

# Linear Polymers with Sulfur in the Main Chain III. Synthesis of Polythioesters by Polycondensation of bis(4,4'-mercaptophenyl)sulfide with Various Acid Dichlorides and Their Properties

Hiroshi Hirano, Seiji Watase, Mitsuaki Tanaka

Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan

DOI 10.1002/app.21472

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Synthesis and properties of sulfur-containing linear polythioesters derived from bis(4,4'-mercaptophenyl)sulfide (MPS) and various acid dichlorides (AC) have been studied to evaluate the effect of the thioester group in comparison with corresponding linear polyesters. Polycondensations between MPS and azelaoyl chloride (AZC) chosen as a model reaction system were investigated under various conditions by solution polycondensation, to find optimal conditions to get high molecular weight and quantitative yield. The obtained polymer using chloroform as a solvent indicated the highest molecular weight, determined by gel permeation chromatography (GPC). Thus the polythioesters from MPS and AC were synthesized under the above-mentioned conditions. The thermal properties of polythioesters including the MPS moiety

were evaluated by thermogravimetry/differential thermal analysis (TG/DTA), and differential scanning calorimetry (DSC). Those indicated that the polythioesters including the MPS moiety were crystalline polymers with relatively high heat resistance. These polythioesters were found to show an odd-even effect with the glass transition temperature, melting point, and oxygen permeability based on the methylene numbers. The tensile strength and storage modulus decreased with the number of methylene units. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 508–515, 2005

**Key words:** polycondensation; polythioester; thermal properties; mechanical properties; odd-even effect

## INTRODUCTION

Engineering plastics containing sulfur atoms, such as poly(phenylenesulfide), poly(ethersulfone), and polysulfone have been put into practical use because they have superior mechanical properties and excellent resistance to heat and chemicals. Thus, the incorporation of sulfur into polymers is expected to result in improved properties, including mechanical properties and resistance to heat and chemicals.

Recently, the number of studies on linear polymers containing sulfur atoms has been increasing. For example, Kobayashi et al.<sup>1,2</sup> studied the polyaddition reaction of dithiols to dialkenes and to dialkynes. Sato et al.<sup>3–5</sup> also studies polyaddition of dithiols to bis(alkoxyallene)s or diallenylbenzene. Koizumi et al.<sup>6</sup> synthesized polysulfide by the polyaddition reaction of dithiol and epoxide. The syntheses of polythioesters by interfacial polycondensation of aromatic and aromatic-aliphatic dithiols with aromatic and aliphatic acid dichlorides have been reported by Podkoscielny et al.<sup>7–12</sup> Shaffer and

Percec<sup>13</sup> found that polythioethers and copolythioethers with methylene numbers of 2–10 derived from 4,4'-biphenyldithiol and  $\alpha,\omega$ -dibromoalkanes exhibited thermotropic liquid crystalline characteristics. Chen et al.<sup>14</sup> reported that incorporation of 4,4'-thiodiphenol (TDP) improves the flexibility of polyarylate with poor impact strength.

In our previous work,<sup>15</sup> the copolycondensation of TDP/bisphenol-A (BPA) with adipoyl dichloride (APC) improved the mechanical properties. In particular, the brittle quality of the homopolymer between TDP and APC was greatly improved. The excellent properties mentioned above were also achieved by introducing sulfur into polyesters, as we reported.<sup>15</sup> Polyesters between TDP and acid dichloride having various numbers of methylene units showed excellent properties, especially barrier property against oxygen gas compared with PET.<sup>16</sup> The polyesters also showed an interesting odd-even effect in properties.

In this paper, synthesis and properties of the polythioesters by polycondensations between bis(4,4'-mercaptophenyl)sulfide (MPS) and acid dichlorides having various numbers of methylene unit are studied to evaluate the effect of substitution of the thioester group.

Correspondence to: H. Hirano (hirano@omtri.city.osaka.jp).

## EXPERIMENTAL

### Reagents

MPS was offered from Sumitomo Seika Chemicals Co. Ltd. It was used after vacuum drying without further purification. Commercially available reagents (Tokyo Kasei Kogyo Inc.) were used for succinyl dichloride (SCC), suberoyl dichloride (SUC), and azelaoyl dichloride (AZC). Adipoyl dichloride (APC), sebacoyl dichloride (SBC), isophthaloyl dichloride (IPC), and terephthaloyl dichloride (TPC) were obtained from Nacalai Tesque Inc. Glutaryl dichloride (GLC) and pimeloyl dichloride (PMC) were purchased from Sigma-Aldrich Co. All aliphatic acid dichlorides were distilled immediately before use. Isomeric phthaloyl dichlorides were recrystallized and dried just before use. Chloroform (Kanto Chemical Inc.), stabilized with amylene, was dried and distilled before using as a solvent. 5-*tert*-Butyl-1,3-benzenedicarbonyl chloride (BIPC), synthesized by reaction of 5-*tert*-butyl-1,3-benzenedicarboxylic acid (Fischer Scientific Inc.) with thionyl chloride, was also recrystallized just before use.

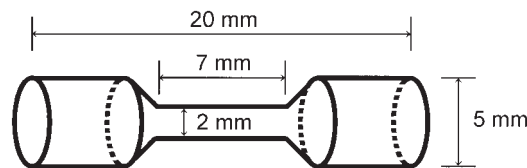
### Synthesis of polythioesters derived from MPS

MPS (30 mmol) was dissolved in 60 mL of chloroform in a 200-mL round-bottom flask equipped with a condenser and a dropping funnel. Under nitrogen atmosphere, triethylamine (63 mmol) was added into the flask and then acid dichloride (31.5 mmol) in 50 mL of the solvent was slowly added through the funnel at room temperature with vigorous stirring by a magnetic stirrer. After 30 min, the flask was heated up to 60°C and stirred for 30 min. White powder, precipitated by pouring the reaction mixture into a large amount of methanol, was washed with water, acetone, and methanol, respectively, and dried under vacuum. When the white powder was deposited in the flask, it was washed with those solvents, respectively, and dried under vacuum. For further purification, the polymers were dissolved into chloroform or PhOH/TCE (1 : 1, w/w) and then reprecipitated by pouring the solution into methanol.

Purified polymers were compression molded to films for the gas permeation and dynamic mechanical measurements.

### Analysis and measurement

The specific viscosity of the solution of polythioesters (10 g L<sup>-1</sup>) in a phenol-tetrachloroethane mixture (1 : 3 in w/w) was measured with an Ubbelohde viscometer at 35°C. Infrared spectra were measured on KBr discs with an Impact-420 Fourier-transform spectrophotometer (Nicolet). <sup>1</sup>H-NMR spectra were recorded on a JEOL NMR-270Q to confirm the structure of the poly-



**Figure 1** Sample shape of the polythioesters for tensile testing.

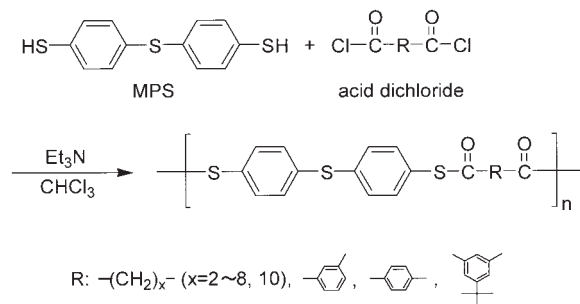
thioesters. Gel permeation chromatography (GPC) was conducted with a Toyo-soda HLC-8020 using tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL min<sup>-1</sup>. Polystyrene standards were used to calibrate the molecular weights.

To evaluate heat resistance, thermogravimetric and differential thermal analyses (TG/DTA) were conducted under an air flow (200 mL min<sup>-1</sup>) at a heating rate of 10 K min<sup>-1</sup>. The melting points and glass transition temperatures of the polythioesters were determined using a SSC-5200 differential scanning calorimeter (Seiko Instrument, Inc.) at a heating rate of 10 K min<sup>-1</sup> under a nitrogen flow (40 mL min<sup>-1</sup>). Dynamic mechanical analysis (DMA) was made with a DMS-200 viscoelastic spectrometer (in tensile mode, Seiko Instrument Inc.) at a frequency of 1 Hz and a heating rate of 2 K min<sup>-1</sup>. The films with ca. 100 μm thickness for DMA were prepared by compression molding at 120–265°C and then annealed at the temperature that was 10°C higher than the corresponding crystallizing point, for 1 h.

The specimens for the tensile test were prepared with a CS-183MMX Minimax Mold System (CSI Co., Ltd.). All materials were vacuum dried at 80°C for 3 h and then injection molded at 125–260°C. The shape of the injection-molded specimens is shown in Figure 1. The tensile test was performed with a universal testing machine (Shimadzu AG-50kN Autograph) at a testing rate of 5 mm min<sup>-1</sup>. Tensile elongation at break was calculated from the moving distance of the cross-head since small test pieces make it difficult to measure the elongation.

Oxygen permeability (*i.e.*, gas permeation coefficient) of the films prepared by compression molding was measured with a Toyo-seiki GTR meter M-C3 using the differential pressure method at 23°C. The films were prepared by same manner as DMA measurement. A polarized microscope, Olympus BH-2, equipped with a Mettler FP82 temperature-control unit was used for observation of the melting of the polythioesters.

The crystallinity of the polythioesters was determined from wide-angle X-ray diffraction traces (WAXD) scanned on a Rigaku X-ray diffractometer RINT 2500 (Rigaku, Inc.), 40 kV-100 mA.



Scheme 1

## RESULTS AND DISCUSSION

### Polycondensation of MPS with various aliphatic acid dichlorides

Polycondensation between MPS and AZC chosen as a model reaction system was investigated to evaluate the effect of reaction solvents (Scheme 1), to find optimal conditions to achieve a high molecular weight and almost quantitative yield. The yields of the polycondensation and molecular weight of obtained polymers by GPC measurement are shown in Table I.

All polycondensations between MPS and various acid dichlorides were carried out according to Scheme 1, because chloroform solvent obtained the highest molecular weight of polycondensate between MPS

**TABLE I**  
Polycondensation between MPS and Azelaoyl Dichlorides

Solvent	Yield (%)	$M_n^a$ ( $\times 10^3$ )	$M_w^a$ ( $\times 10^3$ )	$M_w/M_n^a$
Methylenedichloride	97	14.3	29.3	2.04
1,1,2,2-Tetrachloroethane	88	6.0	16.4	2.73
Chloroform	98	15.1	32.2	2.13
Tetrachloromethane	94	8.7	19.1	2.20
Tetrahydrofuran	98	14.4	28.7	1.99
Dimethylformamide	87	2.5	8.9	3.56
Benzene	91	4.0	9.8	2.45

<sup>a</sup> Determined by GPC relative to polystyrene standards.

and AZC. The polymer yields were relatively high and almost quantitative (Table II). The chemical structures of the produced polymers were confirmed by IR spectra and <sup>1</sup>H-NMR spectra.

For example, the FTIR spectrum of the product of polycondensation between MPS and azelaoyl chloride (Run 6) shown in Figure 2. In the FTIR spectra of the product, the absorptions based on the thiol group (around 2550  $\text{cm}^{-1}$ ) of MPS and the chloro carbonyl group (1795  $\text{cm}^{-1}$ ) of AC disappeared, while a new thioester carbonyl band at 1705  $\text{cm}^{-1}$  appeared, confirming the formation of polythioester by polycondensation. The <sup>1</sup>H-NMR spectrum also suggests the structures of the polythioesters, for example, polythioester (Run 6), as shown in Figure 3.

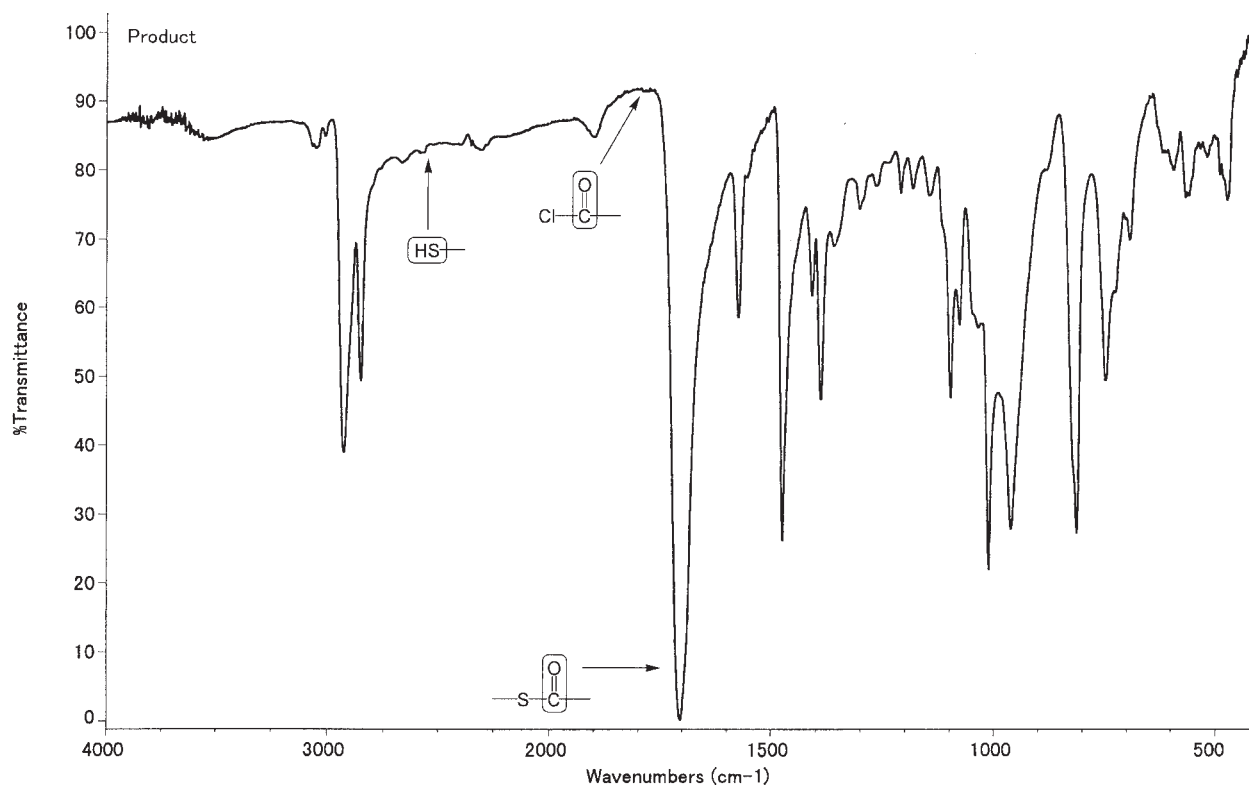


Figure 2 FT-IR spectrum of the polythioester derived from MPS and azelaoyl dichloride (Run 6).

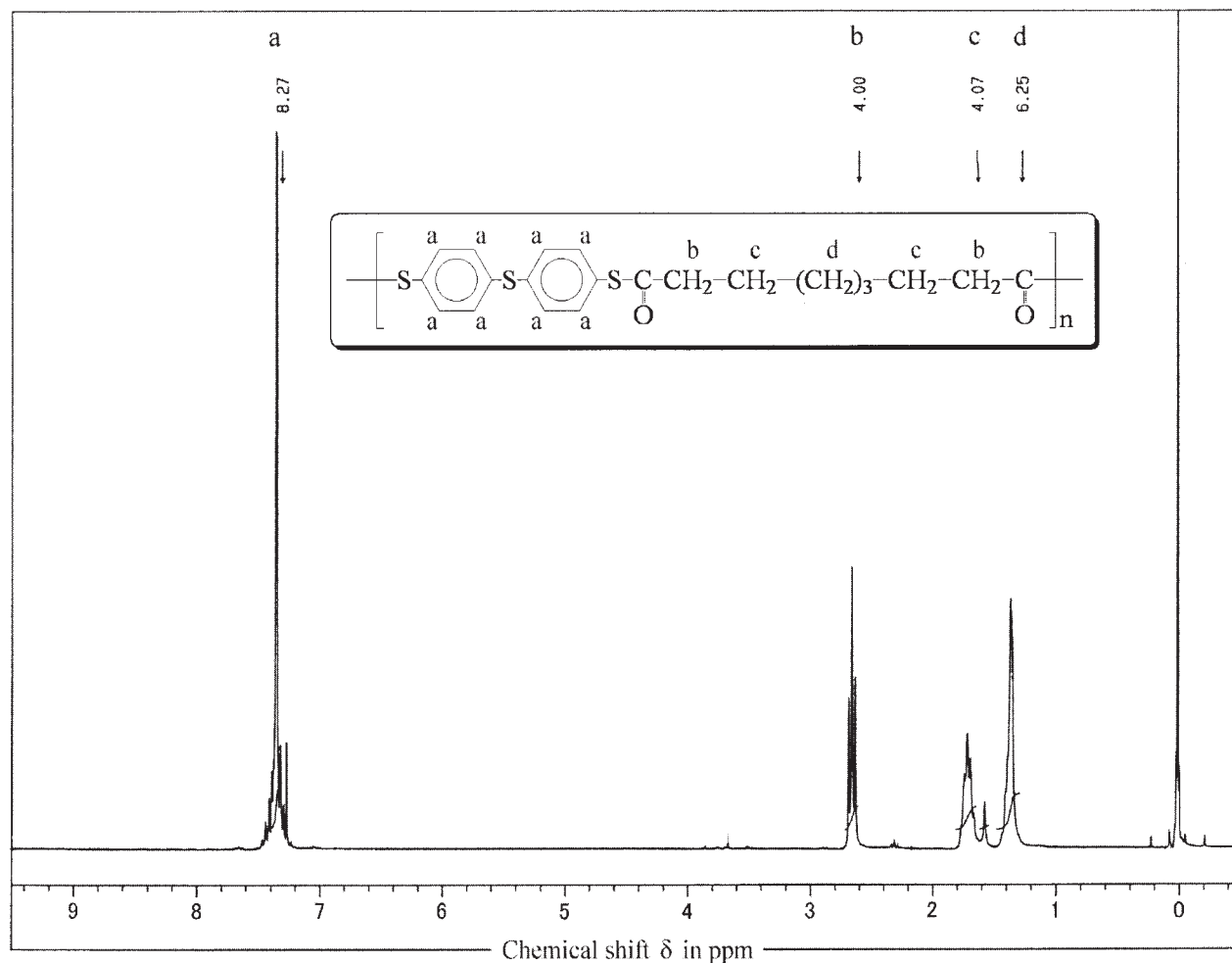


Figure 3  $^1\text{H-NMR}$  spectrum of the polythioester derived from MPS and azelaoyl dichloride (Run 6).

TABLE II  
Characterization of Polymers Derived from MPS and Several Acid Dichlorides

Run	Acid dichloride	Methylene number	Yield (%)	$\eta_{sp}^a$	$M_n^c$ ( $\times 10^3$ )	$M_w^c$ ( $\times 10^{-3}$ )	$M_w/c M_n$
1	Succinyl	2	97	0.32	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
2	Glutaryl	3	97	0.43	11.0 <sup>d</sup>	29.8 <sup>d</sup>	2.71 <sup>d</sup>
3	Adipoyl	4	99	0.63	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
4	Pimeloyl	5	99	0.76	19.4 <sup>d</sup>	53.5 <sup>d</sup>	2.75 <sup>d</sup>
5	Suberoyl	6	99	0.56	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
6	Azelaoyl	7	98	0.61	15.1 <sup>d</sup>	32.2 <sup>d</sup>	2.13 <sup>d</sup>
7	Sebacoyl	8	98	0.75	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
8	Dodecandieryl	10	95	0.49	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
9	Isophthaloyl	—	99	0.74	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>
10	<i>t</i> -Butylisophthaloyl	—	99	1.12	88.1 <sup>d</sup>	185.4 <sup>d</sup>	2.11 <sup>d</sup>
11	Terephthaloyl	—	98	— <sup>b</sup>	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>

<sup>a</sup> 35°C, PhOH/TCE = 1/3 (w/w), 1 g/dL.

<sup>b</sup> Insoluble in PhOH/TCE.

<sup>c</sup> Determined by GPC relative to polystyrene standard.

<sup>d</sup> Soluble in THF.

<sup>e</sup> Insoluble in THF.

TABLE III  
Thermal Properties of the MPS Polythioesters

Run	Acid dichloride	Initial mass loss temperature (°C)	5% mass loss temperature (°C)	$T_g^a$ (°C)	$T_m^b$ (°C)
1	Succinyl	276	290	70.3	185
2	Glutaryl	302	318	44.0	136 <sup>c</sup>
3	Adipoyl	308	321	46.8	194
4	Pimeloyl	311	328	28.3	119 <sup>c</sup>
5	Suberoyl	319	335	31.4	154
6	Azelaoyl	318	334	16.2	102 <sup>c</sup>
7	Sebacoyl	313	330	19.8	135
8	Dodecanedioyl	312	327	11.8	126
9	Isophthaloyl	364	389	141.7	249
10	<i>t</i> -Butylisophthaloyl	363	379	167.7	— <sup>d</sup>
11	Terephthaloyl	367	437	— <sup>d</sup>	— <sup>d</sup>

<sup>a</sup> Determined by DSC.

<sup>b</sup> Observed in the DSC curves on second heating.

<sup>c</sup> Observed in the DSC curves on first heating.

<sup>d</sup> Not observed in the DSC curve.

Since the polythioesters with odd numbers and 5-*tert*-butyl-1,3-benzene unit were soluble in THF, GPC measurements were performed in relation to polystyrene standards. The results of polycondensation between MPS and various acid dichlorides are summarized in Table II. The measurement clarifies that polythioesters have a high molecular weight ( $M_w = 29,800$ – $185,400$ ).

### Thermal properties

The heat resistance of the polythioesters was examined by TG/DTA. The temperatures of the 5% mass loss and the initial mass loss were deduced from the curves, as shown in Table III. The 5% mass loss temperatures are close in aliphatic polythioesters because of the similar structures of the polythioesters from aliphatic acid dichlorides. On the contrary, the rigid aromatic polythioesters from the aromatic acid dichlorides showed higher 5% mass loss temperatures than those of the aliphatic polythioesters using aliphatic acid dichlorides. These temperatures were lower than those of corresponding polyesters derived from TDP in our previous paper.<sup>16</sup> This fact indicates that thermal resistance of the polythioesters is inferior to that of the corresponding polyesters. The thioester group would be readily oxidized in comparison with the ester group, because the sulfide bond is larger and more flexible than the ether bond. The sulfide moiety of the thioester group is readily oxidized to sulfones or sulfonic acids and further cleaved in comparison with the ether moiety of the ester group.

The glass transition temperatures ( $T_g$ s) were determined from the DSC curves (Fig. 4 and Table III). The  $T_g$ s decrease as the methylene numbers of the polythioesters increase. The  $T_g$ s of the polythioesters with even

methylene numbers are obviously higher than those of the polythioesters with odd methylene numbers, as shown in Fig. 5. This is evidence of the existence of an odd–even effect between the  $T_g$ s and the methylene numbers. Similarly, in the poly(alkylene terephthalates)<sup>17</sup> and polyesters shown in our previous report,<sup>16</sup> both the melting points ( $T_m$ s) and the  $T_g$ s were reported to exhibit an odd–even effect on the basis of the methylene numbers. This fact certainly indicates that the conformation of the polymers having even methylene numbers is regular, in contrast to those having odd methylene numbers.

All the polythioesters from aliphatic acid dichlorides were confirmed to be crystalline polymers. This is because they show an endothermic peak on heating in the DSC curves attributed to the melting point on the polarized microscope observations. The polythioesters with even number of methylene units show an endothermic peak on the first heating scan but only one peak was observed on the first cooling or second heating. The polythioesters having an odd number of methylene units only show an endothermic peak on the first heating in the DSC curves but they don't show any exothermic peaks due to crystallization on the first cooling and endothermic peaks on the second heating. Since this phenomenon is probably attributable to very slow crystallization, after cooling of molten polythioesters with an odd number of methylene units, the cast films were prepared from chloroform solution and then the DSC measurement was made again. The cast films indicated an endothermic peak in the DSC curves on heating at around the respective melting point on first heating. Thus, it was clarified that the polythioesters with an odd number of methylene units have an extremely slow rate of crystallization from the molten state. An odd–even effect was also confirmed

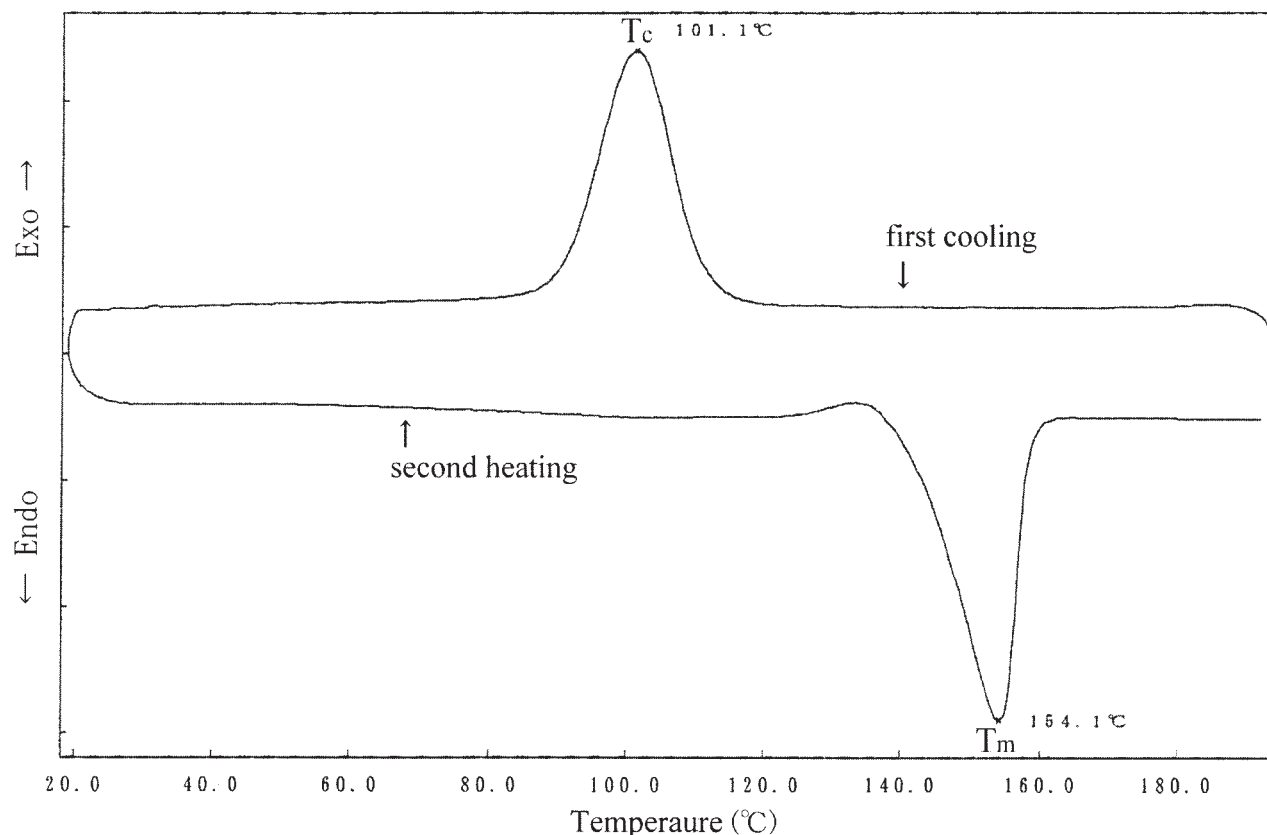


Figure 4 DSC curve of the polythioester from suberoyl dichloride (Run 5) on first cooling and second heating.

between  $T_m$  and the methylene numbers (Fig. 5), similar to the reference.<sup>16,17</sup>

The polythioester from isophthaloyl chloride (Run 9) is also a crystalline polymer since it showed an endothermic peak due to melting. The polythioester from terephthaloyl chloride (Run 11) didn't indicate an endothermic peak in the DSC measurement in the range of 0–320°C and also in the DTA curve under the initial

temperature of thermal degradation. However, this polythioester is also defined to be a crystalline polymer since crystalline peaks were observed in the WAXD pattern. These two aromatic polythioesters are rigid, brittle, and insoluble in solvents without phenol/tetrachloroethane mixture and pentafluorophenol. To improve their solubility, introduction of a substituent group into the aromatic ring of isophthaloyl dichloride was investi-

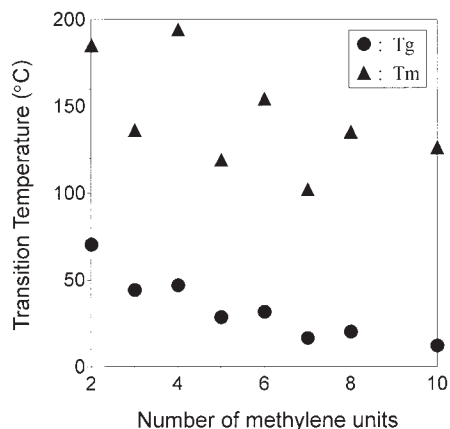
TABLE IV  
Properties of the Polythioesters Derived from MPS and Several Acid Dichlorides

Run	Acid dichloride	Tensile strength <sup>a</sup> (MPa)	Elongation <sup>a</sup> (%)	Tan $\delta$ peak <sup>b</sup> (°C)	Storage modulus <sup>c</sup> (GPa)	Oxygen permeability ( $\text{cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$ )
1	Succinyl	17.2	2	81.4	2.76	—
2	Glutaryl	45.6	3	58.6	1.42	$6.2 \times 10^{-15}$
3	Adipoyl	36.5	6	58.0	1.86	$7.8 \times 10^{-15}$
4	Pimeloyl	24.5	8	41.7	1.49	$1.3 \times 10^{-14}$
5	Suberoyl	27.4	9	48.0	1.65	$1.1 \times 10^{-14}$
6	Azelaoyl	23.4	43	34.8	1.39	$2.5 \times 10^{-14}$
7	Sebacoyl	24.3	14	38.4	1.58	$1.6 \times 10^{-14}$
8	Dodecanedioyl	26.0	276	21.9	0.88	$4.4 \times 10^{-14}$
9	Isophthaloyl	68.7	36	150.5	2.56	—
10	<i>t</i> -Butylisophthaloyl	53.2	10	184.4	3.62	—
11	Terephthaloyl	—	—	—	—	—

<sup>a</sup> Tensile rate: 5 mm/min.

<sup>b</sup> Determined by viscoelastic spectrometer.

<sup>c</sup> Determined by viscoelastic spectrometer at 25°C.



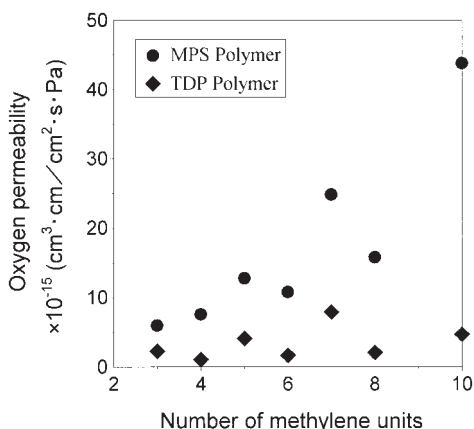
**Figure 5** Dependence of number of methylene units on transition temperature.

gated. The polythioester synthesized from MPS and *t*-butyl-isophthaloyl chloride (Run 10) has a high molecular weight and was soluble in chloroform, tetrahydrofuran, and so on. The DSC measurement around the melting temperature observed by microscope and WAXD evidenced that the polythioester with the bulky *t*-butyl group (Run 10) is an amorphous polymer. This would be because the bulky *t*-butyl group in the polymer disturbed its crystallization. It has high thermal resistance despite the amorphous polymer.

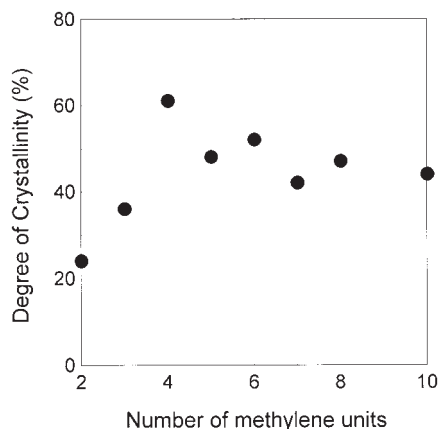
### Mechanical property and gas permeability

The tensile strengths, storage moduli,  $\tan \delta$  peaks, and oxygen permeabilities of the MPS polythioesters derived from aliphatic acid dichlorides are summarized in Table IV.

The tensile strengths at the breaking point of the MPS polythioesters become weak with an increase of the methylene numbers. The MPS polythioesters would soften and the tensile strengths decrease with



**Figure 6** Oxygen permeability of the sulfur-containing polymers.

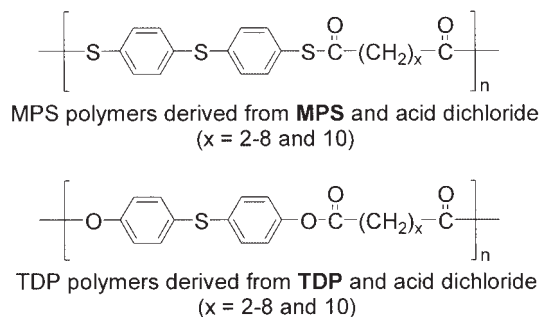


**Figure 7** Degree of crystallinity of the polythioesters.

longer methylene units. The MPS polythioesters of Runs 6–8 have  $T_g$ s similar to the testing temperature or lower, therefore, easily inducing plastic deformation resulting in low tensile strengths and high elongation.

The  $\tan \delta$  peaks due to their  $T_g$ s were slightly different from those determined by DSC measurement. An odd–even effect between the  $\tan \delta$  peaks and the methylene numbers was also observed. At 25°C, the storage moduli were relatively high and showed a similar relationship with the methylene numbers, as did the tensile strength.

The oxygen permeabilities (oxygen permeation coefficient) of the MPS polythioester films were plotted against the methylene numbers, as shown in Figure 6. The gas barrier property of the MPS polythioesters against oxygen permeation decreased with the increase of the methylene numbers. Furthermore, the oxygen permeabilities of the MPS polythioesters with even methylene numbers were lower than those of the MPS polythioesters with odd methylene numbers. Thus, the oxygen permeabilities of the MPS polythioesters also exhibited an odd–even effect based on the methylene numbers. In general, the rate of permeation of the gas molecule through the amorphous segments in the semicrystalline polymer is much faster than that through the crystalline segments. Accordingly, an increase of crystallinity generally gives an improvement of the gas barrier property. WAXD was used to determine the crystallinity of the specimens for measurement of oxygen permeability since the estimation of crystallinity is helpful to assess the odd–even effect. As shown in Figure 7, the crystallinity slightly decreases with increasing the methylene numbers of the polythioester. In addition, the crystallinity of the polythioesters with even methylene numbers is higher than that with odd methylene numbers. Thus, it was found that the odd–even effect for oxygen permeability of the polythioesters showed good correlation with the crystallinity.



Scheme 2

The oxygen permeabilities of the TDP polyester films in our previous paper<sup>16</sup> were also plotted against the methylene numbers, as shown in Figure 6. MPS polythioesters indicated higher oxygen permeabilities compared with TDP polyesters. This would be because the polythioesters have larger sulfur atoms on the thioester bond in the main chain than oxygen atoms on the ester bond of the TDP polyesters and lower polarity of the S–C bond in thioester than that of the O–C bond in ester bond would induce lower crystallization and more flexibility.

## CONCLUSION

MPS polythioesters were synthesized by polycondensation with bis(4,4'-mercaptophenyl)sulfide and a variety of acid dichlorides. The structures of the polythioesters thus prepared were confirmed by FTIR and <sup>1</sup>H-NMR. It was found that the MPS polythioesters have a high molecular weight and relatively high heat resistance.

The oxygen permeabilities of the MPS polythioesters against oxygen permeation are higher than those of the corresponding TDP polyesters and PET (40% crystallinity,  $2.6 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$ ).<sup>18</sup>

The MPS polythioesters with even methylene numbers show a higher  $T_g$ ,  $T_m$ , and oxygen gas barrier property than those with odd methylene numbers. In other words, an odd–even effect between the properties and the methylene numbers was observed also in these MPS polythioesters.

## References

1. Kobayashi, E.; Obata, T.; Aoshima, S.; Furukawa, J. *Polym J* 1990, 22, 803.
2. Kobayashi, E.; Obata, T.; Aoshima, S.; Furukawa, J. *Polym Prep Jpn (English Ed.)*, 1991, 40, E95.
3. Sato, E.; Yokozawa, T.; Endo, T. *Macromolecules*, 1993, 26, 5185.
4. Sato, E.; Yokozawa, T.; Endo, T. *Macromolecules*, 1993, 26, 5187.
5. Sato, E.; Yokozawa, T.; Endo, T. *J Polym Sci, Part A* 1996, 34, 669.
6. Koizumi, T.; Yoshioka, N.; Endo, T. *Macromolecules*, 1994, 27, 1284.
7. Podkoscilny, W.; Kultys, A. *J Polym Sci Polym Chem Ed* 1976, 14, 655.
8. Podkoscilny, W.; Kultys, A. *J Polym Sci Polym Chem Ed* 1984, 22, 1025.
9. Podkoscilny W.; Szubinska, S. *J Appl Polym Sci* 1986, 32, 3277.
10. Podkoscilny, W.; Szubinska, S. *J Appl Polym Sci* 1988, 35, 85.
11. Podkoscilny, W.; Tarasiuk, B. *Angew Makromol Chem* 1993, 207, 173.
12. Podkoscilny, W.; Rudz, W.; *Eur Polym J* 1993, 29, 1115.
13. Shaffer, T.; Percec, V. *J Polym Sci Polym Chem Ed* 1986, 24, 451.
14. Chen, T.; Wang, D.; Chiu, W.; Chen, L. *Angew Makromol Chem* 1996, 239, 133.
15. Hirano, H.; Tanaka, M. *Angew Makromol Chem* 1999, 267, 57.
16. Hirano, H.; Watase, S.; Tanaka, M. *J Appl Polym Sci* 2004, 91, 1865.
17. Yuki, S. *Plastics Age*; Tokyo, Japan, 1982, Vol. 101.
18. Michaels, A. S.; Vieth, W. R.; Barrie, J. A. *J Appl Phys* 1963, 34, 1.