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Molecular design of the polymer forming the complex with metal [I]: design of the hard-segments of thermoplastic elastomers by using model compounds

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Abstract

The six model hard-segments of thermoplastic elastomers containing a pyridine ring were synthesised and the complexation studied with several metal chlorides. It is found that the model compounds containing MPY group (*N*-pyrid-2-ylmethyl amide) form the stoichiometric 1:1 complex with $ZnCl_2$ by means of IR. This stoichiometric complexation is caused by the effective formation of the chelate ring between MPY group and $ZnCl_2$. In addition, the complex structure exhibits strong interaction with each other, so that the melting temperature and enthalpy are remarkably increased. As the result, the MPY–$ZnCl_2$ complex structure is the most suitable structure as the hard-segment of thermoplastic elastomers. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: thermoplastic elastomers; model hard-segment; metal coordination; pyridine units; stoichiometric complexation; melting temperature

A thermoplastic elastomer is polymeric material with the multi-block structures consisting of a glassy or semicrystalline ‘hard-segment’ and a rubbery ‘soft-segment’. Two-phase separation caused by the incompatibility of these segments at room temperature leads to elastic properties [1]. In addition, the hard phase, which acts as multifunctional cross-links, melts thermo-reversibly. The degree of the phase separation and cohesion of the hard-segment significantly influence the mechanical and thermal properties of thermoplastic elastomers. For example, hard domains of thermoplastic polyurethane elastomers partially melt on increasing the temperature, so that the elastic properties decline [2]. The thermoplastic elastomers in which the hard-segments have a remarkably strong cohesive and a single size distribution, such as covalent cross-links, is excellent in mechanical and thermal properties. Usually, four different types of interaction are considered as the driving force for the aggregation of hard-segments [3,4]; van der Waals interaction (in poly (styrene-*block*-butadiene-*block*-styrene) [5]), hydrogen bonding (in thermoplastic polyurethane elastomers [6]), crystallization (in poly (ether ester) thermoplastic elastomers [7]) and ionic interaction (in ionomers [8, 9]). Recently, the metal coordination interactions and crystallization of metal complex as the driving force for the hard-segment aggregation and phase separation have been reported.

Eisenbach et al. [10–12] synthesized telechelic polyethers with bipyridine terminal units, which formed the double-helical complexes of these polymers with

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Cu(I). The complexed polymers were phase-separated at the level of nano to mesoscopic superstructure consisting of copper-bipyridine complex aggregates in polyether matrix [11,12]. The mechanical properties of the complexed polyethers varied with the composition of the copper. These results indicate that the potential of the metal coordination interaction as the driving force for the phase separation of hard segments is large.

Yang et al. [4,13,14] synthesized the segmented polyurethane elastomers having pyridine groups. They investigated the influence of the complexation between the pyridine group and transition metals on the elastic properties. The mechanical properties improved largely when the polyurethanes with the pyridine groups were blended with a metal acetate, especially nickel acetate. The formation of coordinate bonds between the metal and the N atom of the pyridine was confirmed by some spectroscopic methods such as NMR, FT–IR [13] and EXAFS [14]. They suggested that these coordinate bonds acting as cross-links caused the improvement of the material property.

In the present report, we designed suitable molecular structures as the metal complexed hard-segment by using some model compounds. The purpose of this study is to obtain the new type of thermoplastic elastomers with the hard-segment that exhibits the strong cohesive and remarkable phase separation caused by the formation of metal complex.

1. Experimental

1.1. Materials

Zinc chloride (99.9%), manganese chloride tetrahydrate (99.9%), iron(II) chloride tetrahydrate, cobalt(II) chloride hexahydrate (99.9%), nickel(II) chloride hexahydrate (99.9%), and copper(II) chloride dihydrate (99.9%) were purchased from Wako Chemical Co. and used as received. Tetrahydrofuran (THF), *N*,*N*-Dimethylformamide (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 except the following materials.

1.2. Synthesis of 2-MPYAA (bis (N-pyrid-2-ylmethyl) adipoamide) [15] (**1**)

2-aminomethylpyridine (25 g) and anhydrous potassium carbonate (40 g) were dissolved in THF (150 ml). Adipoyl chloride (12.5 ml) in THF (150 ml) was added to the solution, and stirred under a N_2 atmosphere at 0°C overnight. After the solvent was evaporated, the residue was washed with water and methylene chloride. The product was purified by crystallization from acetone and obtained as white crystals (yield 71%). ^{1}H–NMR (DMSO–d_6): δ1.57 (m, 2H, O=CCH$_2$*CH*$_2$), δ2.22 (t, 2H, O=C*CH*$_2$CH$_2$), δ4.38 (d, 2H, Py–*CH*$_2$) δ7.23 (m, 2H, pyH–3,5), δ7.72 (t, 1H, PyH–4), δ8.41, δ8.50 (t + d, 2H, NH + PyH–6).

1.3. Synthesis of 2-PYAA (bis (N-pyrid-2-yl) adipoamide) (**2**)

2-aminopyridine (23 g) and anhydrous potassium carbonate (40 g) were dissolved in THF (150 ml). Adipoyl chloride (12.5 ml) in THF (150 ml) was added to the solution, and stirred under a N_2 atmosphere at 0°C overnight. After the solvent was evaporated, the residue was suspended in water and extracted with methylene chloride. The product was isolated by crystallization from methanol as white crystals (yield 74%). ^{1}H–NMR (DMSO–d_6): δ1.66 (m, 2H, O=CCH$_2$*CH*$_2$), δ2.47 (t, 2H, O=C*CH*$_2$CH$_2$), δ7.08 (t, 1H, pyH–5), δ7.76 (t, 1H, PyH–4), δ8.12 (d, 1H, PyH–3), δ8.30 (d, 1H, PyH–6), δ10.42 (s, 1H, NH).

1.4. Synthesis of 4-MPYAA (bis (N-pyrid-4-ylmethyl) adipoamide) (**3**)

A procedure similar to that for 2-PYAA was used, and the product was obtained as white crystals (yield 89%). ^{1}H–NMR (DMSO–d_6): δ1.58 (m, 2H, O=CCH$_2$*CH*$_2$), δ2.22 (t, 2H, O=C*CH*$_2$CH$_2$), δ4.31 (d, 2H, Py–*CH*$_2$) δ7.26 (d, 2H, pyH–3,5), δ8.44, δ8.50 (d + t, 3H, NH + PyH–2,6).

1.5. Synthesis of 2-MPWA (N-pyrid-2-ylmethyl valeroamide) (**4**)

A procedure similar to that for 2-PYAA was used. The product was purified by chromatography on silica gel using ethyl acetate/methanol (95/5 (v/v)), and obtained as clear liquid (yield 75%). ^{1}H–NMR (DMSO–d_6): δ0.87 (t, 3H, CH_2CH_3), δ1.28 (m, 2H, CH_2CH_3), α1.52 (m, 2H, O=CCH_2CH_2), δ2.18 (t, 2H, O=CCH_2CH_2), δ4.36 (d, 2H, Py-CH_2), δ7.23 (m, 2H, pyH–3,5), δ7.74 (t, 1H, PyH–4), δ8.39, δ8.49 (t + d, 2H, NH + PyH-6).

1.6. Synthesis of 2-MPYHDI (bis (N-pyrid-2-ylmethyl)-N′-1 6-hexyldiurea) (**5**)

2-aminomethylpyridine (25 g) and was dissolved in DMF (200 ml). 1,6-hexamethylene diisocianate (16 ml) in DMF (70 ml) was added to the solution, and stirred under a N_2 atmosphere at 0°C overnight. The reaction mixture was poured into water. The precipitate was filtered off and washed by water. The product was obtained as white crystals (yield 94%). ^{1}H–NMR (DMSO–d_6): δ1.27 (m, 2H, $NHCH_2CH_2CH_2$), δ1.36 (m, 2H, $NHCH_2CH_2CH_2$), δ2.98 (m, 2H, $NHCH_2CH_2CH_2$), δ4.28 (d, 2H, Py–CH_2) δ6.10 (t, 1H, $NHCH_2CH_2CH_2$), δ6.39 (t, 1H, $NHCH_2$–Py), δ7.23 (m, 2H, pyH–3,5), δ7.73 (t, 1H, PyH–4), δ8.47 (d, 1H, PyH–6).

1.7. Synthesis of 2-MPYAE (bis (N-pyrid-2-ylmethyl) adipate) (**6**)

2-hydroxypyridine (25 g) and anhydrous potassium carbonate (40 g) were dissolved in THF (150 ml). Adipoyl chloride (12.5 ml) in THF (150ml) was added to the solution, and stirred under a N_2 atmosphere at 0°C overnight. After the solvent was evaporated, the residue was suspended in water and extracted with methylene chloride. The product was isolated by crystallization from acetone/hexane as white crystals (yield 68%). ^{1}H–NMR (DMSO–d_6): δ1.75 (m, 2H, O=CCH_2CH_2), δ2.45 (t, 2H, O=CCH_2CH_2), δ5.22 (s, 2H, Py–CH_2) δ7.22 (t, 1H, pyH–5), δ7.35 (t, 1H, PyH–3), δ7.69 (d, 1H, PyH–4), δ8.58 (d, 1H, PyH–6).

1.8. Preparation procedure of metal-model compound complex

1.8.1. Method A

The model compound (1 mol) in methanol (10 ml) and metal chloride (1 mol) in methanol (10 ml) was mixed and refluxed for 1 h. The precipitate was filtered off and washed by methanol. In the cases of 2-MPYAA, 2-PYAA, 4-MPYAA and 2-MPYHDI,the complexes were quantitatively obtained by using this method.

1.8.2. Method B

The model compound (1 mol) in methanol (10 ml) and appropriate concentration of metal chloride in methanol (10 ml) was mixed and reflexed for 1 h. The solvent was evaporated, then the complex was obtained.

1.9. General procedure

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

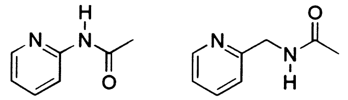
The differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC–7 differential scanning calorimeter. Each sample (*ca*. 5 mg) was measured under a N_2 atmosphere with a DSC-scan rate of 10 K/min. Indium was used as a calibration standard.

The differential thermal analysis (DTA) measurements were performed on a Rigaku TAS–200 thermal analysis system. Each sample (*ca*. 10 mg) was measured under a N_2 atmosphere with a DTA-scan rate of 10 K/min.

2. Results and discussion

2.1. Molecular design of hard segment

In general, free metal ions prevent the formation of the hydrogen bonding or crystallization, thus leading to disaggregate the hard segments of the thermoplastic elastomers. In addition, some metal salts cause the decline of mechanical properties by taking up water. A way to solve these problems is to construct the hard segment capable of forming the stoichiometric complex with a metal in a polymer system. Therefore, we designed the hard segment with the following strategy; 1. introduction of a ligand which coordinate with a metal, 2. formation of a chelate ring so as to form the complex effectively, 3. introduction of a



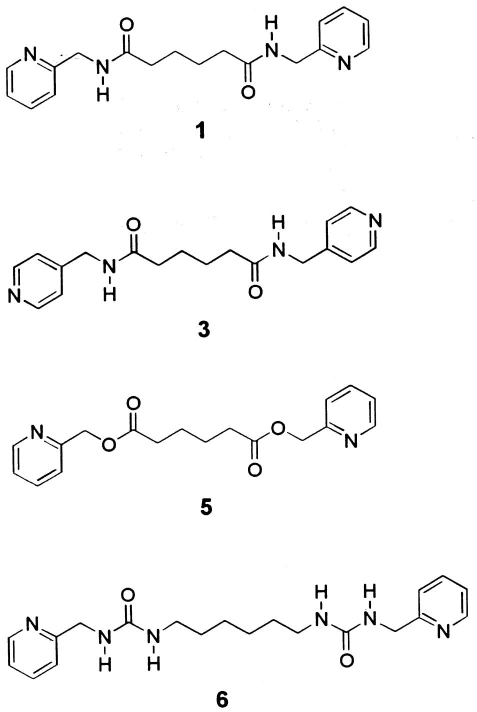
1 **2**

Fig. 1. Structures of the group designed as the hard-segment forming of the metal complex. PY (**1**) and MPY (**2**).

functional group so that the hard segment obtained is easily introduced to a polymer. According to the above-mentioned strategy, we adopt the two types of structures, PY (*N*-pyrid-2-yl amide) and MPY (*N*-pyrid-2-ylmethyl amide) as shown in Fig. 1. While 2-carbon of pyridine is directly connected with an amide group in PY, there is a methylene spacer among 2-carbon of pyridine and the amide group in MPY. We intend that one metal atom coordinated to both the pyridine and the amide group, as a result, the chelate ring is formed. In order to investigate that these structures act as the metal complexed hard-segment effectively, we synthesized six model compounds with a pyridine ring (Fig. 2). While 2-MPYAA (1) and 2-MPYVA (4) consist of MPY group, 2-PYAA (2) consist of PY group. 4-MPYAA (3), in which 4-carbon of pyridine is bound with a methylene spacer, is impossible to form a chelate ring. 2-MPYHDI (5) and 2-MPYAE (6) consist of urea and ester groups, respectively, instead of the amide group. Only 2-MPYVA is obtained as liquid, and other derivatives are solid.

2.2. IR study

Fig. 3 shows the IR spectra of 2-MPYAA and 2-MPYAA-$ZnCl_2$ complex obtained by the method A. The absorption bands at 1473 cm^{-1} (pyridine ring stretching), 600 cm^{-1} (in-plane pyridine ring deformation) and 405 cm^{-1} (out-of-plane pyridine ring deformation) of 2-MPYAA are respectively shifted to 1485 cm^{-1}, 619 cm^{-1} and 418 cm^{-1} by forming the complex with $ZnCl_2$. These shifts are suggested that a Zn atom of $ZnCl_2$ coordinates to a N atom of pyridine ring [16,17]. In addition, the absorption



1 **2** **3** **4** **5** **6**

Fig. 2. Structures of pyridine-containing model compounds. 2-MPYAA (**1**), 2-PYAA (**2**), 4-MPYAA (**3**), 2-MPYVA (**4**), 2-MPYHDI (**5**), 2-MPYAE (**6**).

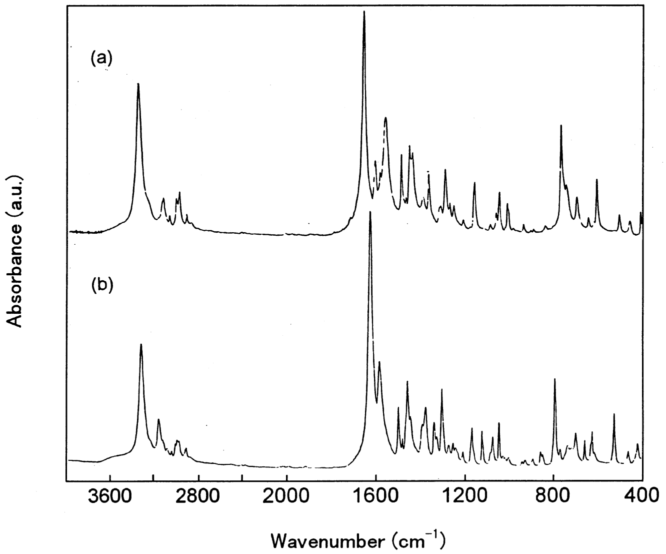


Fig. 3. IR spectra of 2-MPYAA(a) and 2-MPYAA-$ZnCl_2$(b) complex obtained by method A.

bands at 3290 cm^{-1} (N–H stretching), 1639 cm^{-1} (C=O stretching) and 1545 cm^{-1} (C–N stretching) are respectively changed to 3261 cm^{-1}, 1608 cm^{-1} and 1570 cm^{-1} in the complex of $ZnCl_2$. These results indicate that a Zn atom coordinates to an O atom of the amide group [18].

By elemental analysis, a 2-MPYAA-$ZnCl_2$ complex consists of one 2-MPYAA and two $ZnCl_2$s (Found; H 4.01%, C 36.08%, N 9.26%, Cl 23.37%, Zn 19.9%, Calc.; H 3.70%, C 36.09%, N 9.35%, Cl 23.67%, Zn 21.8%,), which suggests that a 1:1 complex is formed between the MPY group and $ZnCl_2$. This supposition is confirmed by the IR measurement of the 2-MPYAA-$ZnCl_2$ complex with various ratios of $ZnCl_2$ to MPY prepared by the method B as shown in Fig. 4. When $ZnCl_2$ is less than the MPY group, the absorption bands from the pyridine ring and the amide group are partially shifted, and a doublet signal from comlexed and uncomplexed 2-MPYAA is detected. Then the IR spectrum of the complex that consisted of a 1:1 ratio of $ZnCl_2$ to MPY is corresponded with the IR spectrum of the 2-MPYAA-$ZnCl_2$ complex obtained by the method A (Fig. 3).

Table 1 shows the characteristic IR wavenumbers of six model compounds with pyridine rings and their complexes of $ZnCl_2$ prepared by the method A. For also 2-MPYHDI, the absorption bands at 1616 cm^{-1} (C=O stretching), 600 cm^{-1} (in-plane pyridine ring deformation) and 398 cm^{-1} (out-of-plane pyridine ring deformation) are completely shifted to 1606 cm^{-1}, 627 cm^{-1} and 417 cm^{-1}, respectively. However, in cases of 2-PYAA and 4-MPYAA, the complete shifts of the absorption bands from amide groups such as the model compounds having the MPY- groups are not detected. These results indicate the unique and the stoichiometric structure is not formed for these complexes. For 4-MPYAA, the 4-carbon atom of pyridine connects with the methylene spacer bound to an amide group, so that a chelate ring is impossible to form with a Zn atom. Therefore, the partial shifts of the bands suggest that the formation of the chelate ring causes the unique complex structure. In the case of 2-PYAA, there is not the methylene spacer, therefore the distance between the N atom of pyridine and the Zn atom is closer than that of 2-MPYAA. The results of IR studies indicate that the presence of a methylene spacer is very important for the formation the unique and the stoichiometric complex structure.

Table 1 also shows the IR spectra of a 2-MPYVA-$ZnCl_2$ complex prepared in the various ratios of $ZnCl_2$ to 2-MPYVA by the method B. The uncomplexed 2-MPYVA is liquid. Since no hydrogen

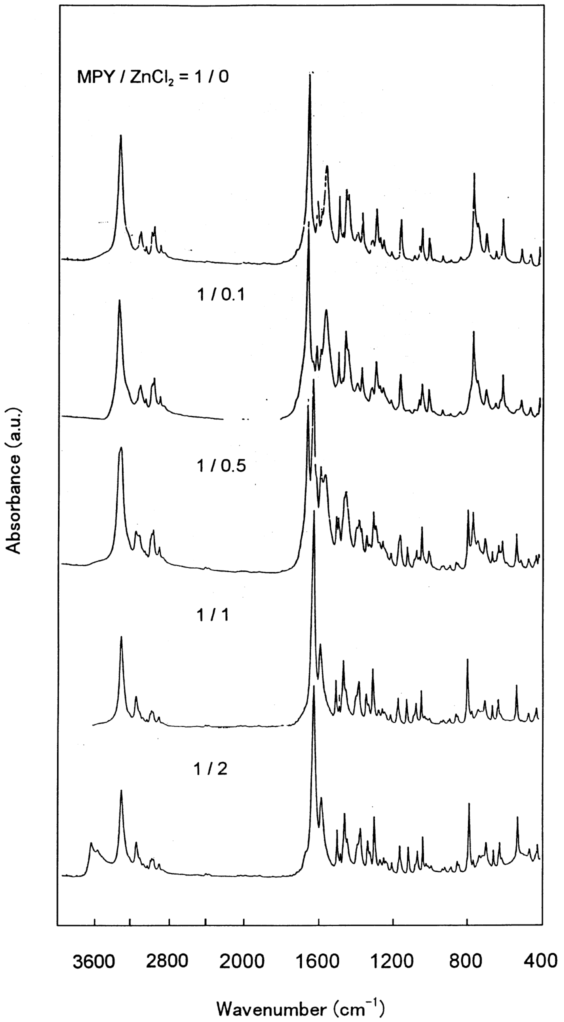


Fig. 4. IR spectra of 2-MPYAA-ZnCl$_2$ complex with various ratio of ZnCl$_2$ to MPY group prepared by method B. The mole ratio of MPY/ZnCl$_2$ is indicated at the left of each spectrum.

bonding of an amide group is formed in 2-MPYVA, the C=O stretching (1651 cm^{-1}) of 2-MPYVA is higher wavenumbers than that of 2-MPYAA (1639 cm^{-1}). No complex of 2-MPYVA is isolated by the method A. However, the stoichiometric 1:1 complex is obtained as a solid by the method B when an equivalent ZnCl$_2$ to the MPY group is added. For 2-MPYAE, a Zn atom is coordinated with the only N atom of pyridine, which indicate that an O atom of an ester group is too week as a Lewis base to coordinate with the Zn atom.

2.3. Thermal analysis

As described in IR studies, the MPY group forms the stoichiometric complex with ZnCl$_2$. These complexes have unique thermal properties. Fig. 5 shows the DTA profiles of the 2-MPYAA-ZnCl$_2$ complex prepared in the various ratios of ZnCl$_2$ to 2MPYAA by the method B. The uncomplexed 2-MPYAA has the endothermic peak from the melt at 136°C. On increasing the amounts of ZnCl$_2$, this peak becomes smaller, and finally disappears in the 1:1 molar ratio of ZnCl$_2$ to MPY. In addition, the new endothermic peak of the 2-MPYAA-ZnCl$_2$ complex appears at 324°C. However, this endothermic peak disappears by adding of an excess of ZnCl$_2$.

Table 2 shows the melting temperatures and the enthalpies of three model compounds containing of the MPY group and their complexes of ZnCl$_2$ by the DSC measurements. The 1:1 complexes of 2-MPYAA and ZnCl$_2$ prepared by both method A and method B indicate the same melting temperature, which suggests that both structures are same in being supported by IR studies. As shown in Table 2, the stoichiometric 1:1 complexes of the model compounds that contain of the MPY group such as 2-MPYAA, 2-MPYVA and 2-MPYHDI have the melting temperature and enthalpy. Furthermore, these melting temperature and enthalpy are remarkable high compared with uncomplexed model compounds. Especially the melting temperature of the 2-MPYVA-ZnCl$_2$ complex is higher than that of the uncomplexed by 129°C. And the enthalpy of the complex is also increased about two orders of magnitude over that of the umcomplexed. These results suggest that the formation of the MPY-ZnCl$_2$ complex give rise to strong interaction, which leads to the increase in the melting temperature.

However, no extra high endothermic peak from melting is observed in any DTA profile with various ratios of the Zn atom to the pyridine ring for the 4-MPYAA-ZnCl$_2$ complex as shown in Fig. 6. This result suggests the increase in the melting temperature is caused by the formation of the chelate ring with the MPY- group and ZnCl$_2$. This suggestion is confirmed by the fact that no endothermic peak is revealed for the 2-MPYAE-ZnCl$_2$ complex that is impossible to form the chelate ring because of the low Lewis basicity of the O atom as presented in IR studies.

Table 1
Characteristic IR wavenumbers (cm^{-1}) of various model compounds of the hard-segment and their $ZnCl_2$ complexes. δ(ip): in-plane of pyridine ring deformation. δ(oop): out-of-plane pyridine ring deformation. ND: not detected

	Amide group			Pyridine ring		
	ν(N–H)	ν(C = O)	ν(C–N)	ν(py)	δ(ip)	δ(oop)
2-MPYAA	3290	1639	1545	1473	600	405
2-MPYAA-$ZnCl_2$	3261	1608	1507	1485	619	418
2-PYAA	3255	1701	1522	1473	613	413
2-PYAA-$ZnCl_2$	3271	1720	1540	1441	644	419
	3232	1654	1481			
4-MPYAA	3328	1641	1554	1498	600	ND
4-MPYAA-$ZnCl_2$	3325	1657	1533	ND	621	ND
2-MPYVA	3292	1651	1547	1475	611	403
2-MPYVA-$ZnCl_2$	3261	1608	1570	1485	619	418
2-MPYHDI-$ZnCl_2$	3334	1616	1579	1479	600	398
	3315					
2-MPYHDI-$ZnCl_2$	3379	1606	1579	1495	627	417
	3300					
2-MPYAE	ND	1730	ND	1481	627	403
2-MPYAE-$ZnCl_2$	ND	1730	ND	1491	650	417

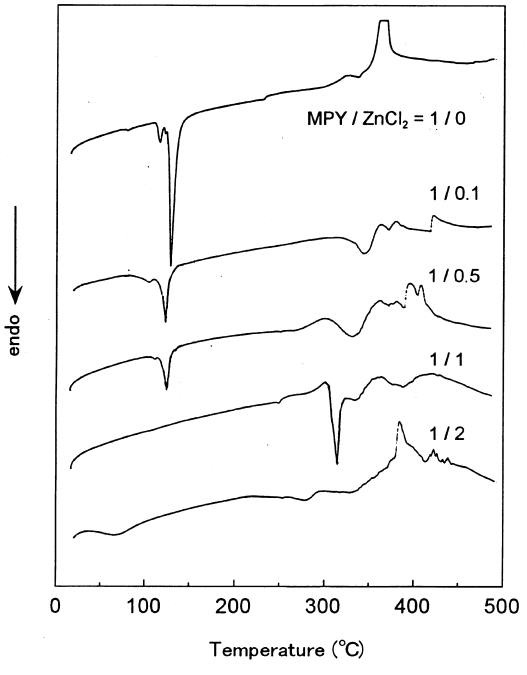


Fig. 5. DTA profiles of 2-MPYAA-$ZnCl_2$ complex with various ratio of $ZnCl_2$ to MPY group prepared by method B. The mole ratio of MPY/$ZnCl_2$ is indicated at the right of each spectrum.

By thermal analyses, we conclude that the MPY group has possibilities to form a complex with $ZnCl_2$, which shows a much higher melting temperature than that of the umcomplexed.

2.4. The complex with other metal halides

The MPY group has possibilities to form a complex with various metal halides. In the cases of $MnCl_2$, $CoCl_2$, $FeCl_2$, $NiCl_2$ and $CuCl_2$, the complex of the MPY to the metal is formed in the 1:0.5 molar ratio. No stoichiometric complex is formed from 2-MPYAA and $CuCl_2$. These findings suggest that the coordination number of $ZnCl_2$ is 4, while those of $MnCl_2$, $CoCl_2$, $FeCl_2$ and $NiCl_2$ are 6. Table 3 shows

Table 2
Melting temperature (Tm), enthalpy (ΔHm) and entropy (ΔSm) of various model compounds containing of MPY group and their $ZnCl_2$ complexes by DSC measurement

	Tm(°C)	ΔHm(J/mol)	ΔSm(J/K·mol)
2-MPYAA	136	3.2×10^4	2.8
2-MPYAA-$ZnCl_2$	324	5.8×10^4	97
2-MPYVA	−70	5.6×10^2	2.8
2-MPYVA-$ZnCl_2$	159	1.4×10^4	32
2-MPYHDI	193	6.5×10^4	140
2-MPYHDI-$ZnCl_2$	249	7.2×10^4	139

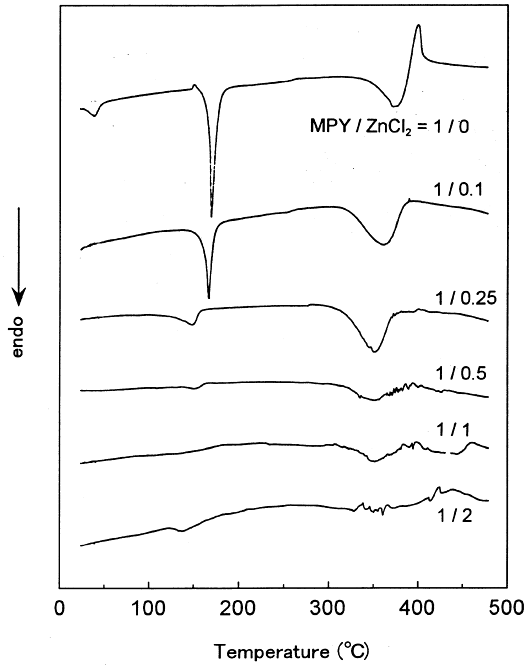


Fig. 6. DTA profiles of 4-MPYAA-ZnCl$_2$ complex with various ratio of ZnCl$_2$ to MPY group prepared by method B. The mole ratio of MPY/ZnCl$_2$ is indicated at the right of each spectrum.

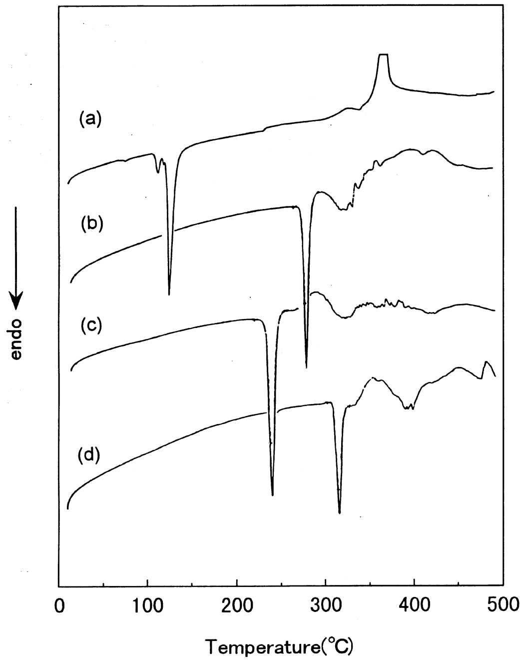


Fig. 7. DTA profiles of the 2-MPYAA (a) and 2-MPYAA complexes with MnCl$_2$(b), CoCl$_2$(c) and ZnCl$_2$(d).

the characteristic IR wavenumbers of the complexes of 2-MPYAA with various metal halides. The magnitudes of the shifts of the IR absorption bands from pyridine ring deformation change in the order of Mn < Fe < Co < Ni, Cu > Zn, which is parallel to the well-known Irving-Williams order. Schmidt et al. [19] reported that this order is related with the coordinate bond energy or stability. On the other hand, the IR wavenumbers of C=O stretching of the amide group change with the coordinated metals in the order of Zn < Cu > Ni > Co, Fe, Mn. The lower wavenumber indicate the formation of the stronger coordinate bond between the metal and the O atom of the amide C=O [18]. The order of the strength of metal coordinate bonds to the O atom of the amide group and the N atom of pyridine is the opposite. We speculate that the competitions of the O atom of amide group and the N atom of pyridine take place in coordinating with metal atom. So the metal which coordinate strongly with pyridine form the weak coordinate bond with the amide group.

Table 3
Characteristic IR wavenumbers (cm^{-1}) of various model compounds of the hard-segment and their metal complexes. δ(ip): in-plane of pyridine ring deformation. δ(oop): out-of-plane pyridine ring deformation

	ν(C = O)	ν(C–N)	δ(ip)	δ(oop)
2-MPYAA	1639	1545	600	405
2-MPYAA-MnCl$_2$	1614	1567	621	418
2-MPYAA-FeCl$_2$	1610	1576	623	426
2-MPYAA-CoCl$_2$	1612	1576	623	430
2-MPYAA-NiCl$_2$	1620	1564	623	438
2-MPYAA-CuCl$_2$	1646	1512 1551	624	436
2-MPYAA-ZnCl$_2$	1608	1570	619	418

Fig. 7 shows the DTA profiles of the 2-MPYAA complex with MnCl$_2$, CoCl$_2$ and ZnCl$_2$. In the cases of FeCl$_2$, NiCl$_2$ and CuCl$_2$, no endothermic peak is observed because of an acceleration of thermal decomposition. The melting temperature of the complex is higher in the order of Zn > Mn > Co. From these results, the MPY-ZnCl$_2$ complex is the most suitable structure as the hard-segment of thermoplastic elastomers. Because this complex has the strong interaction which causes the strong driving force for hard-domain aggregation and phase separation, it also has thermal stability.

3. Conclusions

In the present studies, the six model compounds were synthesized and investigated in relation to their thermal properties and complexation with several metal chlorides. In the IR spectroscopic studies, we found that the MPY group, with a methylene spacer between the 2-position of pyridine and the amide group is able to form the stoichiometric strong complex with $ZnCl_2$. So the melting temperature and the enthalpy are remarkably increased. From these results, we conclude that the MPY-$ZnCl_2$ complex is the most suitable structure as the hard-segment of the thermoplastic elastomer. In a further report, we will study a polymer containing this complex group.

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