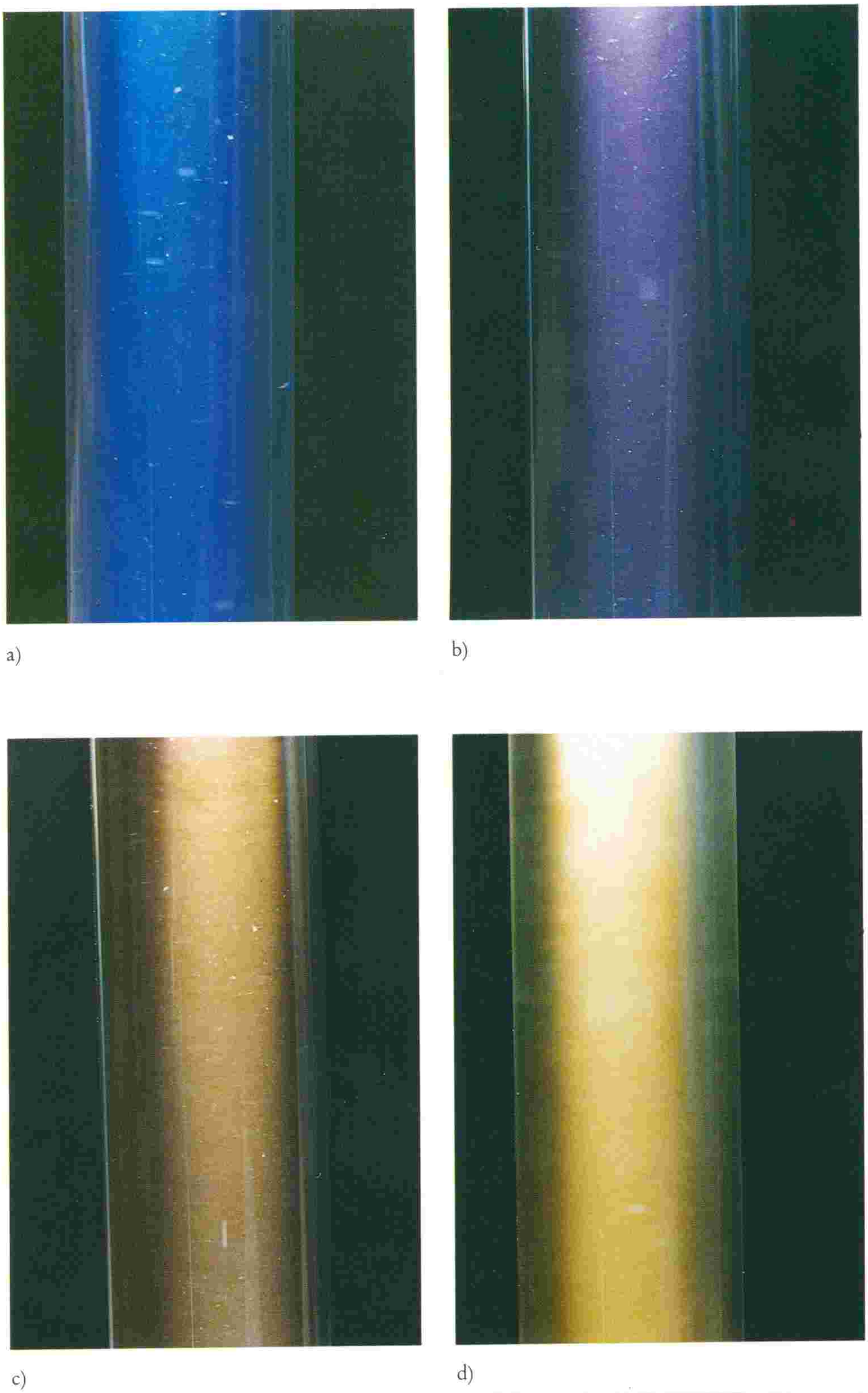


Fig. 7. Thermochromism of 3% polypropylene gel in benzene: colour photographs of scattered light by the gel at (a) 26.6°C; (b) 31.0°C; (c) 36.0°C; and (d) 50.0°C.

all showed clear thermochromism. Photographic plates (a) to (d) in Fig.7 show the thermochromism of 3% PP gel in benzene at 26.6°, 31.0°, 36.0°, and 50.0℃, respectively.

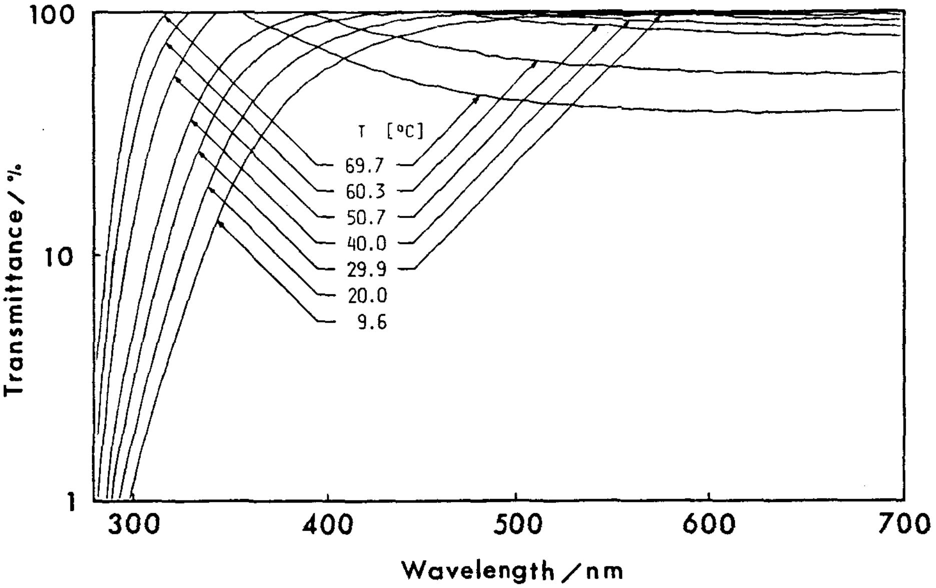


Fig. 8. Transmitted-light spectra of 3% PP gel in benzene.

In order to make this more quantitative, transmitted spectra of the gel were measured. Transmitted-light spectra of 3% PP gel in benzene at various temperatures are showed in Fig.8. Transmittance is plotted as ordinate and wavelength as abscissa. It is apparent that the shape of the spectrum changes with an increase in temperature as well as swollen PP. As PP itself has no chromophore, it is unlikely that PP gel absorbs light in the visible region. The spectra of the light scattered by the gel in the direction perpendicular to the incident light were measured. Fig.9 illustrates the spectra measured in the range of about 26° to 70℃. As

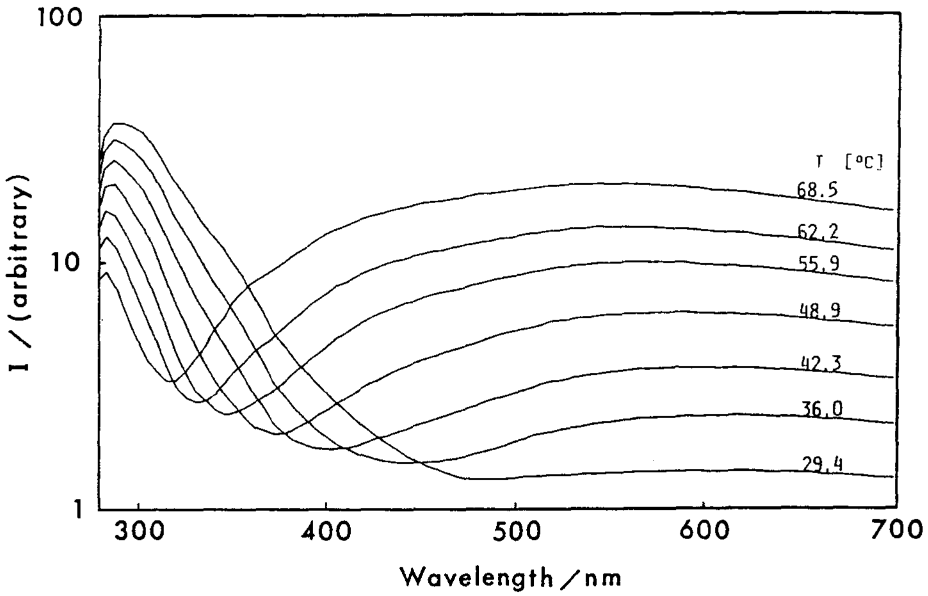


Fig. 9. Scattered-light spectra of 3% PP gel in benzene.

can be seen from Fig.9, the scattered-light spectra are measured and change with an increase in temperature. The spectrum of the light scattered from the gel at 26.5° C has a peak near 300 nm and tailing edge in the wavelength range of 400 to 470 nm. Therefore, the scattered light itself appears to be bluish, resulting in the photographic plate, Fig.7a. As the temperature of the gel is raised, the intensity of the scattered light diminishes and a new broad band with a maximum at 700 nm arises over the wavelength range of 480 to 700 nm at 36.0℃ . In this case, the scattered light appears to be reddish, resulting in the photographic plate, Fig.7c. Further increase in temperature gives rise to an increase of the intensity of the new band over all visible range. The spectrum at 48.8℃ , which has a peak near 580 nm, may be recognized as a yellowish light, giving the photographic plate, Fig.7d. The gels become turbid and white when the temperature is further increased. This is because the intensity of the scattered light increases over all the visible range, as can be seen in the spectrum at 68.5℃ in Fig.9.

From these results, the author may speculate that the colouring phenomenon is due to a selective reflection similar to that in a cholesteric liquid crystal but not due to fluorescence.

The influence of solvents on the thermochromism

In the preceding section, the thermochromism of PP gels in benzene was investigated. In order to examine whether gels in other organic solvents inhibit the thermochromism or not, thirteen solvents which can gel PP were used. Consequently, it has been found that the thermochromic behavior can be classified into two types. One is the type that indicates the thermochromism similar to the gel in benzene, the other is the type that a bluish colour diminishes and the other colour not appear. As the typical example the scattered-light spectra of the gels in *o*-xylene and tetralin are shown in Figs.10, 11, respectively. As can be seen from Fig.10, the spectrum of the gel in *o*-xylene shows the change similar to the gel in benzene with an increase in temperature. In any case, as the temperature is raised, the colour changes in order to blue, violet, red, orange, yellow. But the temperature where the same colour appears is different, that is, o-xylene system changes the same colour at higher temperature than benzene system. The benzene and the benzene-derivatives such as toluene, *o*-xylene, *m*-xylene, *p*-xylene, and tetrachloroethylene systems indicate the same tendency.

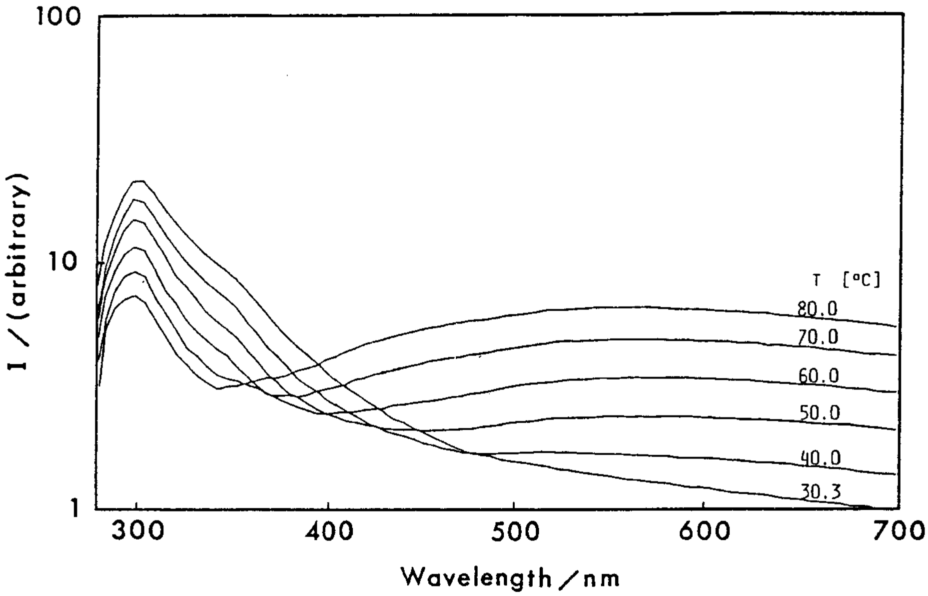


Fig. 10. Scattered-light spectra of 3% PP-4 gel in *o*-xylene.

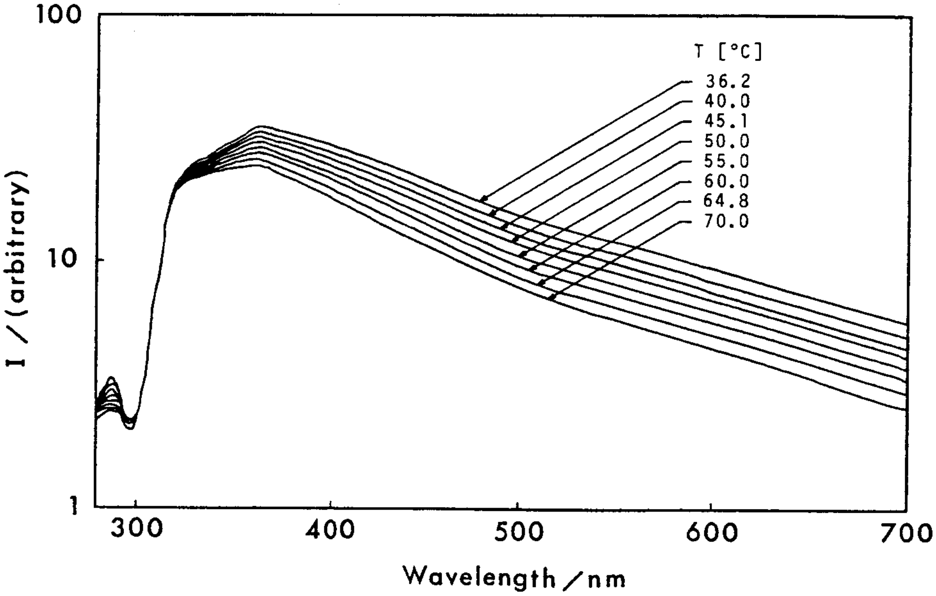


Fig. 11. Scattered-light spectra of 3% PP-4 gel in tetralin.

The spectrum in Fig.11 shows the change in contrast with these systems. That is, The intensity of scattered light only decreases over visible and near-ultraviolet region, and new band not appear with an increase in temperature. The chlorobenzene system indicates the same tendency. The decalin, cyclohexane, *o*-dichlorobenzene, and 1,1,2,2-tetrachloroethane systems form gels but not indicate the thermochromism. And carbontetrachloride does not form a gel and not indicate the thermochromism.

Table 3. List of solvent systems indicated colouring

Solvent	Colouring
benzene	++
toluene	++
o-xylene	++
m-xylene	++
p-xylene	++
decalin	-
tetralin	+
cyclohexane	-
tetrachloroethylene	++
o-dichlorobenzene	-
1,1,2,2-tetrachloroethane	-
chlorobenzene	+
carbontetrachloride	--

All results are tabulated in Table 3. In Table 3, the symbol ++ indicates that the thermochromism is strikingly observed, the symbol + indicates that a bluish colour diminishes and the other colour not appear with an increase in temperature, the symbol - indicates that a gel is formed but not indicate the thermochromism, the symbol -- indicates that a gel is not formed and not indicates the thermochromism.

The influence of the molecular weight of PP on the themochromism

As the thermochromism in the present study is based on polymer, a molecular weight of PP can be expected to influence the thermochromism. In this section, using various molecular weight of PP samples, the influence of the molecular weight of PP on the thermochromism is investigated. As it is difficult to measure quantitatively a scattered-light spectrum, the measurement of transmitted-light spectra was carried out. In Fig.12, the spectra measured at 50℃ for 3g/100cm^3 gels of various samples are plotted, with absorbance as ordinate. The ordinate is enlarged to clarify the dif-

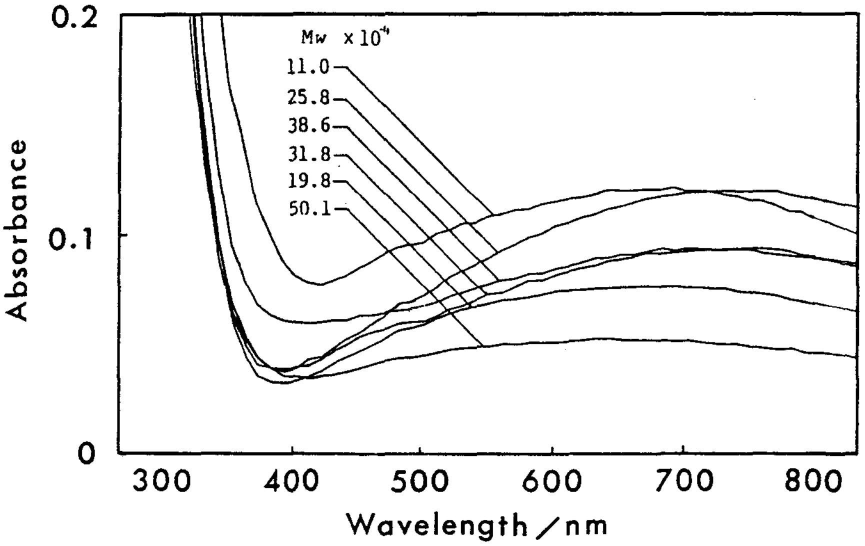


Fig. 12. Transmitted-light spectra of the various gels in benzene at 50° C.

ference of each spectrum in the visible region. As can be seen from Fig.12, each spectrum is apparently different. The degree of brightness in each spectrum is qualitatively evaluated by the ratio of absorbance of a peak in the visible region against that of a valley near 400 nm. Accordingly, the ratio A_p/A_v is plotted against molecular weight of PP sample as a function of temperature in Fig.13. As the ratio is small than 1 over all

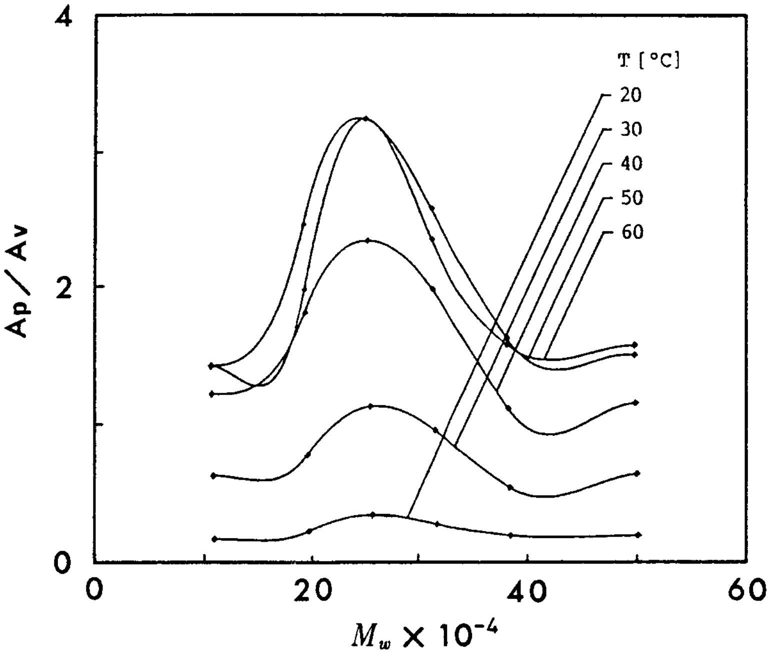


Fig. 13. Plots of A_p/A_v against M_w of PP.

molecular weight region at 20℃, it is found that a scattered light of a short-wavelength in the visible region is relatively larger than that of a long-wavelength. As the temperature is raised, it becomes large than 1. This indicates that a light of a long-wavelength in the visible region is scattered highly than that of a short-wavelength. The curve has a maximum near molecular weight of 25× 10^4 in the case of each temperature. In other words, the gel of PP in a molecular weight of about 25× 10^4 shows a most striking thermochromism. The reason is unknown at the present stage.

The effect of cooling temperature for formation of gels on the thermochromism

In the preceding section, gels formed by cooling at 0℃ were used. As it becomes apparent that gels formed by gradual cooling don't show a striking thermochromism, the effect of cooling temperature for formation of gels on the thermochromism was investigated in detail. After the PP was dissolved completely in benzene at 150℃ and 3 % PP solution was prepared, the solution was quenched in a thermobath kept at 0° , -44° , -195℃ .

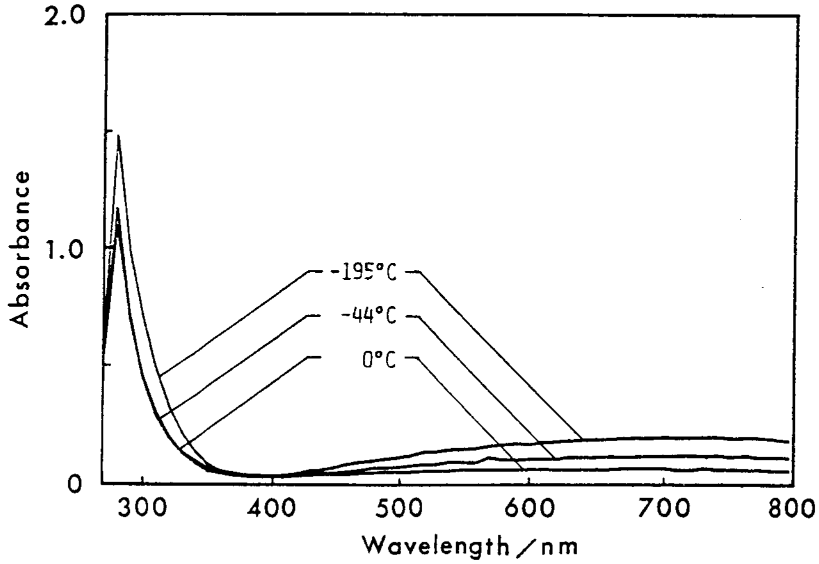
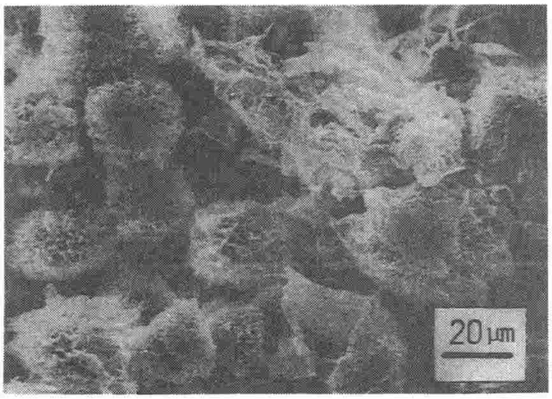
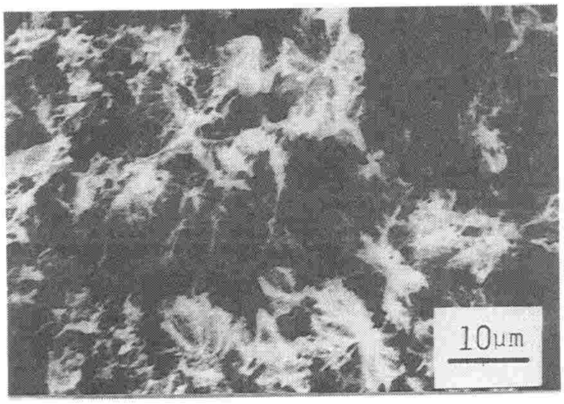


Fig. 14. Effect of gelation temperatures on the selective reflection of the PP-4 gel in benzene at 50°C.

Transmitted-light spectra of these gels at various temperatures were measured. As an example, spectra measured at 50℃ are plotted in Fig.14. Gel quenched to lower temperature shows a spectrum with a higher absorbance of peak in both near ultraviolet and visible



(a)



(b)

Fig. 15. Electron micrographs of replicas from 2% PP-4 gel in benzene; gelation temperature: (a) 0°C, and (b) -195°C.

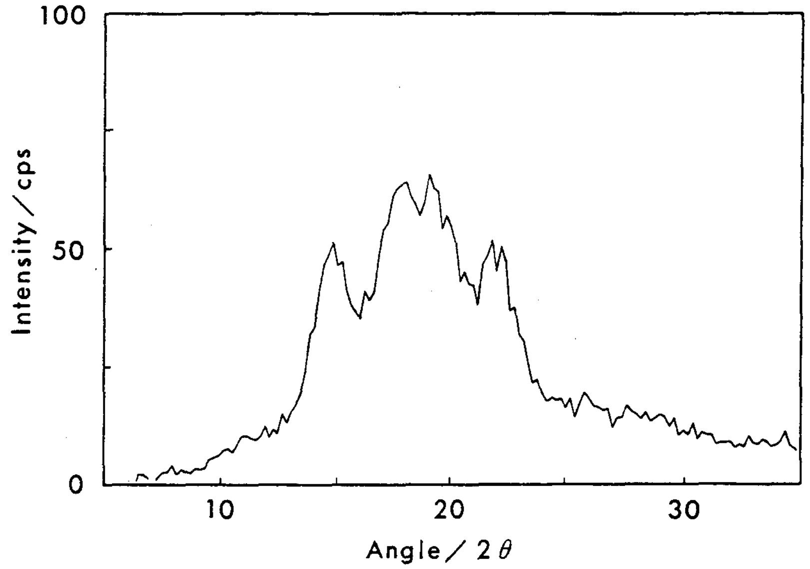


Fig. 16. X-ray diffraction pattern for 3% PP-4 gel in benzene formed by quenching rapidly to 0° C.

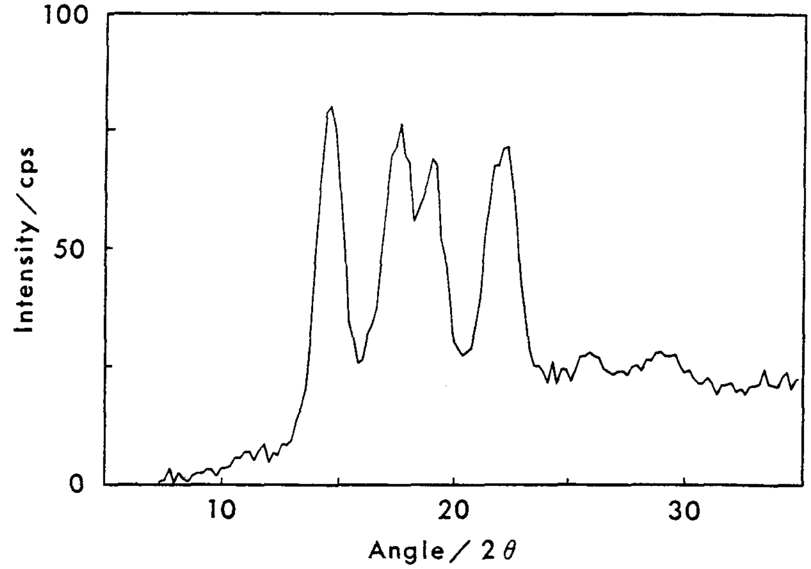


Fig. 17. X-ray diffraction pattern for 3% PP-4 gel in benzene formed by quenching rapidly to -195° C.

region. The result suggests that gel structure formed by quenching at lower temperature closely relates with the thermochromism.

Then, lyophilized gels were observed by a SEM. Examples of electron micrographs of specimens from 2 % gels in benzene formed at 0° ,-195℃ of cooling temperature are shown in Figs.15(a) and (b), respectively. In Fig.15(a), spherulites are observed. On the other hand, in Fig.15(b), an amorphous structure is observed, but not a spherulite. Furthermore, in order to examine these crystalline states, X-ray diffraction of each gel was performed. Examples of X-ray diffraction patterns for 3 % gels in benzene quenched at 0° and -195℃ are shown in Figs.16 and 17, respectively. These are patterns after subtracting the diffraction intensity of the solvent from that of gels. The gel formed by quenching at -195℃ shows the broad pattern than that of the gel at 0℃ . This indicates that the size of micro-crystallines in the gel formed at -195℃ is smaller, or the packing of micro-crystallines is in disorder than that of the gel at 0℃ . Taking into account the results observed by a electron microscope, it seems reasonable to consider that the packing is in disorder.

From results described above, it was proved that the thermochromism closely relates to an amorphous structure in gels.

I -4 Summary

The colouring and thermochromism of the swollen and gelled PP were studied. The results obtained were summarized as follows:

1. Swollen and gelled isotactic PP in some solvents such as benzene derivatives, tetrachloroethylene, tetralin, and chlorobenzene shows a colouring phenomenon.

2. It shows a thermochromism. There are two types of the thermochromism. One is the type that the colour changes strikingly in the order of blue, violet, red, orange, and yellow under natural light, as the temperature rises. The other is the type that a bluish colour diminishes, as the temperature rises.

3. The colouring of the gels is due to selective reflection, but not to optical absorption.

4. The gel of PP in a molecular weight of about 25×10^4 shows a most striking thermochromism.

5. Amorphous structure of PP crystalline in gel closely relates to the present thermochromism.

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CHAPTER II

THERMOCHROMISM OF POLY-1-BUTENE AND POLYMETHYLPENTENE GELS

II -1 Introduction

In chapter 1, the thermochromism of the swollen and gelled isotactic polypropylene in some organic solvents was investigated, it was revealed that the colouring phenomenon was due to selective scattering, but not to optical absorption. Polyethylene gels in organic solvents do not exhibit such a colouring phenomenon. Accordingly, it is interesting to examine whether other kinds of polyolefins show thermochromism or not. In the present chapter, the thermochromism of poly-1-butene and polymethylpentene gels is investigated by measurements of scattered- and transmitted-light spectra in the visible and near-ultraviolet region, X-ray diffraction, differential scanning calorimetry, and electron microscopic observation.

II -2 Experimental

Material

Poly-1-butene used is a homo-polymer of molecular weight $82x10^4$, and polymethylpentene used is a homopolymer of molecular weight $64x10^4$.
These were supplied by Dr.Fuji of Exploratory Polymer Research Laboratory, Mitsui Petrochemical Industries, LTD. The sample was dissolved in xylene at the boiling

point and precipitated in cooled methanol with stirring. It was then dried under reduced pressure until a constant weight was attained.

All the chemicals used in the present experiments were originally of the Wako special grade. The solvents (benzene, toluene, o-xylene, m-xylene and p-xylene) were purified by the following procedure: Each original solvent was mixed concentrated sulfuric acid by the portion of 10 %. The solvent layer was washed with water and then with a sodium hydrate solution. It was then dehydrated with calcium chloride and finally distilled. The o-dichlorobenzene was distilled before use.

Methods

Poly-1-butene and polymethylpentene gels were prepared in glass tubes as follows: A definite weight of the polymer samples and a definite volume of the solvent were sealed in each glass tube. After the polymers were dissolved completely at 150° C, the solutions were quenched in a thermobath kept at 0°, -50°, -195° C. The polymer concentration in gels was 3 g/cm^3 in all systems.

When natural light was radiated from behind of the glass tubes, thermochromism in the visible region was easily detected with naked eyes.

The wavelength-dependent transmittance was measured by a Shimadzu MPS-2000 spectrophotometer. The temperature was controlled by circulating water through the cell jacket. The spectrum of the light scattered by the gel in the direction perpendicular to the incident light was recorded by the same spectrometer which has the attachment of a double beam fluorescence apparatus. The sample temperature was controlled by the electric heater buried in the cell jacket. Each series of these spectral measurements was carried out within about two hours. The reproducibility of these spectra has been confirmed.

Melting temperatures of the gels were measured by a Rigaku 8240 differential scanning calorimeter. The rate of heating was 1°C per minute.

Observation of poly-1-butene crystallites was carried out using an Akashi Model ALPHA-10A scanning electron microscope. The specimen for SEM measurement was prepared as follows: After a gel was lyophilized, it was coated with a thin layer of gold by the vacuum evaporation technique. The specimen of powdery poly-1-butene was also prepared in the same method.

X-ray diffraction of a gelled and lyophilized poly-1-butene was performed on a Rigaku Geigerflex 2028 diffractometer equipped with a scintillation counter and a pulse height analyzer, using CuKα radiation.

II -3 Results and Discussion

The influence of solvents on the thermochromism of poly-1-butene gels

Poly-1-butene flakes swollen in benzene, toluene, o-xylene, m-xylene, p-xylene and tetrachloroethylene exhibited thermochromism, just as polypropylene flakes did [1]. As the temperature increased, the colour changed in the order of blue, violet, red, orange and yellow under irradiation of natural light. The temperature range was different for each colour. Because of the

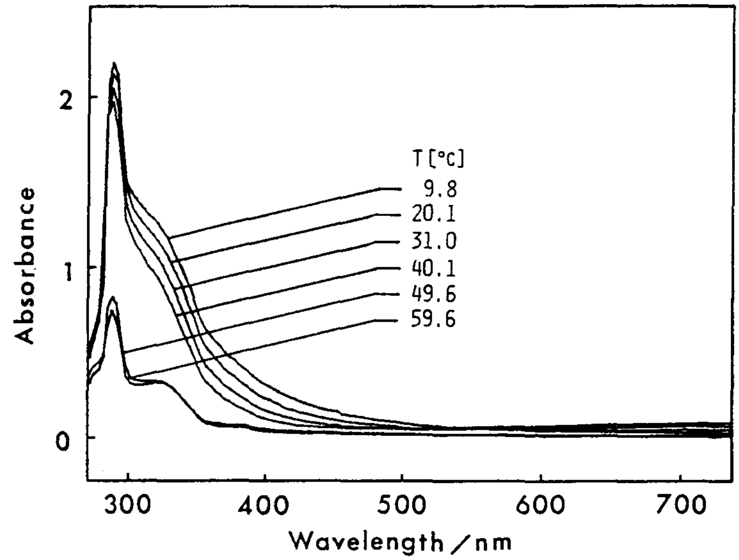


Fig. 1. Transmitted-light spectra of 3% poly-1-butene gel in benzene.

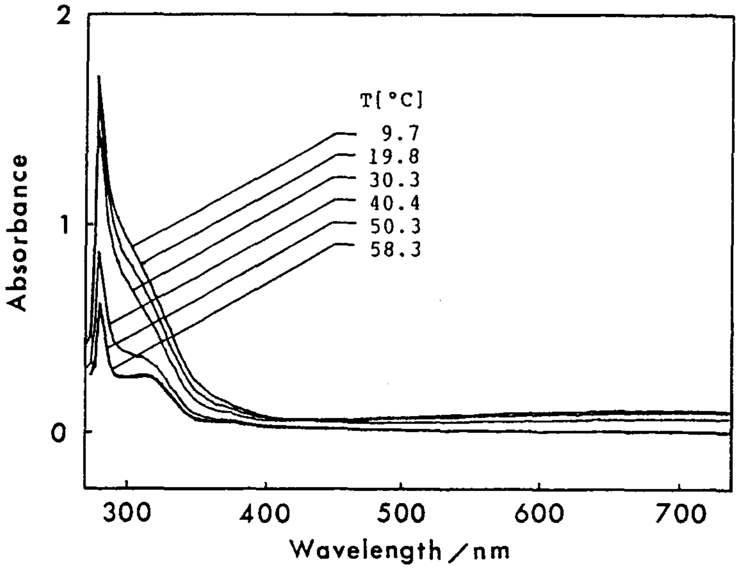


Fig. 2. Transmitted-light spectra of 3% poly-1-butene gel in toluene.

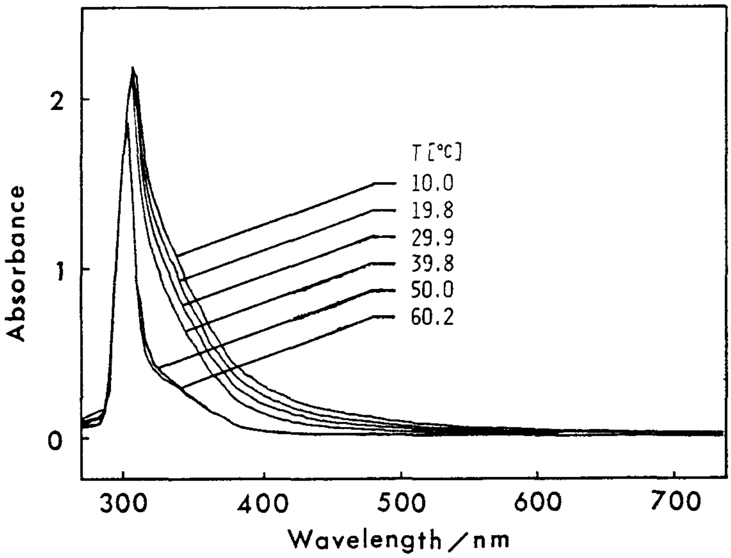


Fig. 3. Transmitted-light spectra of 3% poly-1-butene gel in *o*-xylene.

heterogeneity, no quantitative measurement was attempted. Fortunately, poly-1-butene dissolved in these organic solvents formed gels, and all of these gels exhibited thermochromism. These colour changes occur instantaneously with temperature, and colour remains unaltered for a long period when the temperature is kept constant.

The transmitted-light spectra of the gels in benzene, toluene and tetrachloroethylene are plotted in Figs 1,2 and 3, respectively. In measuring these spectra, the corresponding solvents were placed in the reference cell of the double-beam apparatus in order to cancel the absorption due to the solvents. These spectra show absorptive peaks around 280 nm and trailing edges in the wavelength range of 400 to 500 nm at lower temperatures.

The temperature dependence for the tetrachloroethylene and the *o*-xylene systems has quite a different characteristic. As an example, the spectra of *o*-xylene gel are shown in Fig.3. In this case, the intensity of the transmitted light increases over all the visible range, as the temperature increases. This corresponds to the diminishing of blue colour, leading to a colourless transparent gel.

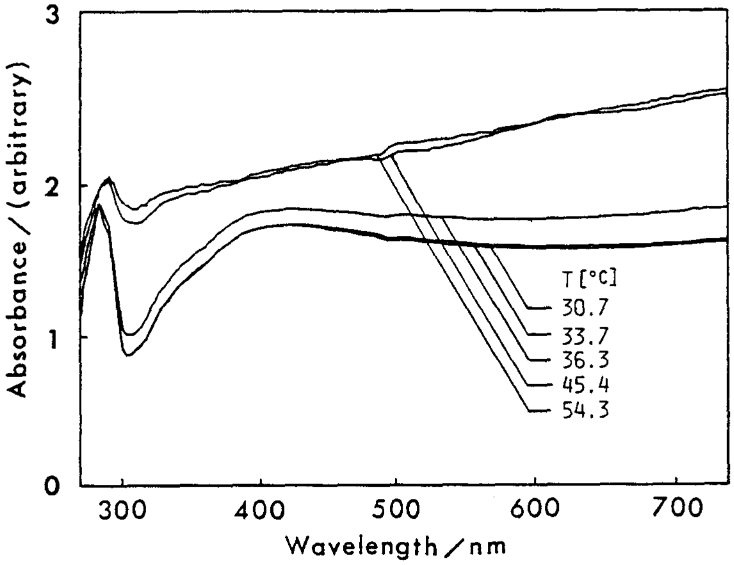


Fig. 4. Scattered-light spectra of 3% poly-1-butene gel in toluene.

As poly-1-butene itself has no chromophore, it is unlikely that the swelled and gelled poly-1-butene absorbs a light in the visible region. Fig.4 illustrates the spectra of the light scattered by the toluene gel in the direction perpendicular to the incident light. Note that these spectra approximately form a reflected image of the spectra in Fig.2, although the position of the peak at 300 nm is slightly shifted. The change of the spectrum in its shape with temperature corresponds to the change of the colour observed with eyes. The author concludes that the colouring phenomenon of the gels is due to a selective scattering, but not to an optical absorption.

The influence of thermal history on the thermochromism of poly-1-butene

As the temperature increases in benzene and toluene systems, the transmittance increases and broad absorptive bands become apparent. This temperature dependence of the spectrum suddenly changes its character beyond a certain temperature. That is, the intensity of the transmitted light begins to increase over all the wavelength range. In Fig.5, apparent absorbances of the absorptive peaks near 280 nm in Figs.1 and 2 are plotted against the temperature. Both curves indicate

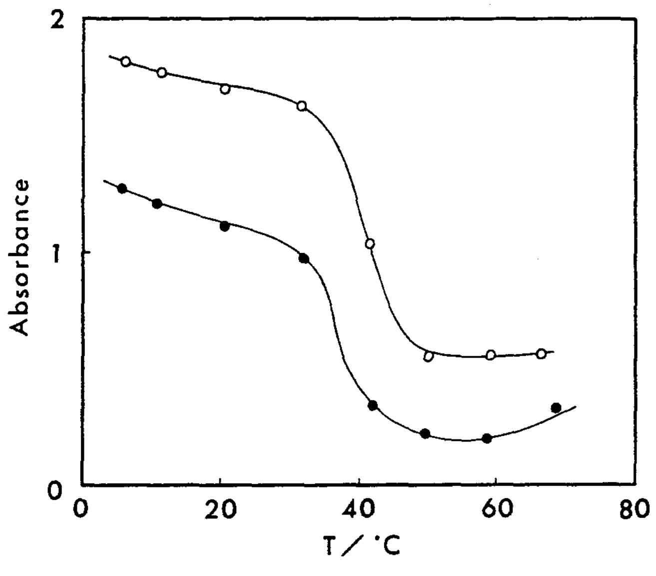


Fig. 5. Temperature dependence of the apparent absorbance of the peak at 280 nm : 3% poly-1-butene gels in (○) benzene and (●) toluene.

similar changes with temperature. The existence of two inflection points (the point at lower temperature is defined as T_1, the point at higher temperature is defined as T_2) in these plots indicates that the temperature dependence is of two steps for these systems. This suggests the existence of two micro-structures of the polymer in the gels. We have therefore carried out the thermal analyses of the gels by using the DSC method.

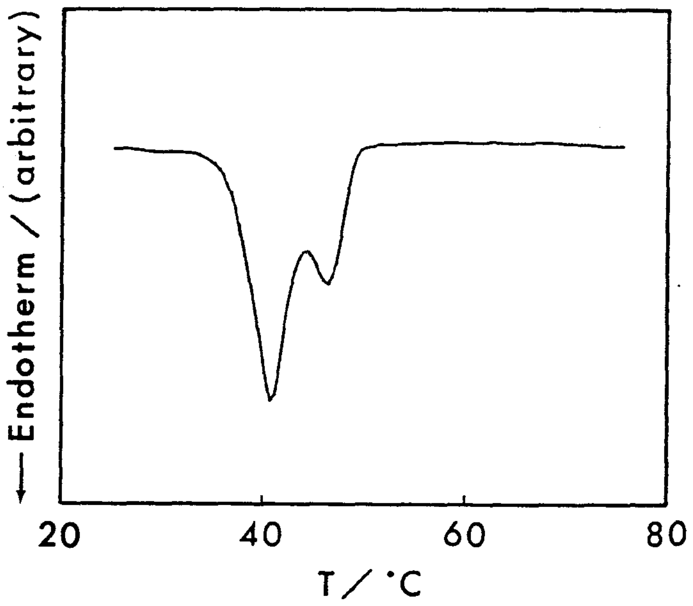


Fig. 6. DSC thermogram for 3% poly-1-butene gel in benzene.

Fig.6 shows DSC thermogram for 3% poly-1-butene gel in benzene. The thermogram indicates two endothermic peaks. The similar thermogram was also obtained for the gel in toluene. The temperatures of two endothermic peaks in each case are 41.9° and 47.4° C for the gel in benzene, 41.0° and 47.8° C for the gel in toluene. In Fig.6, a gradual shift of endothermic appears about 34℃ .

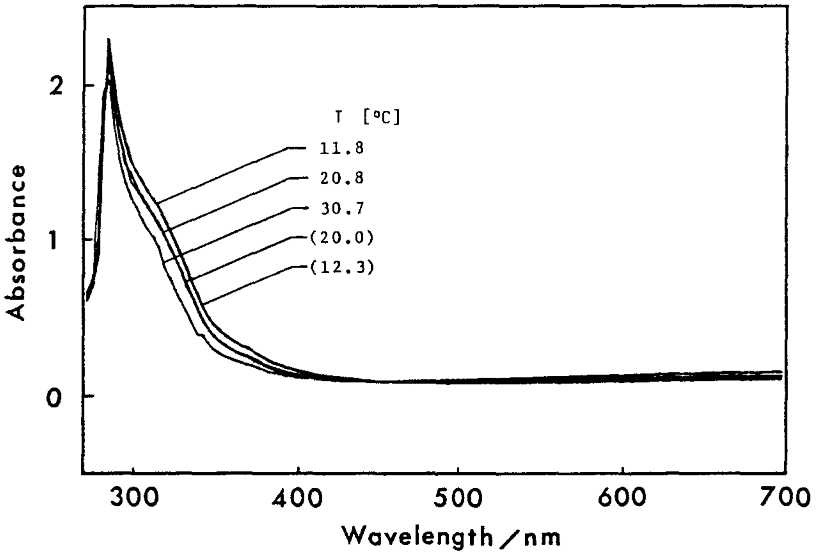


Fig. 7. Reproducibility of the spectrum of 3% poly-1-butene gel in toluene when heated to 30°C.

It agrees with the temperature T_1 from which the absorbance in Fig.5 rapidly begin to decrease. The higher temperatures of the endothermic peaks, i.e. 47.4°C for the gel in benzene and 47.8°C for the gel in toluene gel, agree with temperatures T_2 at which the gradual change of the absorbance curve in Fig.5 begins to appear again. They also agree with temperatures at which these gels turn to the sols [13]. These peaks are probably due to the melting of the polymer in two different deformations. This view has been deduced from the known results of the thermal analyses of other polyolefins such as polyethylene [2,3] and polypropylene [4-12].

If such idea hold good, it may be expected that the a thermal history of a gel influence on a thermochromism. First thermo-reversibility below T_1 was examined. The spectra of the gel were measured as the temperature is raised from about 10°C to about 30°C at

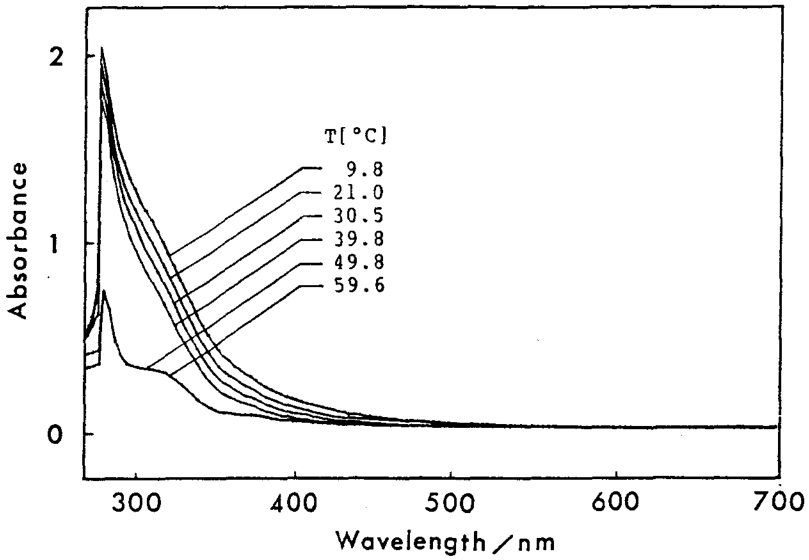


Fig. 8. Reproducibility of the spectrum of 3% poly-1-butene gel in toluene when heated to 60° C.

10° intervals. Again the spectra of the gel were measured as the temperature is decreased. These results are shown in Fig.7. The absorbance is plotted as ordinate and the wavelength as abscissa. The parentheses in Fig.7 indicate the spectra measured as the temperature is decreased. As can be seen from Fig.7, the spectrum measured with an increase in temperature approximately agree with that measured with an decrease in temperature. Further measurements with an increase in temperature resulted in the same spectra although these are not demonstrated. After a gel was heated at 60° C once, it was cooled at 10° C. The spectra of the gel were measured as the temperature is raised again. The results are shown in Fig.8. This suggests that a structure, which is responsible for the scattered light in the visible region, diminishes together with the melting of the gel. These results are probably due to either the melting of the polymer crystalline in the two different deformations or the difference of the mechanism for light scattering. This view has been deduced from the known results of the thermal analysis of other polyolefins such as polyethylene [2,3] and polypropylene [4-12].

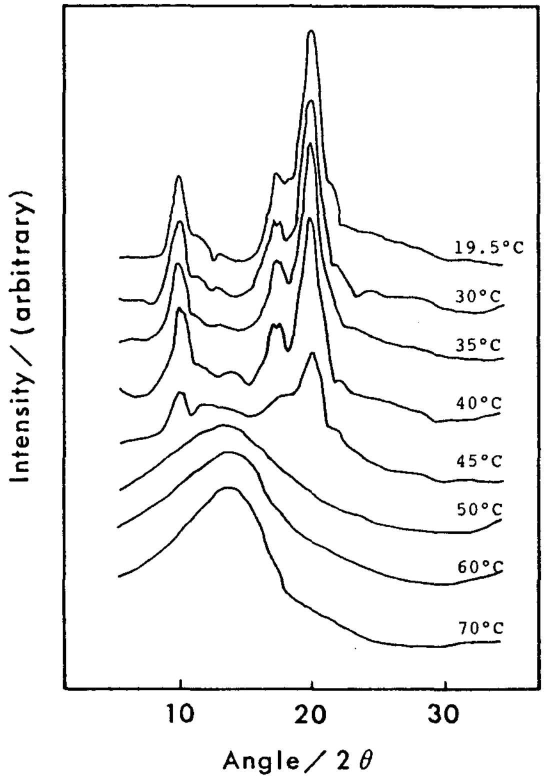


Fig. 9. X-ray diffraction pattern of 5% poly-1-butene gel at various temperatures.

X-ray diffraction of the gel were performed under the same conditions as spectra in Figs.7 and 8 were measured. Fig.9 shows X-ray diffraction patterns at various temperatures. These are patterns after subtracting the diffraction intensity of the solvent from that of the gel. The diffraction pattern scarcely change within the temperature from 10° to 40° C. But, at 45° C sharp peaks characteristic of poly-1-butene crystalline begin to decrease, further, these peaks diminish beyond 50℃ . Although unshown here, the spectrum remains unchanged, that is, spectra measured at each temperature are the same as the spectrum at 70° C, when the temperature is lowered again.

Taking into account both results regarding spectra and X-ray patterns, the scattered light in the near-ultraviolet region is believed to be due to an amorphous structure in the gel, in the visible region a macroscopic structure in the gel.

The influence of cooling temperature for the formation of gels on the thermochromism

In the preceding section, gels formed by cooling at 0° C were used. As it becomes apparent that gels formed

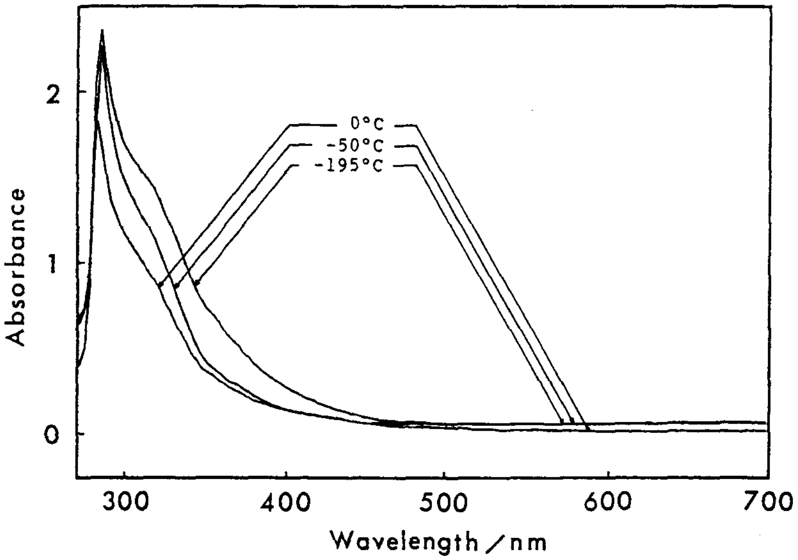
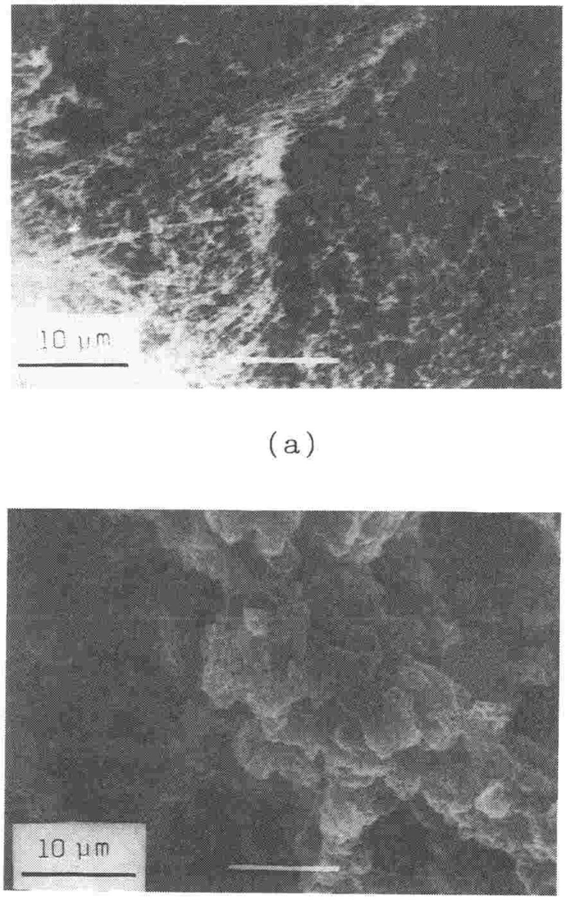


Fig. 10. Spectra of poly-1-butene gels formed by quenching rapidly to 0, -50, and -195° C.

by gradual cooling don't show a striking thermochromism, the effect of cooling temperature for formation of gels on the thermochromism was investigated in detail. After poly-1-butene was dissolved completely in toluene at 140°C and 5 % poly-1-butene solution was prepared, the solution was quenched in a thermobath kept at 0°, -50°, and -195°C. Transmitted-light spectra of these gels at various temperatures were measured. As an example,



(a)

(b)

Fig. 11. Electron micrographs of specimens obtained by freeze-drying of poly-1-butene gels formed by quenching rapidly to -195°C (a), and 0°C (b).

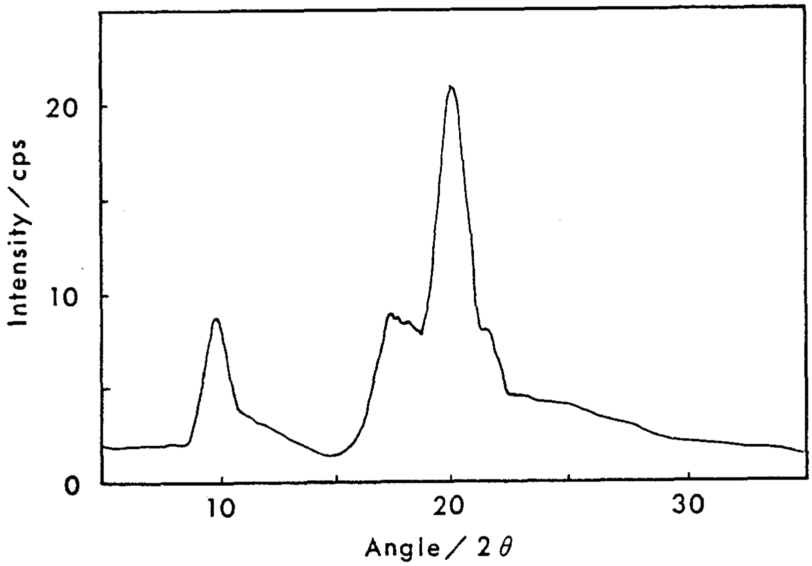


Fig. 12. X-ray diffraction pattern of 5% poly-1-butene gel in toluene formed by quenching rapidly to 0°C, at 20°C.

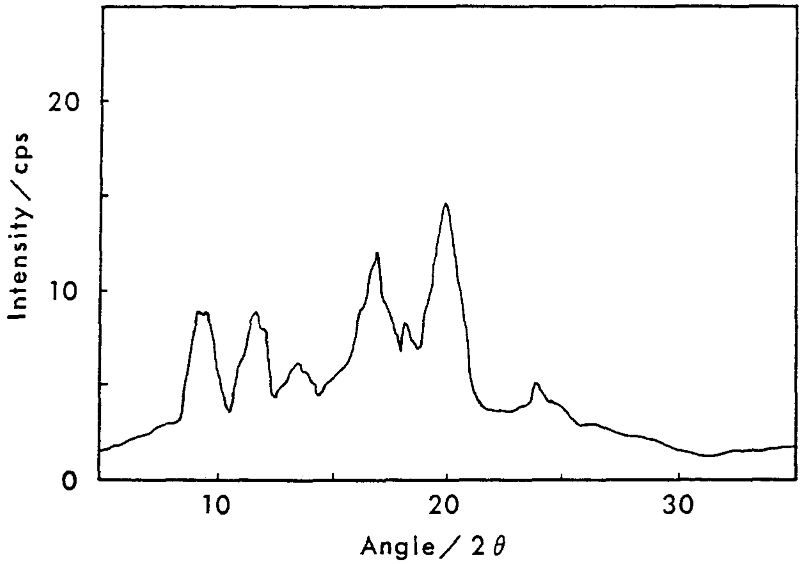


Fig. 13. X-ray diffraction pattern of 5% poly-1-butene gel in toluene formed by quenching rapidly to -195°C, at 20°C.

spectra measured at 10° C are plotted in Fig.10. Gel quenched to lower temperature shows a spectrum with a higher absorbance of peak in both near-ultraviolet and visible region. The result suggests that gel structure formed by quenching to lower temperature closely relates with the thermochromism.

Then, lyophilized gels were observed by a SEM. Examples of electron micrographs of specimens from 5 % gels in toluene formed at 0°, -195° C of cooling temperature are shown in Figs.11(a) and (b), respectively. In Fig.11(a), spherulites are observed. On the other hand, in Fig.11(b), micro-spherulites are observed. Furthermore, in order to examine these crystalline states, X-ray diffraction of each gel was performed.
Examples of X-ray diffraction patterns for 5 % gels in toluene quenched to 0° and -195° C are shown in Figs.12 and 13, respectively. These are patterns after subtracting the diffraction intensity of the solvent from that of gels. The gel formed by quenching rapidly to -195° C shows the broad pattern than that of the gel at 0° C. This indicates that the size of micro-crystallines in the gel formed at -195° C is smaller, or the packing of micro-crystallines is in disorder than that of the gel at 0° C. Taking into account the results observed by a electron microscope, it seems reasonable to consider that the packing is in disorder.

From results described above, it was proved that the thermochromism closely relates to an amorphous structure in gels.

Thermochromism of polymethylpentene

In the preceding section, optical characteristics of poly-1-butene gels in some solvents were examined in detail. Further, the author examined whether other kinds of polyolefins inhibit a thermochromism or not. Consequently, it was found that a gel of polymethylpentene inhibits a thermochromism. In the present section, optical characteristics of polymethylpentene gels were investigated. First, solvent in which polymethylpentene gels was sought. It was found that polymethylpentene forms gels in toluene, o-xylene, tetrachloroethylene, and chlorobenzene. The gel in toluene of these solvents inhibited a thermochromism.

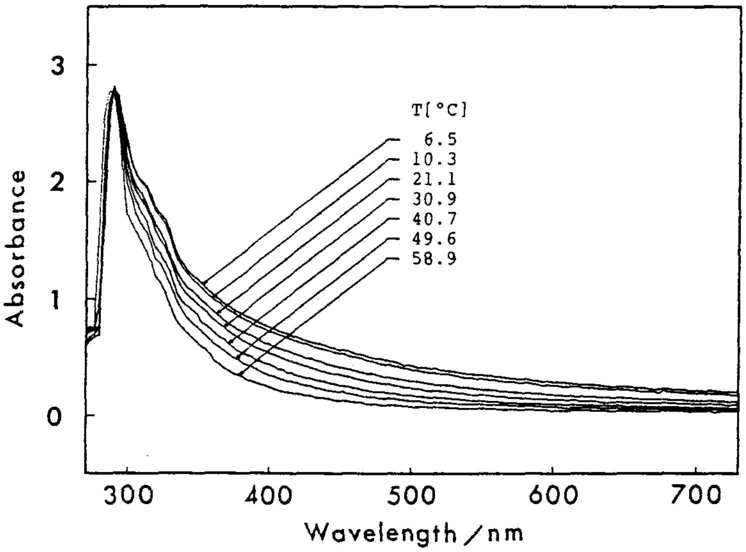


Fig. 14. Transmitted-light spectra of 3% polymethylpentene gel in toluene.

After the polymer was dissolved completely at 150° C, the gel quenched 0° C used to measure a transmitted-light spectrum in the visible and near-ultraviolet region. Spectra measured at various temperatures are plotted in Fig.14, with absorbance as ordinate.

As can be seen from Fig.14, The change of the spectrum with an increase in temperature is analogous to that of Fig.3. That is, the absorbance of the transmitted-light decreases over all wavelength region as the temperature increases. This corresponds to the diminishing of the blue colour, leading to a colourless transparent gel.

II -4 Summary

The thermochromism of poly-1-butene and polymethylpentene in some organic solvents was studied. The results obtained are summarized as follows:

1. Both gelled and swollen poly-1-butene in some solvents of benzene derivatives and tetrachloroethylene show colouring phenomena under natural light.
2. They show thermochromisms exhibiting a sequence of striking colour changes in the order of blue, violet, red, orange and yellow under natural light, as the temperature rises.
3. When the gel is heated below the temperature which endothermic shift in DSC thermogram appears, optical characteristics of the gel are thermo-reversible. When the gel is heated beyond the temperature of endothermic peak at higher temperature in DSC thermogram, the spectra in the visible region in the figure are not reproduced, but the spectra in the near-ultraviolet region are reproduced.
4. The colouring of the gels is due to a selective scattering, but not to an optical absorption.
5. The gel formed by quenching rapidly to lower temperature inhibits a more deep colour.
6. The thermochromism has been partially explained by the possible existence of two different microstructures of the polymer crystal.

7. Polymethylpentene gel in toluene also show the same thermochromism.

II -5 References

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CHAPTER III

ADHESIVE EFFECT OF HIGH DENSITY POLYETHYLENE GELS ON POLYETHYLENE MOLDINGS

III -1 Introduction

It is well known that securing a good adhesion between polyethylene plate and other materials, especially between two polyethylene plates, is difficult because of polyethylene's non-polarity and high crystallinity. To increase the strength of the adhesion of a material to a polyethylene moldings, Various methods such as chemical [1,2], thermal [3], electrical [4,5], or radiation [6] treatments for the activation of the surface of the polyethylene moldings had been devised. However, such methods have disadvantages that the adhesive strength is often unsatisfactory, that the effects due to the treatments diminish with time and, furthermore, expensive and complex procedures are required.

It has been reported that concentrated solutions of polyethylene in mixed solvents [7] and in single solvents [8-10] gel. In these papers, it is indicated that polyethylene dissolved in the solvents above the boiling points formed thermo-reversible gels. If these gels interposed between two polyethylene plates are heated, an adhesive effect is expected. Because these gels satisfy three fundamental conditions [11] for an adhesion. First, an adhesive is of a fluid material, and can wet the material to be joined. Second, an adhesive solidifies after coating. Third, an adhesive itself has an appropriate strength. However, as polyethylene is non-polarity, intermolecular interactions such as hydrogen bond, polarization force can not be expected. If there is an inter-molecular interaction expected for polyethylene, that is of London's dispersion force which is calculated as 0.16 kcal per one unit of $-CH_2-$. Because that can interact between non-polar molecules. Using polyethylene gels, it is thought that the intermolecular interaction based on London's dispersion force can be utilized effectively for an adhesion between polyethylene plates. However, a polyethylene gel did not inhibit an adhesive effect at room temperature. In order to satisfy truly conditions described above, heating shall be required.

In the present chapter, using polyethylene gels as an adhesive, the influence of heating conditions, the solvents, and physical properties of polyethylene samples on the adhesive effect have been investigated in detail by strain rate meter, differential scanning calorimeter (DSC) and electron microscope techniques.

III -2 Materials and Methods

Materials

Four samples of unfractionated high density polyethylene (HDPE) were used as an adhesive. The samples were supplied and characterized by Motegi of the Ohita Laboratory, Showa Denko Co. Typical physical properties of the samples are shown in Table I.

Polyethylene plates to be joined were 3 mm thick and composed of HDPE of molecular weight $10x10^4$ (Mitsui Petro Chemical Co.).

Solvents used in this study were the Wako reagent grade of decalin, tetralin, and *o*-dichlorobenzene, and were purified according to the usual method before use in order to avoid the influence of impurities.

Table 1. Typical Physical Properties of High Density Polyethylenes

Sample	Density (g/cm^3)	M_w X 10^{-4}	M_n X 10^{-4}	M_w/M_n	T_m (°C)	α (%)
HDPE-1	0.936	12.5	1.8	6.9	125.2	52.7
HDPE-2	0.946	13.7	1.7	8.0	127.3	62.9
HDPE-3	0.961	5.7	1.1	5.2	130.1	73.1
HDPE-4	0.960	7.9	1.4	5.8	131.3	76.4

M_w, the weight-average molecular weight determined by GPC method.
M_n, the number-average molecular weight determined by GPC method.
T_m, the melting temperature determined by DSC method.
α, the crystallinity determined by DSC, provided that the heat of fusion of the completely crystallized PE is 68.5 cal/g.

Purification of the sample was carried out as follows: Pellets of the polyethylene samples were dissolved completely in purified xylene at its boiling point in a flask with a reflux condenser. The solution was then poured into cooled methanol while stirring. After washing with purified methanol, the sample was dried under reduced pressure at 60℃ until a constant weight was attained.

Methods

Polyethylene gels were prepared in glass tubes as follows: A definite weight of polymer and a definite volume of solvent were placed in the glass tube which was then sealed. After polymer was dissolved completely at 140℃ , the polymer solution was cooled in a thermobath kept at 0℃ until a gel was formed. The polymer concentration in gels used as an adhesive was 8 g/100cm^3 in all systems.

Gels prepared by the procedure described above were interposed between polyethylene plates, 100 mm in length and 20 mm in width, as shown in Fig.1. The effective adhesive area was 4 cm^2. After 2 h of heating in an oven controlled at 5° C-intervals in the temperature range 90°-120° C, the samples were left stand for 24 h at room temperature. (It was determined in advance that 2 h was sufficient for all solvents to diffuse out.)

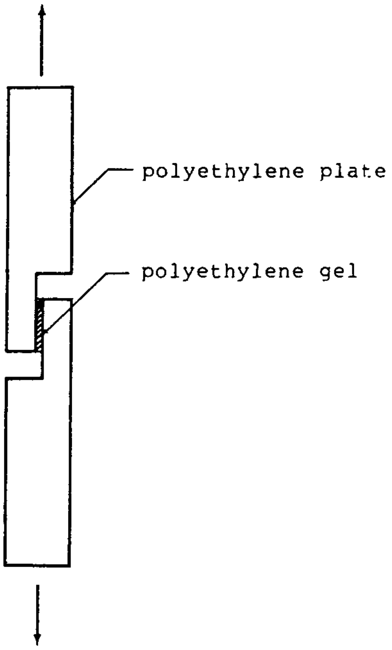


Fig. 1. The scheme of polyethylene plate for tensile shearing test (by ASTM D906-64).

The adhesive strength as a tensile shearing stress was continually measured according to ASTM D906-64 at the shearing rate of 5mm/min, using a Shimadzu RES-2 strain rate meter.

The surface of polyethylene plates immersed in heated solvents was observed by an Akashi ALPHA-30A scanning electron microscope with a Robinson detector in low vacuum environment.

The thermal behavior of gels was measured at the rate of 6°C/h, 1°, 2°, 5°, 10°, 15° and 20°C/min, and at the sensitivity of 0.5 mcal/sec, using a Rigaku Denki 8240B differential scanning calorimeter. The concentration of the gels is similar to those used as an adhesive.

The dissolution behavior of the molded polyethylene in solvents was directly measured at a heating rate of 1°C/min using the same DSC. Volume fraction of solvent to the molded polyethylene prepared in a cell is about 0.8 in each system.

The gel melting temperature was measured by the falling-ball method. The dependence of the gel melting temperature on the size of a steel ball was examined by a preliminary experiment, and that of a 2mg weight was selected. The steel ball was moved carefully to the surface of gel was warmed slowly at a heating rate of about 6°C/h, while the height of the steel ball from a reference level was recorded by a cathetometer as a function of temperature. When the gel melted, or converted to a sol, the steel ball begins to rapidly to fall downward. An example of measurements is illustrated in Fig.4. The temperature at which the horizontal and vertical straight lines intersected was defined as the gel melting temperature.

The solubility parameter (SP) of solvents was estimated as follows: Heat of vaporization ΔH is related to vapor pressure P by the Clapeyron-Clausius equation,

$$(d\ln P/dT) = \Delta H/RT^2 , \qquad (1)$$

where $(d\ln P/dT)$ can be obtained from the given P-T curve

[12]. Cohesive energy density (CED) can be calculated, when the heat of vaporization is substituted in

$$(\mathrm{CED}) = (\Delta H - RT)/V , \qquad (2)$$

where V is a molar volume of the solvent at the temperature T. The relation between SP and CED is defined as

$$(\mathrm{SP}) = (\mathrm{CED})^{1/2} . \qquad (3)$$

To obtain V in the eq.2, densities of the solvents were measured by a Shibayama SS-D-200 density meter; SP value were then obtained by substituting the CED values in eq.3.

The SP value of the molded polyethylene was estimated by a maximum intrinsic viscosity method at 140℃ as follows: Intrinsic viscosity of the polyethylene solutions in various organic solvents possessing various SP values was measured by Ubbelohde's viscometer. Intrinsic viscosities were then plotted against SP values of the solutions. An SP value corresponding to maximum intrinsic viscosity can be estimated as that of the molded polyethylene.

Ⅲ-3 Results and Discussion

In Fig.2, the values obtained by shearing stress tests are plotted against the heating temperature for PE gels in tetralin. Filled circles in Fig.2 indicate that polyethylene plate itself have given rise to a necking without being stripped from the jointing. Neither of the samples showed effective adhesive strength when heated at 100℃, as can be seen from Fig.2.

However, the adhesive strength increases as the heating temperature rose. It is apparent that the adhesive strength in the HDPE-1 system increases to over

36 kg/cm^2 when heated at 110℃ , and all of the systems begin to indicate significant adhesive strength when heated at 120℃ . The temperatures at which an adhesive strength begins to increase differ depending upon the samples. On comparing these results with physical properties in Table 1, the adhesive strength for the samples possessing a lower crystallinity is found to begin to increase at lower temperatures. Transition from gel to sol by means of the heating may first be required for adhesion. Because a correlation between crystallinities of the polymer samples and sol-gel transition temperatures is expected, the thermal behavior of the gels were examined by differential thermal analysis, in order to obtain a sol-gel transition temperature. As an example of the results, the thermogram for 8 g/100

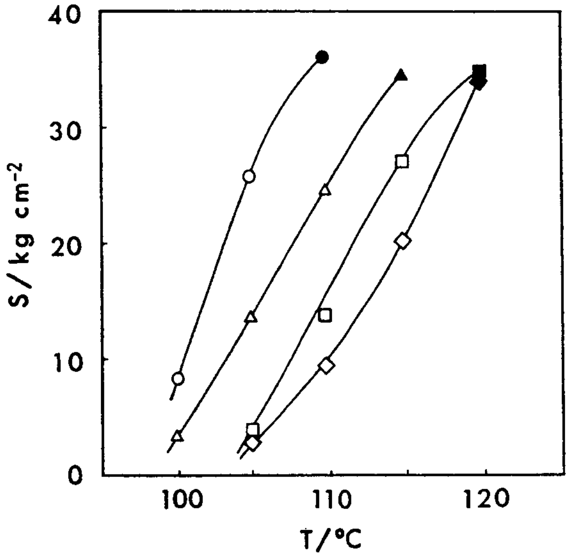


Fig. 2. Effect of the heating temperature on the adhesive strength of the HDPE gels in tetralin; -○-:HDPE-1, -△-: HDPE-2, -□-: HDPE-3, -◇-: HDPE-4. Filled symbols represent the results of polyethylene plates themselves giving rise to necking.

cm^3 of the HDPE-4 gel in tetralin at a heating rate of 6° C/h is shown in Fig.3. Two endothermic peas were observed, as can be seen from Fig.3. In Fig.4, the movement of a steel ball with an increase in temperature is shown when heated at a rate of about 6° C/h. It was confirmed that the peak at higher temperature in Fig.3 agrees with the sol-gel transition temperature obtained and shown in Fig.4. Heating rate dependence of the peak position was observed. Taking into account the experimental fact that the peak does not shift when heated at a rate of over 10° C/min, and the experimental condition that a test piece for adhesion is heated in an oven previously controlled at a definite temperature, that is, it is heated rapidly, the peak temperature at a heating rate of 10° C/min was adopted as the gel-melting temperature. All of the gel-melting temperatures obtained by DSC method for 8 g/100cm^3 of the gels are summarized in Table 2. Gels of the samples possessing

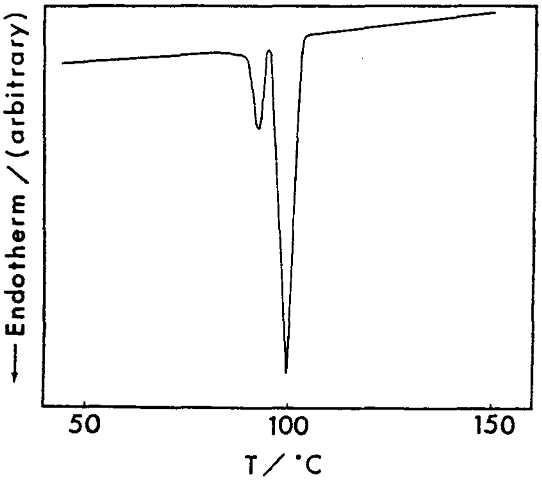


Fig. 3. DSC thermogram for HDPE-4 gel in tetralin.

Table 2. Sol-gel transition temperature estimated by DSC method.

Solvent	Polymer	Tm(°C)
Tetralin	HDPE-1	95.7
	HDPE-2	97.3
	HDPE-3	99.4
	HDPE-4	100.7
Decalin	HDPE-1	93.2
	HDPE-2	94.8
	HDPE-3	95.3
	HDPE-4	97.8
o-Dichlorobenzene	HDPE-1	97.7
	HDPE-2	100.0
	HDPE-3	100.0
	HDPE-4	100.2

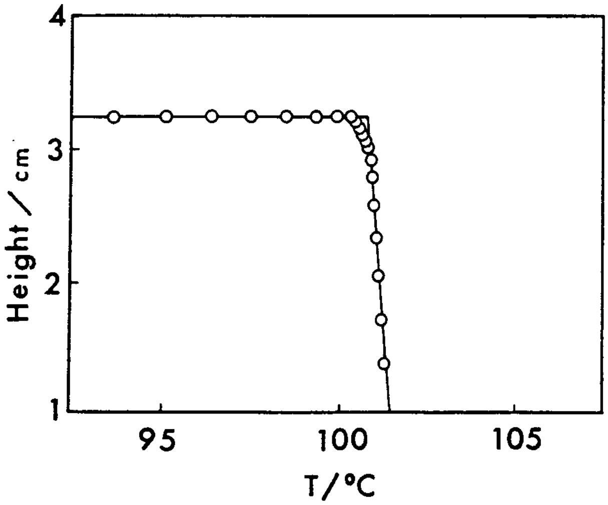
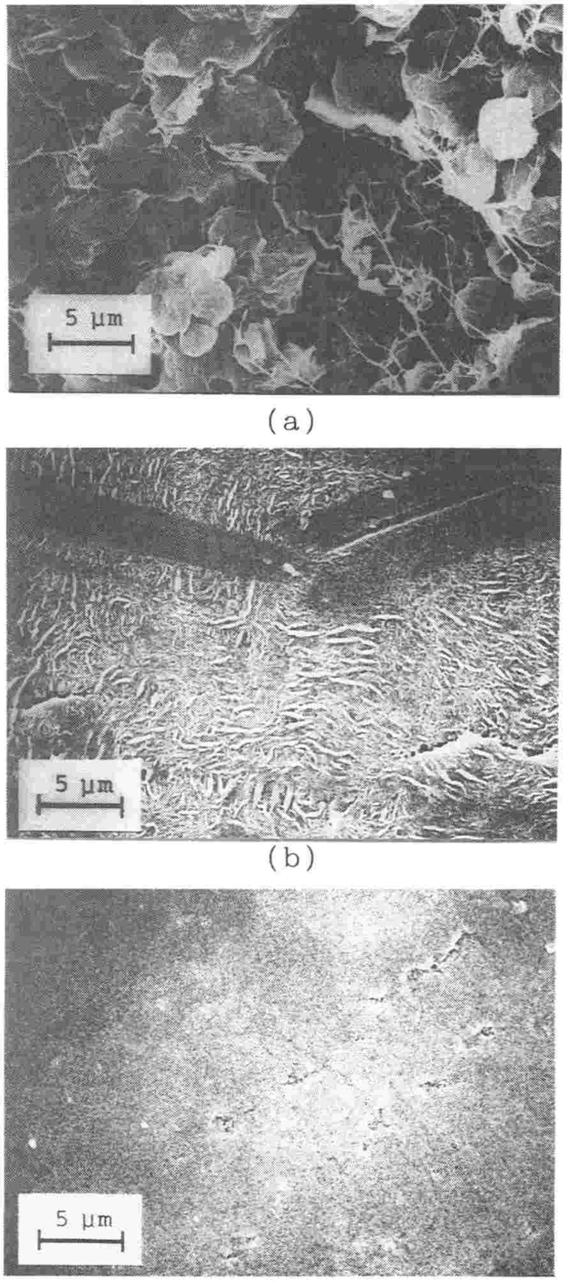


Fig. 4. Example of measurement of gel-melting temperature by the falling-ball method; HDPE-4-tetralin system at the concentration of 8 g/10^2cm^3.

lower crystallinities indicate the lower sol-gel transition temperatures. The temperature at which the adhesive strength begins to increase agrees approximately with the temperature of the endothermic peak at higher temperature in Fig.3. Therefore, it has become apparent that the gel exhibits an adhesive effect when it is heated at a higher temperature than the sol-gel transition temperature. These results suggest that great adhesive strength is obtained, even at a lower heating temperatures, if a polyethylene gel possessing a low crystallinity is used as adhesive. It has become apparent that the transition from gel to sol is required for adhesion.

On the other hand, the condition of the surface on the polyethylene plate must be considered, because it is difficult to imagine that the polyethylene, which is non-polar material, joins without the change of the surface condition. When the gel interposed between polyethylene plates was heated, the condition of the surface on the polyethylene plates was expected to change because of the solvent contained in the gel.

In order to examine how the surface of the polyethylene plate is affected by the solvent included in the gel, electron microscopic measurements were carried out. As an example of the results, electron micrographs of the surface of the polyethylene plate immersed in tetralin heated at 100° and 80℃ for 1 h are showed in Figs.5 (a) and (b), respectively. Fig.5 (c) shows the injection-molded untreated surface of the polyethylene plate. It is apparent that the surface of the polyethylene plate in Figs.5 (a) and (b) is severely etched or eroded, compared with Fig.5 (c); in the case of the treatment at higher temperature (Fig.5a),the surface is remarkably eroded— this is probably due to the liquefaction of an amorphous or low molecular weight portion from a molded polyethylene surface by the heated solvent.



(a)

(b)

(c)

Fig. 5. Electron micrographs of the surface of the polyethylene moldings immersed in tetralin heated at (a) 100°C, (b) 80°C, for 1 h, and (c) non-treated.

In Fig.6, the values of the adhesive strengths for HDPE-1 gels are plotted against heating temperatures for three different solvents. It is apparent that the temperature at which the adhesive strength begins to increase differs depending upon the solvent. In Fig.6 the adhesive strength begins to increase in the neighborhood of the gel-melting temperatures listed in Table 2.

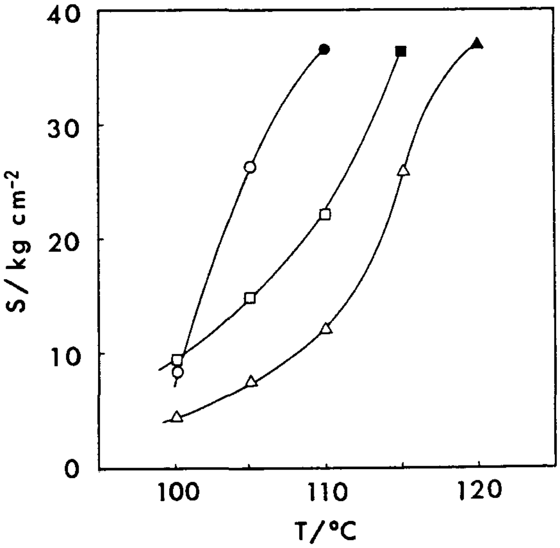


Fig. 6. Effects of the heating temperature on the adhesive strength of HDPE-1 gels in various solvents; -○-: tetralin, -△-: *o*-dichlorobenzene, -□-: decalin. Filled symbols represent the results of polyethylene plates giving rise to necking.

However, temperature curves of the adhesive strength cross each other. In the case of the decalin system, the adhesive effect is obtained at the lowest heating temperature, while at higher temperatures the adhesive strength is greater in the other systems than in the decalin system. This suggests that the solvents contained in gels have different solubilities in the polyethylene plate at a temperature.

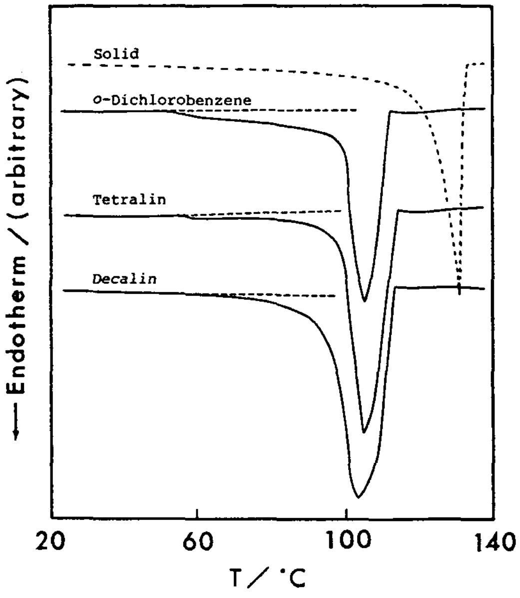


Fig. 7. DSC thermograms of the molded polyethylene in decalin, tetralin, *o*-dichlorobenzene, and solid of the molded polyethylene.

It is known that the melting temperature depression of crystalline polymer occurs [13] when crystalline polymer is in equilibrium with the dilute solution. To examine the melting temperature depression in the present systems, dissolution behavior of the molded polyethylene in the solvents accompanying a heating was measured by DSC method. In Fig.7, DSC thermograms of the molded polyethylene in decalin, tetralin, *o*-dichlorobenzene, and solid of the molded polyethylene are showed. The endothermic peaks in Fig.7 seem to indicate the dissolution process of the molded polyethylene. The temperatures of the endothermic peak in decalin, tetralin, and *o*-dichlorobenzene are 130.4°, 105.2°, and 105.2°C, respectively. The melting temperature depression is apparently observed, as the melting temperature of the molded polyethylene is 103.2°C.

These endothermic shifts occur around 50° C. The abrupt shift of the endothermic occurs around 90° C in each system— this indicates that a thin layer of the molded polyethylene surface is dissolved by the solvent contained in the gel at somewhat lower temperature than it at which the gel begins to indicate the adhesive effect. The melting temperatures estimated as the peak temperature are approximately equal. Consequently, the difference in the adhesive strength, depending upon the solvent, cannot be interpreted only by the results.

Table 3. Estimated values of SP and parameters for various solvents at 110°C, the molded HDPE at 140°C

Sample	dnD/dT	Density (g/cm^3)	V (g/mol)	ΔH (cal/mol)	CED (cal/cm^3)	SP ($[cal/cm^3]^{1/2}$)	ΔSP ($[cal/cm^3]^{1/2}$)
Tetralin	0.03983	0.89546	147.63	11.61	73.5	8.6	0.5
Decalin	0.03346	0.81763	169.09	9.75	53.2	7.3	0.8
o-Dichlorobenzene	0.03796	1.20538	121.95	11.01	84.5	9.2	1.1
HDPE	—	—	—			8.1	—

Now, in order to evaluate solubility or compatibility, the author used another method based on a solubility parameter. According to the method described above, the SP values of the solvents used for the gelation and of the molded polyethylene at 110 °C were estimated. The SP values obtained and the difference between the SP values of the solvents and that of the molded polyethylene, Δ SP, are tabulated in Table 3. It is well known that the closer the SP values of a solvent and a solute are, the more miscible they are [14], and the closer the SP values of an adhesive and a material to be joined are, the stronger they join [15]. On the other hand, it is known that the relation between the solubility and a solubility parameter deviates from theoretical values, especially in the case of the solvents such as a polar solvent and chloride-added hydrocarbon. But, on comparing Table 3 with Fig.6, it is found that the less Δ SP is, the larger the adhesive strength is, even at the same temperature. The melting temperature is scarcely different, as can be seen from Fig.7. However, the adhesive strength depends upon the difference of the solubility parameters. Consequently, it is considered that the difference of the solubility parameters, Δ SP, dictates the compatibility between a gel and the molded polyethylene, rather than the solubility.

When the experimental facts are put together, the following mechanism is proposed for the adhesion of a polyethylene molding by use of the polyethylene gel: When the gel interposed between polyethylene plates is heated, the gel undergoes transition to sol, and the solvent contained in the gel dissolves locally the surface of the polyethylene moldings. Subsequently, after polyethylene molecules in both the gel and the surface of the polyethylene plate are diffused and entangled, they recrystallize as the solvent evaporates. As a result, the two polyethylene plates are left in a strong adhesion.

III -4 Summary

The adhesive effect between polyethylene moldings by use of high density polyethylene gels in organic solvents was studied. The results obtained were summarized as follows:

1. High density polyethylene gels in solvents such as decalin, tetralin and *o*-dichlorobenzene are effective for adhesion of a pair of polyethylene plates, when heated at 100℃ or over.
2. When heated at 110° C for 2 h, the tetralin gel shows such a strong adhesive strength (over 36 kg/cm^2) that polyethylene plates give rise to necking, enough for practical use. Other gels also show a strong adhesive strength, when heated at 120° C.
3. Temperatures at which an adhesive strength begins to increase agree with temperatures of endothermic peaks, that is, temperatures corresponding to the gel-melting temperatures.
4. The closer the SP values of solvents used for the gelation are to that of the molded polyethylene, the stronger the adhesion of the polyethylene moldings is.

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CHAPTER Ⅳ

ADHESIVE EFFECT OF LOW DENSITY POLYETHYLENE GELS ON POLYETHYLENE MOLDINGS

Ⅳ-1 Introduction

It is well known that securing a good adhesion between a polyethylene plate and other materials, especially between two polyethylene plates, is difficult because of the non-polarity and high crystallinity of polyethylene. To increase the adhesive strength of materials to polyethylene moldings, various methods such as chemical [1,2], thermal [3], electrical [4,5], or radiative [6] treatments have been devised to active the molded polyethylene surface. However, these methods are often unsatisfactory in that enough adhesive strength is not attained and that the effects due to the treatments diminish with time.

In chapter 3, it was proved that the polyethylene and polypropylene moldings can be joined with polyethylene gels, and that the gels exhibit adhesive effects when heated over about 100℃. In order to avoid softening of HDPE moldings, it is necessary to lower the heating temperature. Fortunately, it has been found that the HDPE sample possessing a lower crystallinity exhibits an adhesive effect at lower heating temperature in chapter 3. This suggests that low density polyethylene (LDPE) which has crystallinity lower than HDPE should exhibit an adhesive effect at lower heating temperature.

In the present chapter, LDPE gels are used as adhesives, and the adhesive effects of the gels on HDPE moldings are investigated using a strain rate meter, a differential scanning calorimeter (DSC) and an electron microscope.

IV -2 Experimental

Materials

Three samples of unfractionated LDPE were used as adhesives. The samples were supplied by Motegi of the Ohita Laboratory, Showa Denko Co. together with the physical data shown in Table 1.

Table 1. Physical properties of LDPE and HDPE

Sample	Density (g/cm^3)	$M_w \times 10^{-4}$	T_m (°C)	α (%)
LDPE-1	0.920	11.5	108.5	34.0
LDPE-2	0.922	7.2	112.0	37.0
LDPE-3	0.920	10.0	111.0	34.9
HDPE-1	0.936	12.5	125.2	52.7

α ,the crystallinity determined by DSC, when the heat of fusion of the completely crystallized PE is 68.5 cal/g.

Polyethylene plates to be joined were 3 mm thick and composed of HDPE of molecular weight 10×10^4 (Mitsui Petro Chemical Co.).

Solvents used in the present study were the Wako reagent grade of decalin, tetralin, and o-dichlorobenzene.

Purification of the LDPE samples was carried out as follows: Pellets of the LDPE samples were dissolved completely in purified xylene at its boiling point in a flask with a reflux condenser. The solution was then poured into cooled methanol with stirring to precipitate LDPE. After washed with purified methanol, the LDPE was dried under a reduced pressure at 60℃ until a constant weight was attained.

Methods

Polyethylene gels were prepared in glass tubes as follows: A definite weight of the LDPE and a definite weight of the solvent were placed in a glass tube which was then sealed. After the LDPE was dissolved completely at 140° C the solution was cooled in a thermobath kept at 0° C until a gel was formed. The LDPE concentration in gels was 8 g/100cm^3 in all systems.

Gels prepared by the procedure described above were interposed between HDPE plates, 100 mm in length and 20 mm in width. The effective adhesive area was 4 cm^2. After 2 h of heating in the oven at constant temperature, temperature taken at 5° C intervals between 70° and 110° C, these were left stand for 24 h in room temperature. (It was determined in advance that 2 h were sufficient for all solvents to diffuse out.)

The adhesive strength was measured according to ASTM D906-64 at the shearing rate of 5mm/min using a Shimadzu RES-2 strain rate meter. The adhesive strength data were reproduced within ± 1kg/cm^2 for different samples.

The surfaces of the HDPE plates immersed in heated solvents were examined by an Akashi ALPHA-30A scanning electron microscope.

The thermal behavior of gels was measured at the rate of 6° C/h, and 1°, 2°, 5°, 10°, 15°, 20° C/min, and at the sensitivity of 0.5 mcal/sec, using a Rigaku Denki 8240B differential scanning calorimeter. The LDPE concentration in gels was comparable with that used as an adhesive.

The sol-gel transition temperature was measured by the so-called falling-ball method [12] at heating rate of 6℃ /h.

Ⅳ -3 Results and Discussion

Heating temperature dependences of the adhesive strength

Well known fundamental conditions required for adhesives are as follows: an adhesive is in liquid state, can get materials to be joined wet, and solidifies through a process such as evaporation, cooling, and chemical reaction. For polyethylene gel to satisfy these conditions as an adhesive, it is necessary that polyethylene crystals in the gel are melted to liquid and the solvent in the gel is evaporated so that polyethylene recrystallizes. Heating operation is necessary to accomplish these. The effects of the heating temperature on the adhesion strength were investigated.

In Fig.1, the adhesive strengths obtained by shearing stress tests are plotted against the heating temperature for LDPE gels in tetralin. The experimental results for HDPE gels are also shown in Fig.1. No samples show a significant adhesive effect when heated below 70° C, as can be seen from Fig.1. However, the adhesive strength increases with the heating temperature.

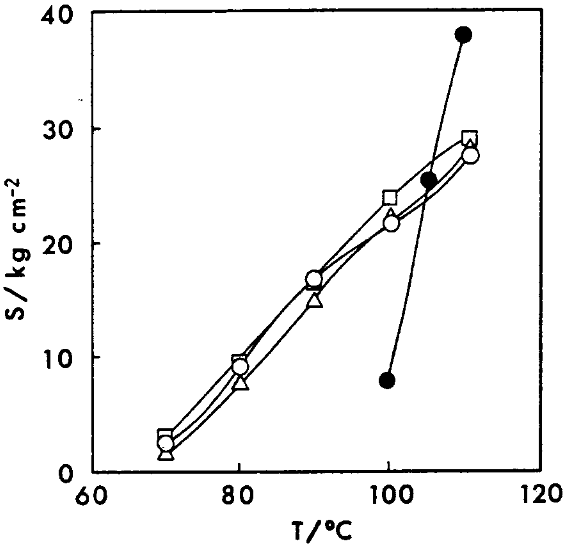

Fig. 1. Effects of the heating temperature on the adhesive strength of various gels in tetralin; -○-: LDPE-1, -△-: LDPE-2, -□-: LDPE-3, -●-: HDPE.

It is apparent that all of the systems show a strong adhesive strength when heated at 110° C. These values are very satisfactory for many practical uses. The curves of adhesive strength in Fig.1 are independent of LDPE samples within the range examined. The temperature at which the heated gel begins to exhibit the adhesive effect is about 70° C. It was suggested in the preceding chapter that a HDPE sample possessing lower crystallinity might exhibit an adhesive effect at lower heating temperature. The present results prove the validity of the suggestion. Table 1 shows the crystallinities of the LDPE, which are much lower than those of HDPE.

As LDPE is non-polar, the LDPE gel may not exhibit an adhesive effect even though it contacts with the polyethylene moldings. The dissolution of polyethylene crystals in both the polyethylene molding and the polyethylene gel is necessary in order for LDPE gel to exert an adhesive effect. Accordingly, adhesion of the polyethylene moldings takes place under two conditions: (i) The polyethylene gel used as an adhesive melts under heating, and at the same time (ii) the surface of the molded polyethylene to be joined is eroded or dissolved.

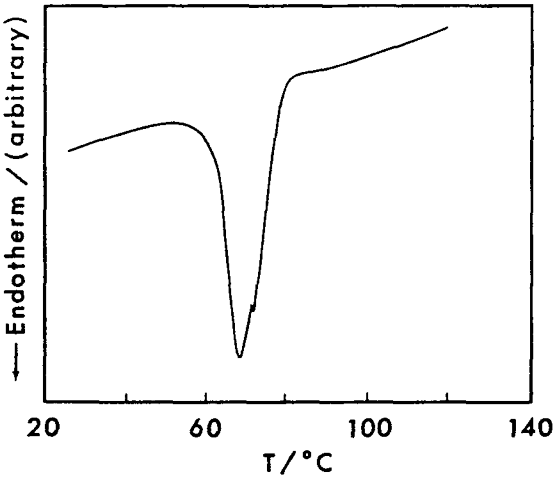

Fig. 2. DSC thermogram for LDPE-1 gel in tetralin.

The first condition requires that the transition from gel to sol should occur from heating. To measure the sol-gel transition temperature, the thermal behavior of the gel was examined by a differential scanning calorimetric technique. As an example of the results, the thermogram for 8 g/100cm^3 of the LDPE-1 gel in tetralin at a heating rate of 6°C/h is shown in Fig.2. The endothermic change composed of two peaks is observed, as is seen in Fig.2. The sol-gel transition temperature obtained by the so-called falling-ball method is 74°C at the same heating rate. The higher peak temperature in Fig.2 agrees approximately with the sol-gel transition temperature. The heating-rate dependence of the peak position on the DSC thermogram was observed. Considering the experimental fact that the peak does not shift when heated at the rates over 5° C/min, the peak temperature at heating rate of 5° C/min was used as gel melting temperature. The temperature at which a endothermic shift rapidly begins to occur also agrees approximately with the temperature at which the adhesive strength begins to increase. While the adhesive effect was observed above the gel melting temperature in HDPE gel, for LDPE gel in the present study the adhesive effect is observed at temperature lower than the gel melting temperature. This may be because the gelation mechanism of LDPE is different from that of HDPE. Okabe and co-workers [7] found that for LDPE gel the peak at higher temperature is in fair agreement with the gel melting temperature in a concentration region above 4%, and the peak at lower temperature agrees with that in the concentration region below 4%. They proposed that the peak at lower temperature is due to the dissolution of intermolecular entanglements and the peak at higher temperature is due to the dissolution of intermicrocrystalline networks. Therefore, in the case of our study the LDPE gel may exhibits adhesive effect at temperature lower than the gel melting temperature because polyethylene molecules solved from entanglement contribute to adhesion.

The second condition requires that the state of the molded HDPE surface is affected by the solvent contained in the gel when the gel interposed between the HDPE plates was heated. In order to examine how the surface of the molded HDPE was affected by the solvent, electron microscopic examinations were carried out. The surface of the molded HDPE immersed in tetralin heated at 10° intervals in the range of 70 to 110° C was observed by an electron microscope. The results are similar to those indicated in the preceding chapter. That is, the surface of the HDPE plate treated at a higher temperature is severely eroded, but only slightly when treated at a lower temperature. This is probably due to the liquefaction of amorphous components or low-molecular-weight components of HDPE from the molded HDPE surface by the heated solvent.

Putting these experimental results together, the following mechanism is proposed for the adhesion of molded HDPE's with LDPE gel: When the gel interposed between HDPE plates is heated up to the temperature where a rapid shift of endothermic occurs, the motion of polymer molecules in gel is likely activated, and the solvent contained in the gel locally dissolves the surface of the molded HDPE. Subsequently, after polyethylene molecules in both the gel and the surface of the molded HDPE are diffused and entangled, they recrystallize as the solvent evaporates. As a result, the two HDPE plates are left in a strong adhesion.0

Influence of the solvent on the adhesive effect

As the solubility of polyethylene depends upon a solvent used, the difference of the solubility may influence the adhesive strength. We investigated the influence of the solvent on the adhesive effect.

In Fig.3, the adhesive strengths of LDPE-2 gels are plotted against the heating temperatures for three different solvents. The adhesive strengths depend upon the solvents. However, in the systems of decalin and tetralin, they do not appreciably differ. The gel melting temperatures obtained for the 8 g/100cm^3 gels are

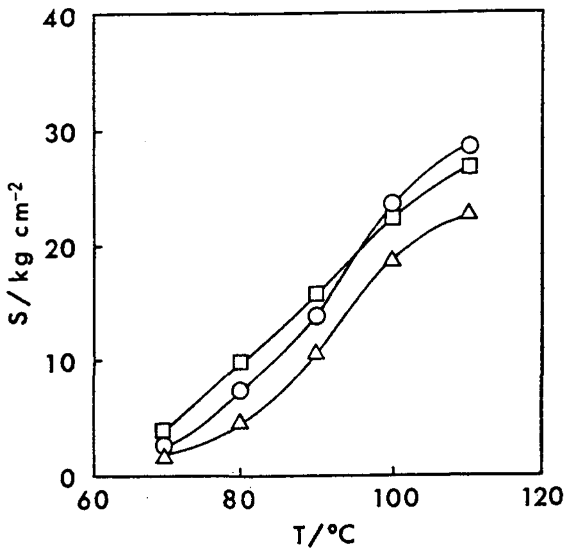

Fig. 3. Effects of the heating temperature on the adhesive strength of LDPE-2 gels in various solvents; -○-: tetralin, -△-: *o*-dichlorobenzene, -□-: decalin.

Table 2. Gel-melting temperatures determined by DSC

Gel		T_m
Solvent	Polymer	(°C)
Tetralin	LDPE-1	75.3
	LDPE-2	79.1
	LDPE-3	77.8
Decalin	LDPE-1	69.1
	LDPE-2	75.8
	LDPE-3	75.5
o-Dichloro-benzene	LDPE-1	75.8
	LDPE-2	79.8
	LDPE-3	78.8

summarized in Table 2. The lower the gel melting temperature is, the higher the adhesive strength at the low temperature is. It is also apparent that the gel exhibits an adhesive effect when it is heated beyond the temperature at which endothermic peak begins to appear in DSC thermogram. In the case of the HDPE gel indicated in the preceding chapter, the solvent dependence of the adhesive strength was explained in terms of the difference of the solubility in the HDPE plate, and the solubility parameter was introduced to evaluate it. The solubility in the HDPE plate decreases in the order of tetralin, *o*-dichlorobenzene and decalin. But, in the present study, the correlation between the adhesive strength and the solubility in the HDPE plate is not clearly recognized. Although the obvious cause is unknown at present stage, this is probably due to the different states of the LDPE crystals formed during the evaporation of the solvents.

Influence of the gel concentration on the adhesive strength

If the adhesive mechanism described above is correct, an adequate amount of the solvent in gel will be required for the local dissolution of the HDPE plate surface. Then, the concentration of the gel is expected to influence the adhesive effect. In Fig.4, the values of the adhesive strength for LDPE-1 gels in decalin are plotted against the gel concentration for various heating temperatures. When heated over 100° C, the adhesive strength remains constant beyond the concentration of 8 ~ 10 g/100cm^3. When heated at 110° C, the adhesive strength decreases after reaching the maximum. This decrease is perhaps caused by the lack of the solvent which erodes the surface of the molded HDPE. When heated at higher temperatures, such tendency will appear more markedly, because more rapid evaporation of the solvent is expected. The results reveal that the high concentration is not necessarily required to obtain the stronger adhesive strength.

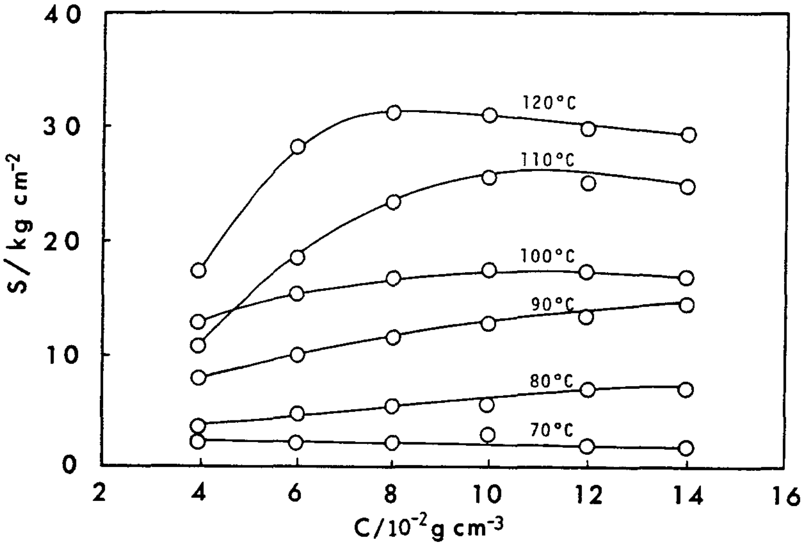

Fig. 4. Effects of the LDPE concentration on the adhesive strength of LDPE-1 gels in decalin at various heating temperatures.

When the concentration of LDPE is high, it is difficult to dissolve the LDPE homogeneously. Also the application of the gel to the molded HDPE becomes difficult, because the gel loses adhesiveness as the concentration increases. Considering these conditions, it is preferable to use the gel of the concentration in the range of 8 to 10 g/100cm^3. In other systems, similar results are anticipated.

Ⅳ-4 Summary

The adhesive effect of LDPE gels in organic solvents on HDPE moldings was studied. The results obtained were summarized as follows :

1. LDPE gels in such solvents as decalin, tetralin and *o*-dichlorobenzene are effective for adhesion of a pair of HDPE plates, when heated at 70° C or over, which is about 30 degrees lower than that required for HDPE gels.
2. When heated at 110° C for 2 hrs, LDPE gels in such solvents as decalin and tetralin show strong adhesive strengths around 30 kg/cm^2, that is strong enough for practical uses.
3. Temperatures at which the heated LDPE gel begins to exhibit the adhesive effect agree with the temperatures at which endothermic peaks appear in DSC measurements.
4. For good adhesion, an appropriate concentration of the gel is necessary. In the case of the gel in decalin, it is in the range of 8 to 10 g/100cm^3.

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CHAPTER V

ADHESIVE EFFECT OF POLYPROPYLENE GELS ON POLYPROPYLENE MOLDINGS

V -1 Introduction

It is well known that securing good adhesion between polypropylene plate and other materials, especially between two polypropylene plates, is difficult because of polypropylene's low polarity and high crystallinity. To increase the strength of the adhesion of a material to a polypropylene molding, it is necessary to activate the polypropylene surface by various methods which involve chemical [1,2], thermal [3], electrical [4-8], or radiation [9] treatments. However, such methods have disadvantages in that the adhesive strength is often unsatisfactory, that the shape of moldings to be treated is restricted, that the effects due to the treatments diminish with time, and, furthermore, that the expensive and complex procedures are required.

In the preceding chapter, it was found that polyethylene moldings can be joined by polyethylene gels. Matsuda and co-workers [10] have indicated the gelation of the concentrated solutions of polypropylene in decalin and tetralin formed thermo-reversible gels. The polypropylene gel is expected to inhibit an adhesive effect for polypropylene moldings.

In the present chapter, using polyethylene gels as an adhesive, the influence of heating conditions, the solvents, and physical properties of polyethylene samples on the adhesive effect have been investigated in detail by strain rate meter, differential scanning calorimeter (DSC) and electron microscope techniques.

Ⅲ -2 Materials and Methods

Materials

Three samples of unfractionated isotactic polypropylene (PP) were used as an adhesive. The samples were supplied by Mitsubishi Layon Co. Typical physical properties of the samples are shown in Table 1.

Table 1. Physical properties of isotactic polypropylenes

Sample	Density (g/cm^3)	$M_w \times 10^{-4}$	T_{mp} (°C)	α (%)
PP-1	0.90	30.0	161.2	34.0
PP-2	0.90	20.0	165.9	35.7
PP-3	0.90	10.0	166.4	34.7

M_w, the weight-average molecular weight determined by GPC method. M_n, the number-average molecular weight determined by GPC method. T_{mp}, the melting temperature determined by GPC method. α, the crystallinity determined by DSC method, provided that the heat of fusion the completely crystallized PP is 62.0 cal/g.

Polypropylene plates to be joined were 3 mm thick and composed of HDPE of molecular weight 4.5×10^4 (Mitsubishi Kasei Co.).

Solvents used in this study were the Wako reagent grade of decalin, tetralin, and *o*-dichlorobenzene, and were purified according to the usual method before use in order to avoid the influence of impurities.

Purification of the sample was carried out as follows: Pellets of the polypropylene samples were dissolved completely in purified xylene at its boiling point in a flask with a reflux condenser. The solution was then poured into cooled methanol while stirring. After washing with purified methanol, the sample was dried under reduced pressure at 60℃ until a constant weight was attained.

Polypropylene gels were prepared in glass tubes as follows: A definite weight of polymer and a definite volume of solvent were placed in the glass tube which was then sealed. After polymer was dissolved completely at 140℃ , the polymer solution was cooled in a thermobath kept at 0℃ until a gel was formed. The polymer concentration in gels used as an adhesive was 8 g/100cm^3 in all systems.

Gels prepared by the procedure described above were interposed between polypropylene plates, 100 mm in length and 20 mm in width. The effective adhesive area was 4 cm^2. After 2 h of heating in an oven controlled at 5° C-intervals in the temperature range 100°-140° C, the samples were left stand for 24 h at room temperature. (It was determined in advance that 2 h was sufficient for all solvents to diffuse out.)

Methods

The adhesive strength as a tensile shearing stress was continually measured according to ASTM D906-64 at the shearing rate of 5mm/min, using a Shimadzu RES-2 strain rate meter.

The thermal behavior of gels was measured at the rate of 6° C/h, 2° , 5° , 10° and 15° C/min, and at the sensitivity of 0.2 mcal/sec, using a Rigaku Denki 8240B differential scanning calorimeter. The concentration of the gels is similar to those used as an adhesive.

The dissolution behavior of the molded polyethylene in solvents was directly measured at a heating rate of 1°C/min, and at the sensitivity of 0.5 mcal/sec, using the same DSC. Volume fraction of solvent to the molded polyethylene prepared in a cell is about 0.8 in each system.

The gel melting temperature was measured by the falling-ball method. The method for the measurement is similar to the preceding chapter.

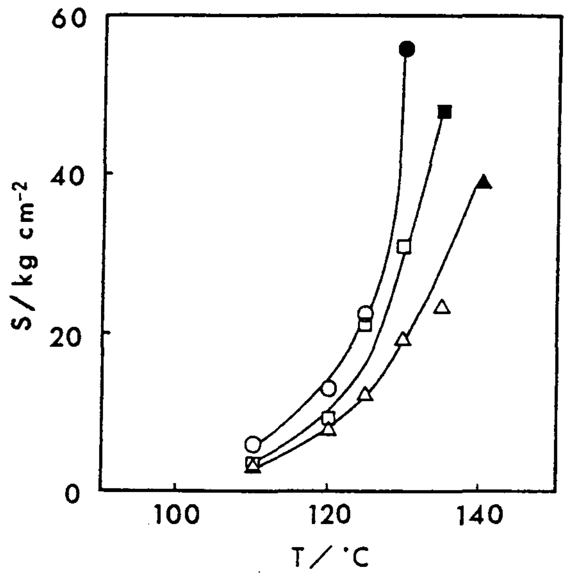

Fig. 1. Effects of the heating temperature on the adhesive strength of various gels in tetralin; -○-: PP-1, -□-: PP-2, -△-: PP-3. Filled symbols represent the results of polypropylene plates themselves giving rise to necking.

Ⅲ-3 Results and Discussion

In Fig.1, the values obtained by shearing stress tests are plotted against the heating temperature for PP gels in tetralin. Filled circles in Fig.1 indicate that polypropylene plate itself have given rise to a necking without being stripped from the jointing. Neither of the samples showed effective adhesive strength when heated at 100℃ , as can be seen from Fig.1.

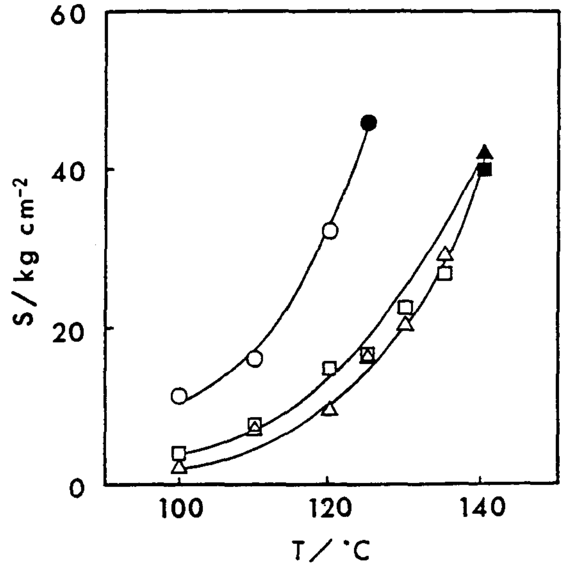

Fig. 2. Effects of the heating temperature on the adhesive strength of various gels in decalin; -○-: PP-1, -□-: PP-2, -△-: PP-3. Filled symbols represent the results of polypropylene plates themselves giving rise to necking.

However, the adhesive strength increases as the heating temperature rose beyond 110° C. It is apparent that the adhesive strength in the PP-1 gel increases to over 56 kg/cm^2 when heated at 120℃ , and all of the systems begin to indicate significant adhesive strength when heated at 140℃ . Adhesive strengths differ depending upon the samples. On comparing these results with physical properties in Table 1, Gels of the sample possessing a higher molecular weight tends to indicate a stronger adhesive strength at the same heating temperature. In Figs.2 and 3, results of the sharing stress tests for gels in decalin and *o*-dichlorobenzene, respectively. In each solvent system, molecular weight dependence of adhesive strength as well as in Fig.1 is found. Especially, In Fig.3 which shows results for PP gels in *o*-dichlorobenzene, the adhesive strength apparently differ depending upon a molecular weight of PP samples.

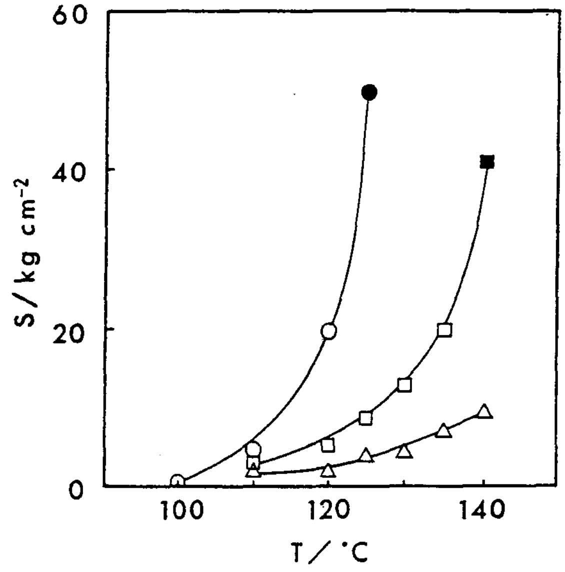

Fig. 3. Effects of the heating temperature on the adhesive strength of various gels in *o*-dichlorobenzene; -○-: PP-1, -□-: PP-2, -△-: PP-3. Filled symbols represent the results of polypropylene plates themselves giving rise to necking.

Accordingly, it is evident that gels of PP possessing a higher molecular weight can join strongly PP moldings even at the same heating temperature. The temperatures at which an adhesive effect begins to be indicated differs depending upon the solvent systems.

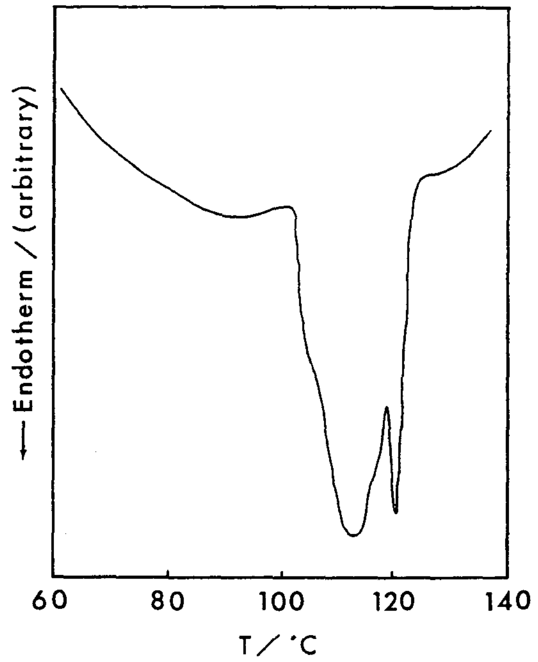

Fig. 4. DSC thermogram for PP-3 gel in tetralin.

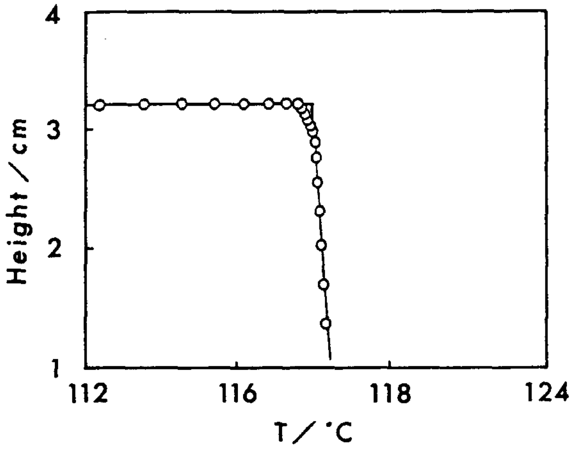

Fig. 5. Example of measurement of gel-melting temperature by the falling-ball method: PP-3-tetralin system at the concentration of 8 g/10^2cm^3.

Transition from gel to sol by means of the heating may first be required for adhesion. The thermal behavior of the gels were then examined by differential thermal analysis, in order to obtain a sol-gel transition temperature. As an example of the results, the thermogram for 8 g/100 cm^3 of the PP-4 gel in tetralin at a heating rate of 6° C/h is shown in Fig.4. Two endothermic peas were observed, as can be seen from Fig.4. In Fig.5, the movement of a steel ball with an increase in temperature is shown when heated at a rate of about 6° C/h. It was confirmed that the peak at higher temperature in Fig.4 agrees with the sol-gel transition temperature obtained and shown in Fig.5. The peak position in DSC thermograms shifts, as shown in Fig.6. In

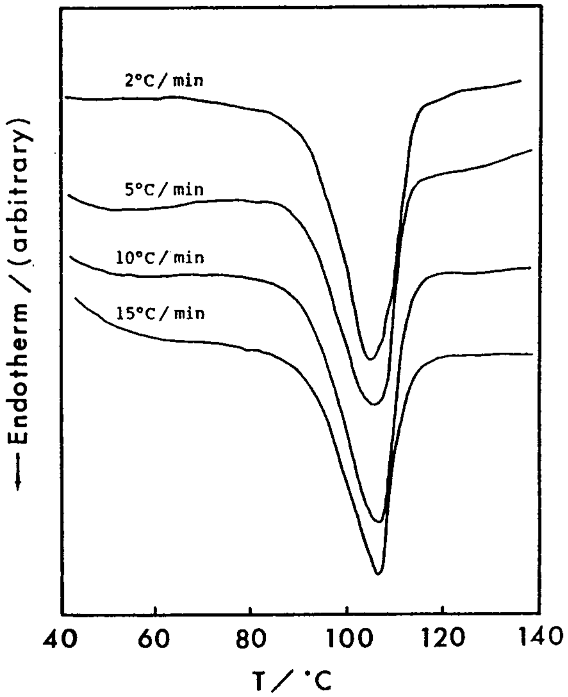

Fig. 6. DSC thermograms for PP-3 gel in tetralin at various heating rates.

order to make clear the heating rate dependence of the peak position, the temperatures at the peak were plotted against the heating rate in Fig.7. It is apparent that the peak does not shift when heated at a rate of over 10° C/min. Taking into account the experimental fact,

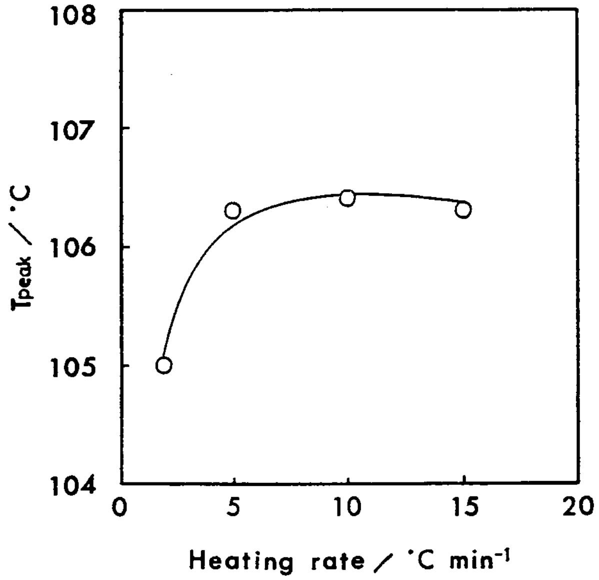

Fig. 7. Heating rate dependence of endothermic peak corresponding to the gel-melting temperature of PP-3 gel in tetralin.

and the experimental condition that a test piece for adhesion is heated in an oven previously controlled at a definite temperature, that is, it is heated rapidly, the peak temperature at a heating rate of 10° C/min was adopted as the gel-melting temperature. All of the gel-melting temperatures obtained by DSC method for 8 g/100cm^3 of the gels are summarized in Table 2. Gels in decalin indicate the lowest sol-gel transition temperatures. The temperature at which the adhesive effect begins to be indicated agrees approximately with the sol-gel transition temperature. Therefore, it has become apparent that the transition from gel to sol is required for adhesion.

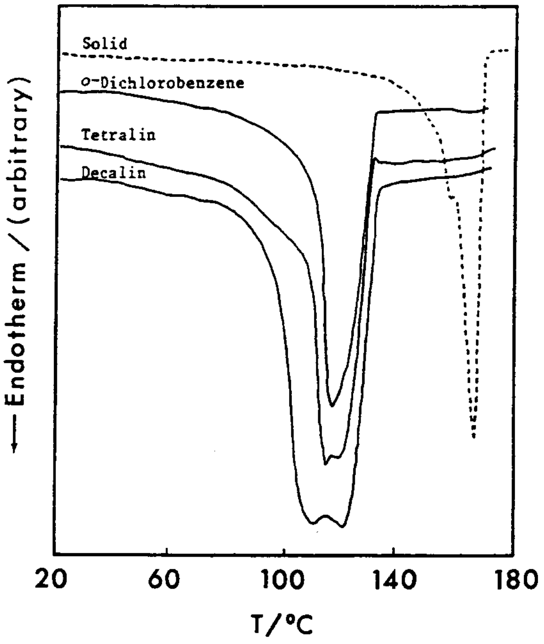

Fig. 8. DSC thermograms of the molded polyethylene in decalin, tetralin, *o*-dichlorobenzene, and solid of the molded polypropylene.

On the other hand, the condition of the surface on the polypropylene plate must be considered, because it is difficult to imagine that the polypropylene, which is low-polar material, joins without the change of the surface condition. When the gel interposed between polyethylene plates was heated, the condition of the surface on the polypropylene plates was expected to change because of the solvent contained in the gel. It is known that the melting temperature depression of crystalline polymer occurs [11] when crystalline polymer is in equilibrium with the dilute solution. To examine the melting temperature depression in the present systems, dissolution behavior of the molded polypropylene in the solvents accompanying a heating was measured by DSC method. In Fig.8, DSC thermograms of the molded polypropylene in decalin, tetralin, *o*-dichlorobenzene, and solid of the molded polypropylene are showed. The endothermic peaks in Fig.8 seem to indicate the dissolution process of the molded polypropylene. The temperatures of the endothermic peak in decalin, tetralin, and *o*-dichlorobenzene are about 120° C in each system. The melting temperature depression is apparently observed, as the melting temperature of the molded polypropylene is about 167° C. These endothermic shifts occur around 50° C. The abrupt shift of the endothermic occurs around 90° C in each system— this indicates that a thin layer of the molded polypropylene surface is dissolved by the solvent contained in the gel at somewhat lower temperature than it at which the gel begins to indicate the adhesive effect. Consequently, for the adhesion of polypropylene moldings using polypropylene gels, the sol-gel transition temperature influences predominantly the temperature at which the adhesive effect begins to be indicated.

When the experimental facts are put together, the following mechanism is proposed for the adhesion of a polypropylene molding by use of the polypropylene gel: When the gel interposed between polypropylene plates is heated, the gel undergoes transition to sol, and the solvent contained in the gel dissolves locally the surface of the polypropylene moldings. Subsequently, after polypropylene molecules in both the gel and the surface of the polypropylene plate are diffused and entangled, they recrystallize as the solvent evaporates. As a result, the two polypropylene plates are left in a strong adhesion.

Ⅲ -4 Summary

The adhesive effect between polypropylene moldings by use of isotactic polypropylene gels in organic solvents was studied. The results obtained were summarized as follows:

1. Isotactic polypropylene gels in solvents such as decalin, tetralin and *o*-dichlorobenzene are effective for adhesion of a pair of polypropylene plates, when heated over 100℃ .
2. When heated at 120° C for 2 h, the decalin gel shows such a strong adhesive strength (over 46 kg/cm^2) that polyethylene plates give rise to necking, enough for practical use. Other gels also show a strong adhesive strength, when heated at 140° C.
3. Temperatures at which an adhesive effect begins to occur approximately agree with the gel-melting temperatures.

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CHAPTER VI

ADHESION OF MOLDED POLYETHYLENE USING POLYETHYLENE GELS BY MICROWAVE HEATING

VI -1 Introduction

It is well known that securing a good adhesion between polyethylene plate and other materials, especially between two polyethylene plates, is difficult because of the non-polarity and high crystallinity of polyethylene.

In the chapter 3, 4, and 5, it has become apparent that the molded polyethylene can be joined by its heating over 60 min at an appropriate temperature, using polyethylene gels as an adhesive. As long as the gel is heated in a hot oven controlled at the prescribed temperature, it may be difficult to drastically shorten the heating time. However, if the solvents which can gel a polyethylene are dielectrics, the solvents can be heated by microwaves. As the molded polyethylene itself act as an insulator for microwave, the gels as an adhesive will be able to be heated in a microwave oven instead of a hot oven with heater.

In the present chapter, using polyethylene gels in various polar solvents, the adhesive effect of the gels on the molded polyethylene by heating with microwaves is investigated.

VI -2 Experimental

Materials and Methods

Unfractionated low density polyethylene (LDPE) was used for the preparation of gels in this study. The sample was supplied by Dr. A. Senuma of the Resin Laboratory, Nippon Unicar Co. Typical physical properties of the sample are shown in Table 1.

Table 1. Physical properties of the LDPE sample

Density (g/cm^3)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	T_{mp} (°C)	α (%)
0.918	94.8	21.4	4.4	111.3	31.9

M_w, the weight-average molecular weight determined by GPC method. M_n, the number-average molecular weight determined by GPC method. T_{mp}, the melting temperature determined by DSC method. α, the crystallinity determined by DSC.

The sample was purified as follows: Pellets of the sample were completely dissolved in xylene at its boiling point under a reflux condenser, and the solution was then poured into an excess of cooled methanol with stirring for precipitation. After being washed with methanol, the sample was sufficiently dried under reduced pressure at 60℃ until a constant weight was attained.

Polyethylene plates to be joined were 3 mm thick and made of high density polyethylene (HDPE) of weight-average molecular weight 10×10^4 (Mitsui Petro Chemical Co.).

Polar solvents used in the present study were *o*-xylene, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, 1,1,1,2-tetrachloroethane, and 1,1,2,2-tetrachloroethane, and were purified from the Wako reagent grade by the usual procedures, before each use, in order to avoid the influence of impurities. The typical physical properties of the solvents are shown in Table 2, where T_b is boiling point.

Table 2. Physical properties of the solvents

Solvent	Dipole moment (D)	Dielectric Constant (ε)	T_b (°C)
Chlorobenzene	1.54	5.649	131.7
o-Dichlorobenzene	2.27	6.828	180.5
m-Dichlorobenzene	1.38	5.040	173.0
o-Xylene	0.44	2.266	144.0
1,1,1,2-Tetra-chloroethane	1.20	5.820	129.2
1,1,2,2-Tetra-chloroethane	1.71	8.000	146.3

Polyethylene gels were prepared in glass tubes as follows: A definite weight of the LDPE and a definite weight of the solvent were placed in a glass tube, which was then sealed. After the polymer was completely dissolved at 140℃ , the solution was cooled in a thermobath kept at 0℃ until gel was formed. Polymer concentrations in the gels were 8 g/100cm^3 in all systems.

The gels were then interposed between polyethylene plates of 100 mm in length and 20 mm in width. The effective adhesive area was 4 cm^2. After heated in a Matsushita NE-M335 microwave oven with the output power of 500 W (2450 MHz) for 5 to 8 min, they were permitted to stand for 24 hrs. The adhesive strength was continually measured according to ASTM D906-64 at the shearing rate of 5 mm/min using a Shimadzu RES-2 strain rate meter.

Ⅵ -3 Results and Discussion

When a dielectric is placed in a microwave field, the electric power consumed in a unit area [2] is expressed by

$$P = (5/9)\times 10^{-10}\cdot f\cdot E^2\cdot \varepsilon_r\cdot \tan\delta\ , \qquad (1)$$

where f is the frequency of the microwave, E is the electric field strength, $\tan\delta$ is the dielectric loss, and ε_r and $\tan\delta$ are characteristic of the material depending upon the temperature and frequency. The electric power in Eq.(1) is dissipated in the form of heat. It is well known that applications of the principle make possible to selectively heat dielectrics. Numerous investigators [2-25] have demonstrated that various plastics and rubbers can be joined by heating metal powder mixed with adhesives in microwave induction heating method, and by heating adhesives with high dielectric loss in microwave dielectric heating method. But adhesive effects of polyethylene gels on the polyethylene moldings are not yet examined by the microwave heating.

It is known that polyethylene itself has only a small dielectric loss [1]. According to Eq.(1), the gel containing a solvent of large ε_r and $\tan\delta$ may be selectively heated without heating of the molded polyethylene.

Solvents of relatively large dipole moments and dielectric constants have been selected out of those solvents which can gel polyethylene. Consequently, six different solvents satisfying the three conditions mentioned above have been selected as listed in Table 1. Using the polyethylene gels in these solvents, the adhesive effects on the polyethylene moldings have been examined by the microwave heating. The values of the shearing stress against irradiated time are shown in

Fig.1. Although each gel does not show only adhesive effect when irradiated for 5 min, it does indicate an adhesive effect when irradiated over 6 min. The adhesive strength increases as the irradiated time increases in each gel. In particular, the polyethylene gel in 1,1,2,2-tetrachloroethane shows so strong adhesion that a polyethylene plate of 3 mm in thick, and 20 mm in width gives rise to necking. As the polyethylene plate is sometimes deformed due to over irradiation of the microwave, the limit of heating time is 8 min.

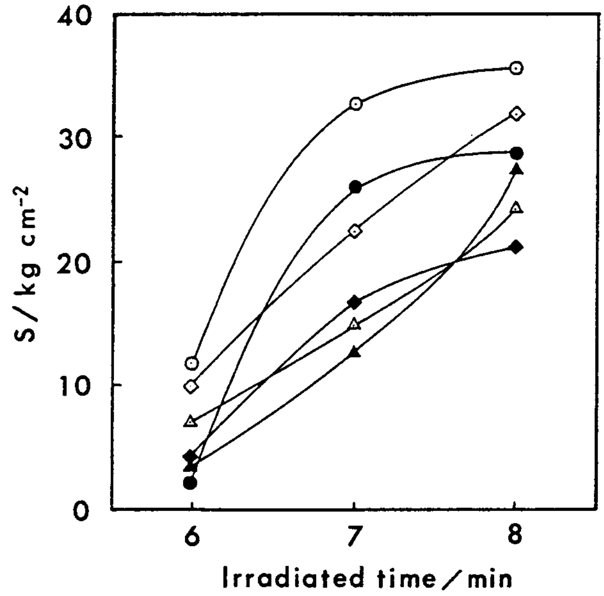

Fig. 1. Effects of irradiated time on the adhesive strength for LDPE gels in various solvents; -○-: 1,1,2,2-tetrachloroethane, -●-: 1,1,1,2-tetrachloroethane, -◇-: chlorobenzene, -◆-: *o*-dichlorobenzene, -△-: *m*-dichlorobenzene, -▲-: *o*-xylene.

It is known [1] that a material of larger dielectric constant has a larger dielectric loss. Values of the adhesive strength for two irradiation times of 7 and 8 min were plotted against the dielectric

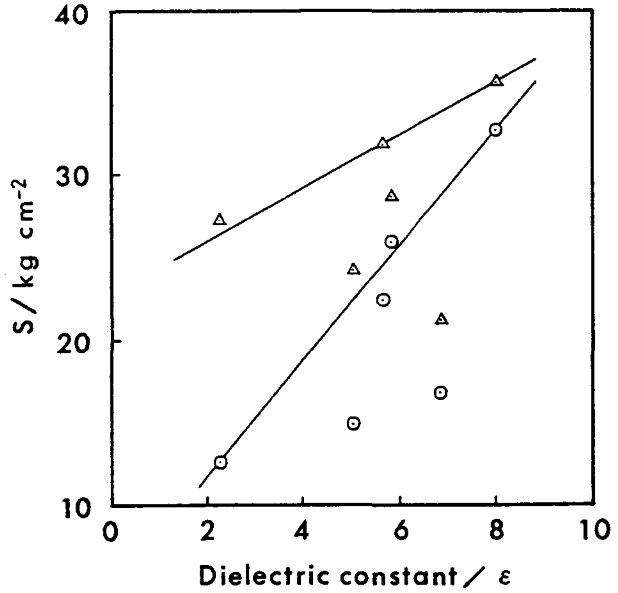

Fig. 2. Plots of the adhesive strength against the electric constant of the solvents as a function of the irradiated time; -○-: 7 min, -△-: 8 min.

constant in Fig.2. A fair correlation between the adhesive strength and the dielectric constant is recognized, except for the *o*-dichlorobenzene and *m*-dichlorobenzene systems. The larger the dielectric constant of the solvent is, the stronger the adhesion of the gel in that solvent is. This is probably due to a high calorific value of the solvent possessing a large dielectric constant. However, the *o*-dichlorobenzene and *m*-dichlorobenzene systems deviate appreciably from the curve in Fig.2. As these solvents have higher boiling points than the other ones, as can be seen from Table 2, they will have difficulty in evaporating during the heating time of the present study, and thus will remain in the gels making the adhesive strength low. Detail on effects of residual solvent on adhesive strength will be reported in the near future.

Ⅵ -4 Summary

It has become apparent that the polyethylene moldings can be joined with polyethylene gels when microwave are applied to heat the gels. Effective polyethylene gels are those in polar organic solvents such as *o*-xylene, chlorobenzene, *o*-dichlorobenzene, *m*-dichlorobenzene, 1,1,1,2-tetrachloroethane, and 1,1,2,2-tetrachloroethane. In particular, the gel in 1,1,2,2-tetrachloroethane showed so strong adhesion that a polyethylene plate of 3 mm in thickness and 20 mm in width gave rise to necking by heating for 8 min in a 500 W (2450 MHz) microwave oven. Gels in solvents possessing larger dielectric constants indicate stronger adhesion even in the same irradiation time of the microwave.

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CHAPTER Ⅶ

ADHESIVE EFFECT OF SWOLLEN POLYETHYLENE FILMS ON POLYETHYLENE MOLDINGS

Ⅶ-1 Introduction

It is well known that securing a good adhesion between a polyethylene plate and other materials, especially between two polyethylene plates, is difficult because of the non-polarity and high crystallinity of polyethylene.

In the chapters 3, 4,and 5, the author have revealed that molded polyethylene can be joined by heating at appropriate temperatures using polyethylene gels, and that molded polypropylene can be also joined by the same method using polypropylene gels without any pretreatment [1-14]. There, it has been revealed that dissolution of the surface of molded polyethylene due to solvents in gels plays an important role in adhesion, and that the gels indicate adhesive effects when heated over the gel-melting temperatures.

The melting temperature of polyethylene gel is ordinarily lower than that of solid polyethylene. It is probably due to the melting point depression of polyethylene incurred by the solvent. It is expected that a polyethylene film swollen in a solvent should also indicate a melting point depression and accordingly indicate an adhesive effect.

In the present chapter, using the polyethylene film swollen in solvents such as decalin, tetralin, and o-dichlorobenzene, the adhesive effect of these films on molded polyethylene are investigated.

Ⅶ-2 Experimental

Materials

The non-elongated 20 μm thick film of unfractionated low density polyethylene (LDPE) was used. The sample was supplied and characterized by Motegi of the Ohita Laboratory, Showa Denko Co. Typical physical properties of the sample are shown in Table 1.

Table 1. Physical properties of the LDPE film

Density (g/cm^3)	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	Mw/Mn	T_{mp} (°C)
0.921	12.0	2.87	4.2	110.0

Solvent used here was Wako reagent grade of decalin, which was purified by the usual method before use in order to avoid the influence of impurities.

The swollen LDPE film was prepared in a glass tube as follows: a suitable size of the film and a solvent were placed in a glass tube. It was then sealed. The film in the glass tube was swollen in the solvent at 65°C in the case of decalin, 75°C in tetralin, and 78°C in *o*-dichlorobenzene until the swelling of the film reach equilibrium state. The swollen film was interposed between high density polyethylene plates, 100 mm in length and 20 mm in width. The effective adhesive area was 4 cm^2.

Methods

After heated in an oven controlled at the prescribed temperature for 2 h, it was permitted to stand for 24 h. The adhesive strength was continually measured according to ASTM D906-64 at the shearing rate of 5 mm/min using a Shimadzu RES-2 strain rate meter.

Thermal behaviors of the solid LDPE film, the LDPE film immersed in decalin and the LDPE film swollen by decalin, tetralin, and *o*-dichlorobenzene were measured at the rate of 2℃/min and the sensitivity of 0.5 mcal/sec using a Rigaku Denki 8240B differential scanning calorimeter(DSC).

Ⅶ-3 Results and Discussion

In order to see whether the LDPE film immersed in decalin would indicate depression of the melting temperature or not, its thermal behavior was measured by the DSC method at the heating rate of 1 ℃/min. 0.008 mg of the film was placed in a DSC cell containing 0.05 cm^3 of decalin, and sealed. The result is shown in Fig.1, together with the result of the solid LDPE film measured at the same heating rate. The endothermic peak of the solid LDPE film is seen at 100℃. It shows the melting point of the LDPE film. On the other hand, the endothermic peak of the LDPE film immersed in decalin appears at 65℃ accompanying its dissolution. This temperature is about 35℃ lower than that of the solid LDPE film, obviously indicating the melting point depression of the LDPE due to decalin. DSC measurements of LDPE films immersed in tetralin and *o*-dichlorobenzene were carried out. The melting point depression was observed also in these solvent systems. The melting points of LDPE films in tetralin and *o*-dichlorobenzene were evaluated from the endothermic peaks, and resulted in 75°, 78° C, respectively.

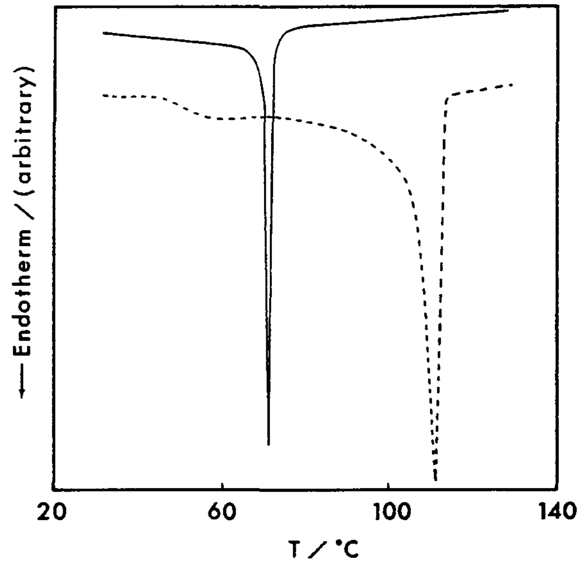

Fig. 1. DSC thermograms of the LDPE film immersed in decalin (solid line) and the LDPE film (dotted line).

It is then thought that the same phenomenon should occur in the polyethylene film swollen in solvent. The DSC measurement of the LDPE film swollen in decalin for 48 h at 65℃ was carried out. Note that this temperature is the same as that of the endothermic peak in the LDPE film immersed in decalin. The result is shown in Fig.2. The behavior of the thermogram is analogous to that of the LDPE film immersed in decalin, but the temperature of the endothermic peak is somewhat higher than that of the LDPE film immersed in decalin.

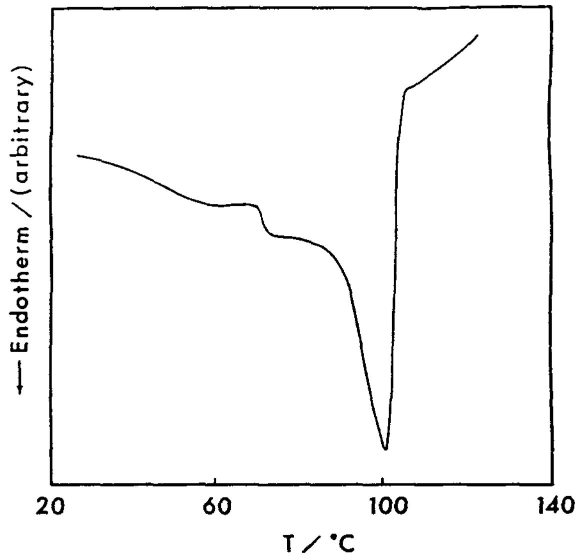

FIg. 2. DSC thermogram of the LDPE film swollen in decalin.

According to Flory [15], when a equilibrium is established between liquid (or dilute solution) and crystalline polymer, the melting point depression of crystalline polymer is given by the equation

$$1/T_m - 1/T_m^o = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2), \qquad (1)$$

where T_m is the equilibrium melting temperature for the mixture, T_m^o is the melting temperature of crystalline polymer, ΔH_u is the heat of fusion per repeating unit, V_u is the molar volume per repeating unit, V_1 is the molar volume of the diluent, v_1 is the volume fraction of the diluent, χ_1 is the interaction parameter. The equation relates T_m to the composition as represented by the volume fraction v_1 of the diluent. The quality $1/T_m - 1/T_m^o$ is approximately proportional to the depression of the melting point and the volume fraction v_1 of the diluent. Hence, the result of the swollen film represented in Fig.2 may be explained by the concentration dependence of the melting point depression. It is then expected that the PE film swollen in the solvent would indicate an adhesive effect for molded polyethylene.

Accordingly, adhesive effects of the swollen LDPE film on molded high density polyethylene (HDPE) were examined. In the present study, the non-elongated LDPE film was used, because it readily swells in decalin. Relation between a degree of swelling of the film and an adhesive strength was examined. The swollen films were prepared by swelling in decalin for 24-144 h at 65° C. After the film was interposed between HDPE plates, it was heated for 2 h at 110° C. The results of shearing tests obtained are plotted against the time in Fig.3.

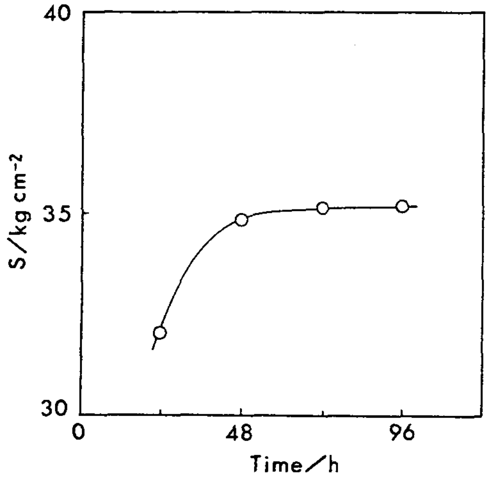

Fig. 3. Plot of adhesive strength against swelling time, in decalin.

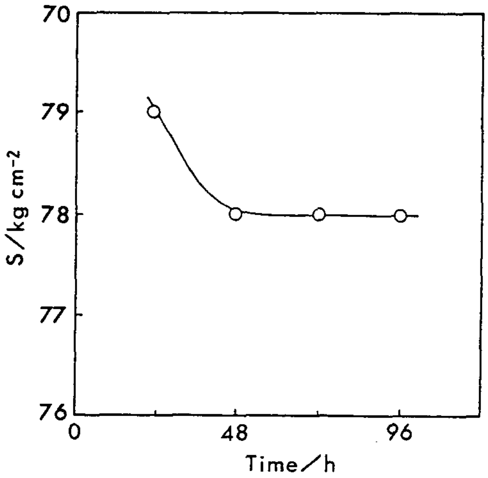

Fig. 4. Plot of the melting point of the swollen LDPE film in decalin against swelling time.

The adhesive strength increases with time, and becomes constant beyond 48 h. This is believed to be due to the influence of the degree of the swelling on the adhesive effect. To confirm this idea, DSC measurements on LDPE films swollen at different times were carried out. As mentioned above, the melting point of a crystalline polymer depends on the concentration. Accordingly, the melting point of the LDPE film will vary with the degree of swelling. In Fig.4, the melting points of LDPE films swollen in decalin are plotted against the swelling time. It can be seen that the melting point decreases with the swelling time, but remains constant beyond 48 h. Comparing the result with that in Fig.3, the adhesive strength is found to be closely related to the degree of swelling of the LDPE film. For the other solvents, the relationship between the degree of swelling of the LDPE film and the adhesive strength was examined.

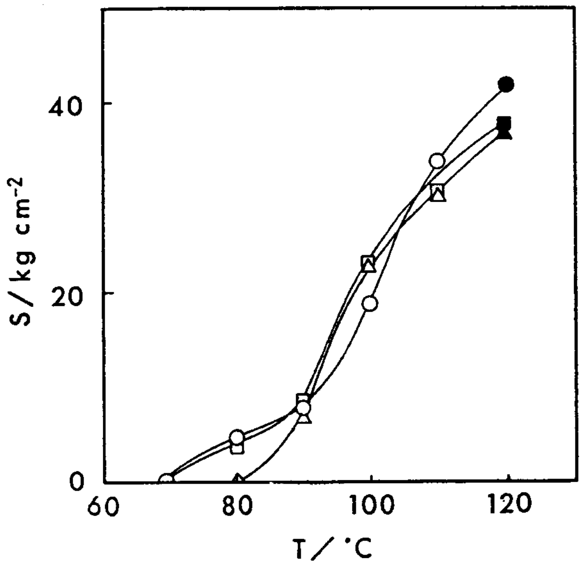

Fig. 5. Effects of the heating temperature on the adhesive strength for the swollen LDPE film in various solvents; -○-: tetralin, -□-: decalin, -△-: *o*-dichlorobenzene. Filled symbols represent the results of the polyethylene plates themselves giving rise to necking.

The time required for the swelling equilibrium was found to be 48 h in both tetralin and *o*-dichlorobenzene. The swollen films which had reached the swelling equilibrium were used for adhesive experiments. It was found that the adhesive strength depended on the heating time. However, it was confirmed that the adhesive strength does not change when heated for more than 1 h at any temperature. Accordingly, joints were heated for 2 h in the subsequent experiments. In Fig.5, adhesive strengths obtained are plotted against the heating temperature. The swollen films in tetralin and decalin indicate the adhesive effect from 80° C. The adhesive strength increases with an increase in temperature. When heated at 120° C, the adhesive strength reaches over 36 kg/cm^2. This is such a strong adhesive strength that polyethylene plates give rise to necking, enough for practical use. On the other hand, the film swollen in *o*-dichlorobenzene shows an adhesive effect when heated beyond 80° C, and adhesive strength is similar to those of the other films beyond the temperature. The results are similar to that obtained in chapter 4, in which the adhesive effect of LDPE gel was investigated. This result suggests that swollen LDPE films may be used instead of polyethylene gels as adhesives. In the case of complicated forms of molded polyethylene, homogeneous coating of the polyethylene gel may be difficult, while this problem is avoided in swollen polyethylene films.

VII -4 Summary

Adhesive effects of the polyethylene film swollen in decalin on the polyethylene molding were examined. It was found that the swollen LDPE film was effective for adhesion of the HDPE moldings. The swollen LDPE film indicates an adhesive effect when heated over 80℃. When heated at 120℃, the adhesive strength goes up to

36 kg/cm^2 , which is equivalent to that of the LDPE gel and is strong enough for practical uses.

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CONCLUSION

The author carried out the studies on the physical properties of polyolefin gels and these applications.

In chapterⅠ through Ⅱ, optical properties of the gels of polyolefins such as polypropylene, poly-1-butene and polymethylpentene were examined. In chapterⅢ through Ⅴ, the adhesive effects of polyolefin gels on polyolefin moldings were examined. In chapter Ⅵ, the study on the adhesion of polyethylene moldings using polyethylene gels by microwave heating was described. In chapter Ⅶ, the adhesive effects of swollen polyethylene films on polyethylene moldings were described.

The principal results and conclusions obtained in this work are summarized as follows.

1. It was found that the swollen and gelled polypropylenes in some organic solvents show a thermochromism, and that gels of poly-1-butene and polymethylpentene also show a thermochromism. The colouring of the gels is due to selective reflection.

2. There are two types of the thermochromism. One is the type that the colour changes strikingly in the order of blue, violet, red, orange, and yellow under natural light, as the temperature rises. The other is the type that a bluish colour diminishes, as the temperature rises.

3. The gel formed by quenching rapidly to lower temperature show a deeper colour.

4. The thermochromism closely relates to an amorphous structure in gels.

5. It was found that polyolefin gels indicate an adhesive effect for polyolefin moldings without

pretreatment when heated at an appropriate temperature.

6. The adhesive strength depends upon solvents used for gelation. When heated at 110° C for 2 h, HDPE gel in tetralin shows such a strong adhesive strength (over 36 kg/cm^2) that polyethylene plates give rise to necking, enough for practical use.

7. LDPE gels indicate the adhesive effect when heated at 70° C or over, which is about 30 degrees lower than that required for HDPE gels.

8. PP gels also indicate the adhesive effect when heated over 100° C. When heated at 125° C for 2 h, PP gel in tetralin shows such a strong adhesive strength (over kg/cm^2) that PP plates give rise to necking, enough for practical use.

9. For the adhesion of polyolefin moldings using polyolefin gels, the following mechanism is proposed: When the gel interposed between polyolefin plates is heated, the gel undergoes transition to sol, and the solvent contained in the gel dissolves locally the surface of the polyethylene moldings. Subsequently, after polyolefin molecules in both the gel and surface of the polyolefin plate are diffused and entangled, they recrystallize as the solvent evaporates. As a result, the two polyolefin plates are left in a strong adhesion. In general, polyolefin moldings can be joined by polyolefin gels.

10. If polar solvent are selected as solvent for the gelation, gels as adhesive are selectively heated by microwaves. A microwave oven instead of a hot-air oven can be used for the heating. When irradiated for 7 min in a 500 W (2450 MHz) microwave oven, LDPE gel in 1,1,2,2-tetrachloroethane shows the strong adhesive strength over 36 kg/cm^2.

11. It was found that the swollen PE films was effective for adhesion of PE moldings as well as PE gels. The method can be applied also for an adhesion of the other polyolefins.

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