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Molecular design of the polymer forming the complex with metal. Part IV. Complexation of pyridine-containing polyisoprene with zinc

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Abstract

Two types of polyisoprenes modified by *N*-pyrid-2-ylmethyl amide (MPY) group were synthesized, and their complexation with $ZnCl_2$ and the thermal property of complexes were investigated. Although these polymers are viscous liquid, the complex is solid at room temperature. MPY modified polyisoprene in which MPY connected a main chain without a spacer (MPYIP) shows the non-stoichiometric complexation, so that the melting temperature of the complex is low (105°C). On the other hand, MPY modified polyisoprene with a C5 spacer (MPYC5IP) shows the high melting temperature (143°C). It is surprising that the glass-transition temperatures of the complexes are almost as same as that of polyisoprene. These results indicate that the presence of the spacer effectively enhances the aggregation of polymers. As a result, MPY is a novel functional structure, since MPY–ZnCl₂ complex functions as an excellent hard-segment in various flexible polymers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermoplastic elastomers; Polyisoprene; Metal coordination; Complexation

1. Introduction

New polymer materials have been developed by the invention of new monomers or catalysts of the polymerization [1]. The chemical modification and functionalization of a polymer have also been performed. The technology of polymer blends is especially an excellent strategy for the effective development of advanced polymer materials [2]. Therefore numerous researches in this field have been reported so far. Most of these investigations were performed with the combination of different types of organic polymers. Recently, blends of an

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organic polymer and an inorganic substance have been of interest as novel functionalized and highperformance polymer materials [3].

A metal-containing polymer is the unique material consisting of the organic polymer with a functionalized group as a ligand [4,5]. The functionalized group forms the complex with a metal. The metal coordination interactions and crystallization of metal complexes obtained by complexation have been recently reported as a new type of the driving force of hard-segment aggregation in thermoplastic elastomers [6–12]. The degree of aggregation of hard-segments and phase-separation rate of hard and soft segments essentially influence on their mechanical and thermal properties [13]. Therefore the high-performance thermoplastic elastomers should be

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obtained by the enhancement of the hard-segment aggregation.

In the previous papers [14-16], we found that the N-pyrid-2-ylmethyl amide (MPY) group, which was introduced to poly(dimethyl siloxane) with the substitution degree of 1.6-9.0 mol% (MPYSI), formed the stoichiometric 1:1 complex with zinc chloride (ZnCl₂). Although the uncomplexed MPYSI was liquid at room temperature, the MPYSI-ZnCl₂ complex had the high melting temperature at about 140°C. The elastic and thermoplastic properties were also observed in this MPYSI-ZnCl₂ complex [15]. By means of the X-ray crystal analysis and EXAFS spectroscopy, we confirmed that the structure of the MPY-Zn complex formed the chelate ring, so that the structure was rigid and planar. In addition, the complex structure had the large dipole moment. Consequently we concluded that the remarkable strong aggregation came from these unique characteristics of the MPY-Zn complex [16].

In the present paper, we synthesized two types of MPY-modified polyisoprene. The complexation of the MPY group and $ZnCl_2$ in these polymers and the thermal properties of the polymer were investigated. The purpose of this study is to clarify the steric influence on the aggregation of the MPY–Zn complex, and to confirm the validity of the new type of hard-segment, that is MPY, to various polymer systems other than poly(dimethyl siloxane).

2. Experimental

2.1. Materials

Zinc chloride (99.9%) was purchased from Wako Chemical Co. and used as received. Polyisoprene (the number-average molecular weight 20 000) was produced by Kuraray Co. and used as received. Tetrahydrofuran (THF), *N*, *N*-dimethylformaide (DMF) and triethylamine were dried with calcium hydride, distilled and then stored over molecular sieves 4A. All other solvents and reagents were used as received from the commercial distributors.

2.2. Synthesis of carboxylic acid-branched polyisoprene (1)

Maleic anhydride (5 g) was added to polyisoprene

(100 g) in an autoclave, and stirred at 180°C for 15 h. After the reaction mixture was cooled to 80°C, methanol (2.7 ml) was added and stirred for 15 h. The unreacted methanol was evaporated under vacuum, then the product was obtained as clear liquid (yield >99%). The degree of substitution was 0.032 (3.2 mol% per isoprene unit) by the ¹H-NMR measurements. ¹H-NMR (CDCl₃): δ 1.3–1.65 (=CH –*CH*₂-, –CH=CHC(*CH*₃)-, –C(*CH*₃)=CH₂), δ 2.0 (–CH=C(CH₃)*CH*₂-), δ 2.2–3.0 (–*CH*(C(=O)OCH₃)) –*CH*(C(=O)OCH₃)) –*CH*(C(=O)OCH)-), δ 3.60 (s, *CH*₃OC=O).

2.3. Synthesis of MPY-branched polyisoprene (MPYIP) (2)

Carboxylic acid-branched polyisoprene (31 g) and DMF (0.5 ml) were dissolved in THF (150 ml). In this solution, excess thionyl chloride was added, and stirred under a N2 atmosphere at room temperature for 2 h. After the unreacted thionyl chloride and the solvent were evaporated, the residue was dissolved in THF (200 ml). Excess of 2-aminomethyl pyridine and triethylamine (18 ml) were added to this solution, and stirred under a N₂ atmosphere at 0°C overnight. The product was precipitated with methanol and dried under vacuum, then obtained as clear liquid (yield 96%). The degree of substitution was 0.031 (3.1 mol% per isoprene unit) by the ¹H-NMR measurements. ¹H-NMR (CDCl₃): δ1.3-1.65 (=CH-CH₂-, -CH= $C(CH_3)-, -C(CH_3)=CH_2), \delta 2.0 (-CH=C(CH_3)CH_2-$), $\delta 2.2 - 3.0 \ (-CH(C(=O)OCH_3) - CH(C(=O)OH) -),$ δ 3.60 (s, CH₃OC=O), δ4.52 (d, -CH₂-Py), δ4.70 (CH₂=C(CH₃)-), δ5.10 (-CH=C(CH₃)-), δ6.7-7.0 $(-NH-CH_2-Py), \delta 7.18, \delta 7.28 (t + d, PyH-3, 5),$ δ7.62 (t, PyH-4), δ8.52 (d, PyH-6).

2.4. Synthesis of 6-(tert-butoxycarbonylamino)hexanoic acid (**3**)

6-aminohexanoic acid (12 g) and triethylamine (19.3 ml) were dissolved in water (60 ml). In this solution, 2-(*tert*-butoxycarbonyloxyimino)-2-pheny-lacetonitorile (25 g) in dioxane solution (60 ml) was added, and stirred at room temperature for 5 h. The product was extracted with ethyl acetate and the solvent was evaporated, then the product was obtained as clear liquid (yield 23 g). ¹H-NMR (DMSO-d₆): δ 1.2–1.6 (–NH–CH₂–*CH*₂*CH*₂*CH*₂–*C*H₂C(=O)OH, (*CH*₃)₃CO–), δ 2.20 (t, –*CH*₂C(=O)OH), δ 2.90

(m, $-CH_2$ NH–), $\delta 6.75$ (t, $-CH_2NH$ –), $\delta 12.05$ (s, $-CH_2C(=O)OH$).

2.5. Synthesis of 1-(N-pyrid-2-ylmethyl)-6-(tertbutoxycarbonylamino)-hexanamide (**4**)

6-(tert-butoxycarbonylamino)-hexanoic acid (22 g) and 2-aminomethylpyridine (9.7 g) were dissolved in ethyl acetate (150 ml). In this solution, triethylamine (13.3 ml) and 1,3-dicyclohexylcarbodiimide (DCC, 19.6 g) in ethyl acetate solution (100 ml) were added at 0°C, stirred at room temperature for 48 h. The reaction mixture was poured into the sodium bicarbonate aqueous solution, and the product was extracted to an organic phase. The product was purified by crystallization from ethyl acetate/hexane, and obtained as white crystals (yield 83%). ¹H-NMR (DMSO-d₆): δ1.2-1.6 (-NH-CH₂-CH₂CH₂CH₂-CH₂C(=O)-, (CH₃)₃CO-), δ2.19 (t, -CH₂C(=O)-), $\delta 2.90 \text{ (m, } -CH_2\text{NH}-\text{)}, \delta 4.38 \text{ (d, } -CH_2-\text{Py}\text{)}, \delta 6.75 \text{ (t, })$ $-CH_2CH_2NH_-$), $\delta 7.25$ (t + d, PyH-3, 5), $\delta 7.76$ (t, *PyH*-4), δ8.40, δ8.50 (t + d, -*NH*CH₂-Py, *PyH*-6).

2.6. Synthesis of 1-(N-pyrid-2-ylmethyl)-6-aminohexanamide (5)

1-(N-pyrid-2-ylmethyl)-6-(tert-butoxycarbonylamino)-hexanamide (22 g) was added to trifluoroacetic acid (58 ml) and water (4.3 ml), and the reaction mixture was stirred at 0°C for 1 h. After the solvent was evaporated, the reaction mixture was neutralized with the sodium bicarbonate aqueous solution. The product was extracted with ethyl acetate and the solvent was evaporated, then the mixture of 1-(Npyrid-2-ylmethyl)-6-amino-hexanamide and sodium trifluoroacetate was obtained as white powder (yield 26 g). The purity of 1-(N-pyrid-2-ylmethyl)-6-aminohexanamide was about 60%. ¹H-NMR (DMSO-d₆): $\delta 1.28$ (m, $-CH_2CH_2CH_2C(=O)-$), $\delta 1.52$ (m, $-CH_2$ $CH_2CH_2C(C=O)-), \ \delta 2.19 \ (t, -CH_2C(=O)-), \ \delta 2.71$ $(m, -CH_2NH_2), \ \delta 4.38 \ (d, -CH_2-Py), \ \delta 7.25 \ (t+d,$ PyH-3, 5), δ 7.76 (t, PyH-4), δ 8.40, δ 8.50 (t + d, -*NH*CH₂–Py, *PyH*-6).

2.7. Synthesis of MPY-branched polyisoprene with C5 spacer (MPYC5IP) (6)

Carboxylic acid-branched polyisoprene (20 g) and 1-(*N*-pyrid-2-ylmethyl)-6-amino-hexanamide (20 g)

2.8. Preparation of zinc complex

An appropriate amount of zinc chloride in methanol solution was mixed to MPYIP or MPYC5IP in THF solution. The solvents were evaporated, then the complex was obtained. The MPYIP–ZnCl₂ complex with the mole ratio (MPY group)/ZnCl₂ = 1:2 was coded MPYIP–ZnCl₂ 1:2.

2.9. General procedure

The FT-IR measurements were performed on a JEOL JIR-5500. The IR spectrum was obtained directly (liquid sample) or from powders in potassium bromide medium (solid sample). Each spectrum was generated by signal averaging 10 scans at a resolution of 2.0 cm^{-1} .

The differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer DSC-7 differential scanning calorimeter. Each sample (ca. 5 mg) was measured under a nitrogen atmosphere with a DSC-scan rate of 10 K/min. Indium was used as a calibration standard.

3. Results and discussion

3.1. Synthesis of MPYIP and MPYC5IP

The synthetic route of MPYIP (2) is shown in Fig. 1. The polymer modified with the MPY group has been obtained by the reaction of 2-aminomethylpyridine and carboxylic acid connected with a



Fig. 1. Synthetic route of MPYIP (2).

polymer [15]. Therefore, in order to introduce the MPY group to polyisoprene, first we synthesized the maleic anhydride-branched polyisoprene by an ene reaction. Next the carboxylic acid-branched polyisoprene (1) was obtained by opening of the maleic anhydride ring with methanol. Then MPYIP (2) was obtained by the reaction with 2-aminomethylpyridine. The MPY-modified polyisoprenes with various substitution degrees are quantitatively synthesized by this procedure. The substitution degree of MPY group to the MPYIP was 3.1 mol% per isoprene monomer unit.

The MPY group of MPYIP is adjacent to the β methyl ester group. In the previous papers [15,16], we indicated that the stoichiometric complexation of the MPY group with ZnCl₂ was necessary to the improvement of the material property. The adjacent methyl ester group possibly prevents the complex formation and/or aggregation by the steric hindrance. In order to clarify this effect, we also synthesized MPYC5IP (6) with a C5 spacer between the MPY group and the isoprene main chain.

The synthetic route of the MPY group with a C5 spacer is shown in Fig. 2. The MPY group with the spacer was obtained from 6-aminohexanoic acid as a starting compound. First the amino group was protected with a tert-butoxycarbonyl group, and then 6-(tert-butoxycarbonylamino)-hexanoic acid (3) was Second 1-(N-pyrid-2-ylmethyl)-6-(tertobtained. butoxycarbonylamino)-hexanamide (4) was obtained by esterification of carboxylic acid of the compound 3 and 2-aminomethylpyridine. Third 1-(N-pyrid-2ylmethyl)-6-amino-hexanamide (5) was obtained by removal of the protecting group of the compound 4 with trifluoroacetic acid. The compound 5 is the MPY group with the C5 spacer. Thus the MPYC5IP (6), which is the MPY-branched polyisoprene with the spacer, was obtained by the reaction of



Fig. 2. Synthetic route of MPYC5IP (6).

the carboxylic acid-branched polyisoprene (1) and the compound 5. The substitution degree of the MPY group in the MPYC5IP is 3.0 mol% per isoprene monomer unit.

Table 1 shows the characteristics of the MPYIP and MPYC5IP. Both the MPY-modified polyisopurenes without $ZnCl_2$ were viscous liquid around room temperature. However, as the amount of $ZnCl_2$ in these polymers increased, the viscosity of the polymer

increased. Finally the ZnCl₂ complexes of MPYIP and MPYC5IP were observed as solid when more than an equivalent ZnCl₂ to the MPY group was added, which is the same behavior as MPYSIs (MPY-modified poly(dimethyl siloxane)) [15].

3.2. IR study

In the previous paper [15], we indicated that the IR

Table 1		
Characteristics	of MPY-modified j	polyisoprene

	Type of modification	Degree of substitution (mol%)	Viscosity ^a (P)
MPYIP	Branched	3.1	1.0×10^4
MPYC5IP	Branched with a C5 spacer	3.0	1.6×10^4

^a Zero-share viscosity (η_0) at 50°C.

	MPY/ZnCl ₂ (mol/mol)	Amide group	Pyridine ring	
		ν (C=O) (cm ⁻¹)	$\delta(py) (cm^{-1})$	
MPYIP	1:0	1664	401	
MPYIP-ZnCl ₂	1:0.5 1:1 1:2	1664, 1645, 1610 1664, 1645, 1610 1664, 1645, 1610	418, 401 418 418	

Table 2 Characteristic IR wavenumbers of MPYIP–ZnCl₂ complexes with various ratios of ZnCl₂ to MPY group

absorption bands of the amide group and the pyridine ring in the MPY group were stoichiometrically shifted when ZnCl₂ was added to various types of the MPYmodified poly(dimethyl siloxane). These shifts of the IR bands mean that the MPY group in the polymer is formed by the complex with ZnCl₂ [17]. Table 2 shows the characteristic IR wavenumbers of the MPYIP-ZnCl₂ complexes with various ratio of ZnCl₂ to the MPY group. The out-of-plane pyridine ring deformation ($\delta(py)$) wavenumber of the MPYIP was 401 cm⁻¹. However, that of the MPYIP–ZnCl₂ was observed at the higher wavenumber (418 cm^{-1}) . As shown in the X-ray crystal analysis of the low molecular-weight model compounds [16], this shift indicates that a Zn atom of ZnCl₂ coordinates to a N atom of the pyridine ring. When an equivalent ZnCl₂ to the MPY group was added, the lower wavenumber (401 cm⁻¹) of $\delta(py)$ disappeared. This result suggests that the ZnCl₂ stoichiometrically coordinates to a pyridine ring so as to form the 1:1 complex.

The C=O stretching (ν (C=O)) wavenumber of the amide group in the uncomplexed MPYIP was 1664 cm⁻¹ (Table 2). When ZnCl₂ was added to the MPYIP, the absorption bands at the lower wavenumber (1645 and 1610 cm⁻¹) were observed. The band at 1610 cm⁻¹ obviously shows the coordination

of the Zn atom to the O atom of the amide group, which suggests that the chelate ring consisted of the Zn atom, the O atom of the amide group and the N atom of the pyridine is formed. However, the absorption bands at the higher wavenumber were still present at the addition of an excess of ZnCl₂ to the MPY group. We do not exactly assign these absorption bands, since the weak absorption band of C=C (of isoprene unit) stretching overlaps. Nevertheless, the absorption band at 1645 cm⁻¹, at least, is probably assigned the uncomplexed and/or hydrogen-bonded amide group. As a result, the uncomplexed amide group of the MPYIP exists even if an excess of ZnCl₂ to the MPY group is added. This indicates that the amide group of the MPYIP forms the nonstoichiometric complex with ZnCl₂ in contrast to the pyridine group above described.

The reason for such a non-stoichiometric complexation in the MPYIP– $ZnCl_2$ system is probably the steric hindrance of the adjacent methyl ester group. In order to clarify this point, we also investigated the complexation of the MPYC5IP, which has the C5 spacer between the MPY group and the isoprene main chain, with $ZnCl_2$ (Table 3). The stoichimetric coordination of $ZnCl_2$ to the pyridine ring was observed like a similar behavior

Table 3

Characteristic IR wavenumbers of MPYC5IP-ZnCl₂ complexes with various ratios of ZnCl₂ to MPY group

	MPY/ZnCl ₂ (mol/mol)	Amide group	Pyridine ring	
		ν (C=O) (cm ⁻¹)	$\delta(py) (cm^{-1})$	
MPYC5IP	1:0	1645	401	
MPYC5IP-ZnCl ₂	1:0.5	1645, 1610	418, 401	
	1:1	1645, 1610	418	
	1:2	1645, 1610	418	

			-	
	MPY/ZnCl ₂ (mol/mol)	$T_{\rm m}$ (°C)	$\Delta H_{\rm m}^{\ a}$ (J/mol)	
MPYIP–ZnCl ₂	1:1 1:2	103 105	3.6×10^3 3.5×10^3	
MPYC5IP–ZnCl ₂	1:1 1:2	111 143	3.4×10^{3} 4.7×10^{3}	

Table 4 Melting temperature (T_m) and enthalpy (ΔH_m) of MPYIP–ZnC₂ and MPYC5IP–ZnCl₂ complexes

^a $\Delta H_{\rm m}$ is calibrated as the value per MPY group sustituted in MPYIP and MPYC5IP.

as the MPYIP. In addition, the shift of ν (C=O) wavenumber of the amide group was observed (1645– 1610 cm⁻¹). These results suggest that ZnCl₂ also coordinates to the O atom of the amide group and the N atom of the pyridine ring in the MPYC5IP– ZnCl₂ system. Unfortunately, it was impossible to prove that the MPY group of the MPYC5IP formed the stoichiomeric complex with ZnCl₂, since the ν (C=O) band of the amide group between the C5 spacer and the isoprene chain overlapped to that of the MPY group.

3.3. Thermal analysis

The MPYIP– $ZnCl_2$ and MPYC5IP– $ZnCl_2$ complexes with more than an equivalent mole ratio of $ZnCl_2$ to the MPY group is obtained as solid at



Fig. 3. DSC profiles of MPYC5IP–ZnCl₂ complexes with the mole ratio of MPY/ZnCl₂, 1:1 and 1:2.

room temperature, although the uncomplexed MPYIP and MPYC5IP are liquid (Table 1). This behavior is similar to that of the MPYSI–ZnCl₂ complex. When an equivalent ZnCl₂ to the MPY group are added, the ZnCl₂ complex of the MPYSI in which the MPY group is branched with more than 4.0 mol% of the substitution degree has the high melting temperature (about 140°C) and enthalpy (about 8.0×10^3 J/mol). The result from the thermal analysis of the MPYSI–ZnCl₂ complex indicates that the MPY–Zn complexes in the MPYSI strongly aggregate each other by the thermal attractive interaction as a driving force.

Table 4 shows the melting temperature (T_m) and enthalpy (ΔH_m) of the MPYIP–ZnCl₂ and MPYC5IP–ZnCl₂ complexes with various mole ratios of ZnCl₂ to the MPY group. The melting temperatures of MPYIP–ZnCl₂ (1:1) and MPYC5IP–ZnCl₂ (1:1) were lower (103 and 111°C, respectively) than expected by the result of the MPYSI–ZnCl₂ system. In addition, even if two times as much ZnCl₂ as the stoichiometric ratio of the MPY–ZnCl₂ complex was added, T_m was still 105°C. On the other hand, the T_m of the MPYC5IP–ZnCl₂ (1:2) was 143°C as expected (Fig. 3). ΔH_m of the MPYC5IP–ZnCl₂ (1:2) was also higher than those of other complexes. Obviously, the MPY–Zn complexes in the MPYC5IP–ZnCl₂ (1:2) strongly aggregate each other.

The degree of aggregation of the MPY–ZnCl₂ complexes is influenced by the structure of the aggregates. In the aggregates with the high T_m , the MPY–Zn complexes orderly line up [16]. However, since the MPY–Zn complex in the MPYIP is adjacent the bulky methyl ester group and isoprene main chain, the MPY–Zn complexes are not able to line up by the steric hindrance. In addition, the steric hindrance causes a non-stoichiometric complexation of the MPY group in the MPYIP with ZnCl₂. This type of complexation has

Table 5 Glass-transition temperature (T_g) of MPYIP, MPYC5IP and their ZnCl₂ complexes

	MPY/ZnCl ₂ (mol/mol)	$T_{\rm g}$ (°C)
Polyisoprene	0:0	-61.2
MPYIP-ZnCl ₂	1:0	-60.4
	1:1	-61.2
	1:2	-57.0
MPYC5IP-ZnCl ₂	1:0	-61.2
	1:1	-62.3
	1:2	-61.9

the defective components such as a non-chelate complex and free Zn salts, which also prevent the complex from forming a well-ordered structure [14].

Since the MPYC5IP has the C5 spacer between the MPY group and the maleic ester group, the MPY group is not hindered from the formation the complex with $ZnCl_2$ by the bulky methyl methyl ester group. The complex structure formed in this way must be the unique chelate structure, so that the strong inter-complex inter-action is shown. As the MPY group is mobile due to the flexible spacer, the MPY–Zn complexes aggregate rather effectively. Thus the MPYC5IP–ZnCl₂ (1:2) has the high T_m . From these results, we confirm that the spacer is so effective to accomplish the strong aggregation of MPY–Zn complexes.

The mole ratio (MPY)/(ZnCl₂) of the MPYC5IP– ZnCl₂ complex with the high T_m at about 140°C is 1:2 (Table 4), which is twice the stoichiometric amount of ZnCl₂ in the MPY–ZnCl₂ complex. The reason is, we consider, that a part of ZnCl₂ coordinates with the maleic amide–ester group connected to the C5 spacer and the isoprene main chain. It is supported from the result that the IR absorption band (ν (C=O)) of the maleic ester group (usually 1740 cm⁻¹) was observed at the additional lower wavenumber (1718 cm⁻¹) when an excess of ZnCl₂ was added.

Table 5 shows the glass-transition temperature (T_g) of MPYIP–ZnCl₂ and the MPYC5IP–ZnCl₂ complexes. The MPYC5IP–ZnCl₂ complex showed the same T_g as the starting polyisoprene and uncomplexed MPYC5IP. This result indicates that the aggregation of the hard-segment (MPY–ZnCl₂ complex) has no influence on the mobility of the soft-segment (isoprene units) of MPYC5IP. Thus the complete phase-separation of hard and soft segments take

place in the MPYC5IP–ZnCl₂ complex. However, T_g of the MPYIP–ZnCl₂ (1:2) was slightly higher than that of the uncomplexed MPYIP. This result suggests that the aggregation of hard-segments has influence on soft-segments in the MPYIP–ZnCl₂ complex with an excess of ZnCl₂ because of the close arrangement of the MPY–Zn complex and the isoprene unit. This result also indicates that the MPY group of MPYC5IP, which has the C5 spacer, is superior as the hard-segment to that of MPYIP.

4. Conclusions

In the present study, two types of polyisoprenes modified by the MPY group, those are the MPYIP and MPYC5IP, were synthesized. The MPY group of MPYIP is closely connected with an isoprene chain. On the other hand, that of MPYC5IP is connected with an isoprene chain through the C5 spacer. Although the uncomplexed MPYIP and MPYC5IP were obtained as liquid state, their complexes with more than an equivalent ZnCl₂ to the MPY groups were solid state. Consequently, the MPY-ZnCl₂ complex was confirmed to enhance the aggregation of the polyisoprene remarkably as well as poly(dimethyl siloxane). Moreover, in the IR spectroscopic studies, we found that the MPY amide group of MPYIP was prevented from forming the complex with $ZnCl_2$ by the steric hindrance. As a result, the ZnCl₂ complex of MPYC5IP showed the higher melting temperature and enthalpy than that of MPYIP. In addition, the better phase-separation between hard and soft segments in the MPYC5IP-ZnCl₂ complex was also observed. From these results, we conclude that the MPY-ZnCl₂ complex functions as a hard-segment of elastomers in various types of polymer system, and moreover the presence of a spacer between the MPY group and the main chain of polymers enhances the aggregation of polymers more effectively.

References

- [1] P. Galli, Macromol. Symp. 89 (1995) 13.
- [2] L.A. Utracki, Polymer Alloys and Blends, Carl Hanser, Munich, 1989.
- [3] E.P. Giannelis, R. Krishnamoorti, E. Manias, Adv. Polym. Sci. 138 (1999) 107.
- [4] W.L. Driessen (Ed.), Macromolecule Metal Complex Macromol. Symp., 131, Huthing and Wepf, Zug, 1998.

- [5] M. Biswas, A. Mukherjee, Adv. Polym. Sci. 115 (1994) 91.
- [6] C.D. Eisenbach, U.S. Schubert, Macromolecules 26 (1993) 7372.
- [7] C.D. Eisenbach, A. Goldel, M. Terskan-Reinold, U.S. Schubert, Macromol. Chem. Phys. 196 (1995) 1077.
- [8] C.D. Eisenbach, W. Degelmann, A. Goldel, J. Heinlein, M. Terskan-Reinold, U.S. Schubert, Macromol. Symp. 98 (1995) 565.
- [9] C.Z. Yang, X. Zhang, E.M. O'Connell, R.J. Goddard, S.L. Cooper, J. Appl. Polym. Sci. 51 (1994) 365.
- [10] E.M. O'Connell, C.Z. Yang, T.W. Root, S.L. Cooper, Macromolecules 29 (1996) 6002.
- [11] B.P. Grady, E.M. O'Connell, C.Z. Yang, S.L. Cooper, J. Polym. Sci. Polym. Phys. Ed. 32 (1994) 2357.

- [12] K. Naka, Polym. Prepr. Jpn 47 (1998) 31.
- [13] G. Holden, N.R. Legge, R.P. Quirk, H.E. Schroeder (Eds.), Thermoplastic Elastomers 2nd ed., Hanser, New York, 1996.
- [14] N. Moriguchi, T. Tsugaru, S. Amiya, J. Mol. Struct. 477 (1999) 191.
- [15] N. Moriguchi, T. Tsugaru, S. Amiya, J. Mol. Struct. 477 (1999) 181.
- [16] N. Moriguchi, T. Tsugaru, S. Amiya, J. Mol. Struct. 523 (2000) 93.
- [17] K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986.