

Linear Polymers with Sulfur in the Main Chain. II. Synthesis of Polyesters by Interfacial Polycondensation of Bis(4,4'-hydroxyphenyl)sulfide with Several Aliphatic Acid Dichlorides and Their Properties

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Received 17 December 2002; accepted 3 June 2003

ABSTRACT: The synthesis and properties of sulfur-containing polyesters derived from bis(4,4'-hydroxyphenyl)sulfide (TDP) and various acid dichlorides (AC) have been studied to evaluate the effect of the incorporation of sulfur in the main chains of polyesters. Polyesters derived from TDP and AC (with methylene numbers of 2–10) were synthesized by interfacial polycondensation in a 1,1,2,2-tetrachloroethane /water mixture using tetra-*n*-butyl ammonium bromide as a phase transfer catalyst. Through the use of gel permeation chromatography, it was determined that the polyesters thus obtained had high molecular weights. The thermal properties of the polyesters including the TDP moiety were evaluated by thermogravimetry/differential thermal analysis and by differential scanning calorimetry. The analyses indicated that the polyesters including the TDP moiety were crystalline polymers with

relatively high heat resistance. These polyesters were found to show an odd–even effect with the glass transition temperature and the melting point based on the methylene numbers. The tensile strength and storage modulus decreased with the methylene numbers. It was further found that the polyesters evidenced excellent barrier properties towards oxygen gas having an odd–even effect. In particular, it was shown that the polyesters with methylene numbers of 3, 4, 6, and 8 of methylene units have lower oxygen permeability than poly(ethylene terephthalate) (PET). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1865–1872, 2004

Key words: interfacial polycondensation; polyesters; sulfur; gas permeation

INTRODUCTION

Engineering plastics containing sulfur atoms, such as poly(phenylenesulfide), poly(ethersulfone), and polysulfone, have been put into practical use because they have superb 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. studied the addition reaction of dithiols to dialkenes and to dialkynes.^{1,2} Koizumi et al. synthesized polysulfide by the polyaddition reaction of dithiol and epoxide.³ The syntheses of polythioesters by interfacial polycondensation of aromatic and aromatic dithiols with aro-

matic and aliphatic acid dichlorides have been reported by Podkoscielny et al.^{4–7} Shaffer et al. found that polythioethers and copolythioethers with methylene numbers of 2–10 derived from 4,4'-biphenyldithiol and α,ω -dibromoalkanes exhibited thermotropic liquid crystalline characteristics.⁸ Chen et al. reported that incorporation of bis(4,4'-hydroxyphenyl)sulfide (TDP) improves the flexibility of polyarylate with poor impact strength.⁹

The excellent properties mentioned above were also achieved by introducing sulfur into polyesters, as we reported.¹⁰ In our previous work,¹⁰ the copolycondensation of TDP/bisphenol-A (BPA) and adipoyl dichloride (APC), improved the mechanical properties. In particular, the brittle quality of the homopolymer between TDP and APC was greatly reduced.

To further reduce the brittleness of the homopolymer, we examined polycondensations between TDP and acid dichloride having various numbers of methylene units (called methylene numbers in this article) as another method. This paper reports on the details of our syntheses of the polyesters by polycondensation between TDP and various aliphatic acid dichlorides, and discusses their properties.

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EXPERIMENTAL

Reagents

Commercially available reagents (Nacalai Tesque, Inc.) TDP and tetra-*n*-butyl ammonium bromide (Bu_4NBr) (or TBAB) were used as a phase transfer catalysts after drying without further purification. Commercially available reagents (Tokyo Kasei Kogyo Inc.), succinyl dichloride (SCC), suberoyl dichloride (SUC), and azelaoyl dichloride (AZC), were also used. 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 dichloride was recrystallized and dried just before use. 1,1,2,2-Tetrachloroethane (TCE, Nacalai Tesque, Inc.), used as a solvent, was dried with CaCl_2 and distilled before use.

Syntheses of polyesters derived from TDP

TDP (50 mmol) was dissolved in 500 mL of aqueous sodium hydroxide solution (0.4 mol L^{-1}) in a 2-L round-bottom flask equipped with a homomixer and a dropping funnel. Bu_4NBr (2.5 mmol) was then added to the solution. A TCE (600 g) solution of acid dichloride (52.5 mmol) was slowly added through the funnel at 10°C with vigorous stirring (8000 rpm) by the homomixer. After 15 min, the mixture was stirred at room temperature for 30 min. After being allowed to stand for 30 min, the reaction mixture in the funnel was separated into water and a cloudy organic layer. A white powder, precipitated out by pouring the organic layer into a large amount of methanol, was washed with water, methanol, and acetone, respectively, and dried under vacuum. For further purification, the polymers were dissolved in PhOH/TCE (1:1 in w/w) and reprecipitated by pouring the solution into methanol.

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

Analysis and measurement

The specific viscosity of the solution of polyesters (10 g L^{-1}) 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 disks with an Impact-420 Fourier transform spectrophotometer (Nicolet).

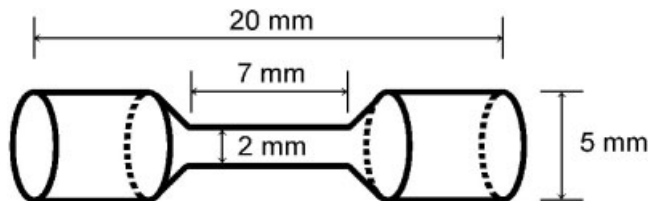


Figure 1 Sample shape of the polyesters for tensile testing.

$^1\text{H-NMR}$ (nuclear magnetic resonance) spectra were recorded on a JEOL NMR-270Q to confirm the structure of the polyesters.

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^{-1} . Polystyrene standards were used to calibrate the molecular weights.

To evaluate the heat resistance, thermogravimetric and differential thermal analyses (TG/DTA) were conducted under an air flow (200 mL min^{-1}) at a heating rate of 10 K min^{-1} .

The melting points and glass transition temperatures of the polyesters were determined using a SSC-5200 differential scanning calorimeter (DSC, Seiko Instrument, Inc.) at a heating rate of 10 K min^{-1} under a nitrogen flow (40 mL min^{-1}).

Dynamic mechanical measurement (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^{-1} . The films with ca. $100 \mu\text{m}$ thickness for DMA were prepared by compression molding at $160\text{--}230^\circ\text{C}$ and then annealed at the temperature, which were 30°C lower than the corresponding T_g s, for 1 h.

The specimens for tensile test were prepared with a CS-183MMX Minimax Mold System (CSI Co., Ltd.). All materials were vacuum dried at 110°C for 3 h and then injection molded at $175\text{--}245^\circ\text{C}$. The shape of injection-molded samples is shown in Figure 1. The tensile test was performed with a Shimadzu AG-50kN Autograph at a testing rate of 5 mm min^{-1} .

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 for DMA measurement.

A polarized microscope, Olympus BH-2, equipped with a Mettler FP82 temperature-control unit was used for observation of the morphology of polyesters.

Degree of the crystallinity of the films was determined from wide-angle X-ray diffraction traces (WAXD) corrected on a Rigaku X-ray diffractometer RINT 2500 40kV-50mA (Rigaku, Inc.).

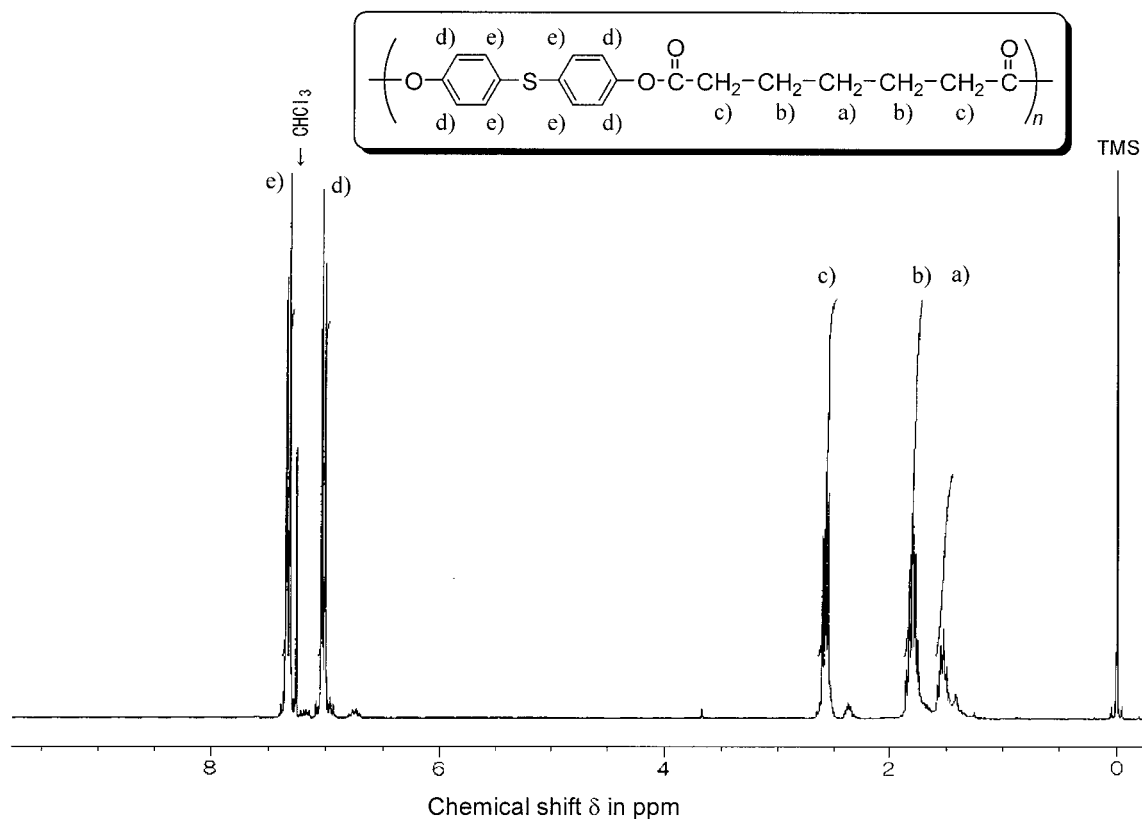


Figure 3 $^1\text{H-NMR}$ spectrum of poly(4,4'-thiodiphenylene pimelate) (run 4).

shown in Table II. The 5% mass loss temperatures are close because of the similar structures of the polyesters from aliphatic acid dichlorides. The rigid polyesters from the aromatic acid dichlorides showed higher 5% mass loss temperatures than those of the polyesters using aliphatic acid dichlorides.

The glass transition temperatures (T_g s) were determined from the DSC curves (Fig. 4 and Table II). The T_g s

decrease as the methylene numbers of the polyesters increase. The T_g s of the polyesters with even methylene numbers are slightly higher than those of the polyesters with odd methylene numbers. 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), both the melting points (T_m s) and the T_g s were reported to exhibit an odd–even effect on the basis

TABLE I
Characterization of Copolymers Derived from TDP and Several Acid Dichlorides

Run	Acid dichloride	Methylene number	Yield (%)	η_{sp}^a	$M_n^c (\times 10^3)$	$M_w^c (\times 10^3)$	$M_w/c M_n$
1	Succinyl	2	96	0.52	— ^e	— ^e	— ^e
2	Glutaryl	3	94	0.38	10.0 ^d	27.1 ^d	2.71 ^d
3	Adipoyl	4	94	1.12	— ^e	— ^e	— ^e
4	Pimeloyl	5	92	0.71	26.4 ^d	46.4 ^d	1.75 ^d
5	Suberoyl	6	91	0.64	— ^e	— ^e	— ^e
6	Azelaoyl	7	93	0.68	21.7 ^d	39.8 ^d	1.84 ^d
7	Sebacoyl	8	96	0.56	— ^e	— ^e	— ^c
8	Dodecandioyl	10	95	0.49	— ^e	— ^e	— ^e
9	Isophthaloyl	—	95	0.79	— ^e	— ^e	— ^c
10	Terephthaloyl	—	98	— ^b	— ^e	— ^e	— ^c

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

^b Insoluble in PhOH/TCE.

^c Determined by GPC.

^d Soluble part in THF.

^e Insoluble in THF.

TABLE II
Thermal Properties of the TDP Polyesters

Run	Acid dichloride	Initial mass loss temp. (°C)	5% mass loss temp. (°C)	T_g^a (°C)	T_1^b (°C)	T_2^b (°C)
1	Succinyl	353	368	69.0	235	— ^c
2	Glutaryl	353	369	56.2	190	— ^c
3	Adipoyl	348	360	50.3	209	218
4	Pimeloyl	330	358	32.2	144	159
5	Suberoyl	352	366	36.9	170	186
6	Azelaoyl	328	362	25.8	138	150
7	Sebacoyl	331	374	24.1	166	— ^c
8	Dodecanedioyl	328	372	8.9	162	— ^c
9	Isophthaloyl	404	436	147.5	— ^d	— ^d
10	Terephthaloyl	419	454	— ^d	— ^d	— ^d

^a Determined by DSC.

^b Observed in the DSC curve on second heating.

^c Not observed in the DSC curve on second heating.

^d Not observed in the DSC curve at temperature of -50 to 300°C.

of the methylene numbers.¹¹ 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 polyesters from aliphatic acid dichlorides were confirmed to be crystalline polymers. This is because they show one or two endothermic peaks on heating in the DSC curves and melt at around the endothermic temperature (T_1) and exothermic peak due to crystallization on cooling. An odd-even effect also exists between T_1 and the methylene numbers, similar to ref. 11. In addition, the polymers having

methylene numbers of 4-7 showed other endotherms on the first and second heating, designated as T_2 . However, only one exothermic peak was observed in the DSC curves of these polymers on cooling. T_2 is estimated to be the melting point of another crystalline state or the transition of the liquid crystalline to the isotropic state. The lower transition in the latter may be induced by the orientation of the higher transition on cooling because of very narrow range between the two transitions.

We assumed the polyesters form a liquid-crystalline phase and a polarized optical microscope was used for

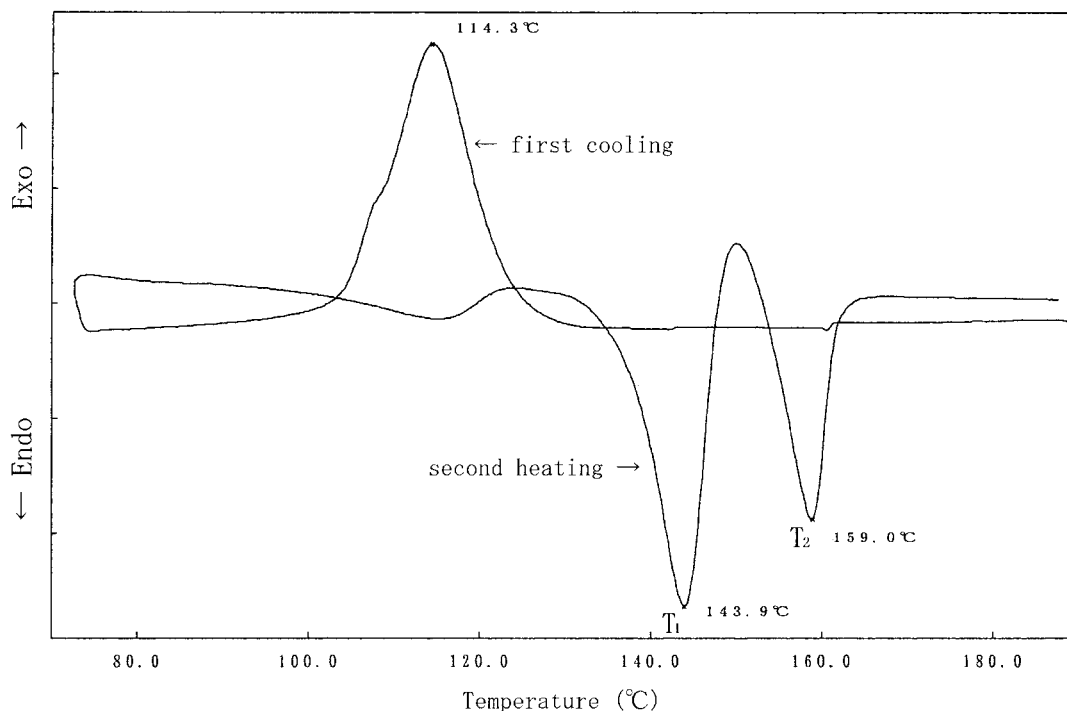


Figure 4 DSC curve of poly(4,4'-thiodiphenylene pimelate) (run 4) on first cooling and second heating.

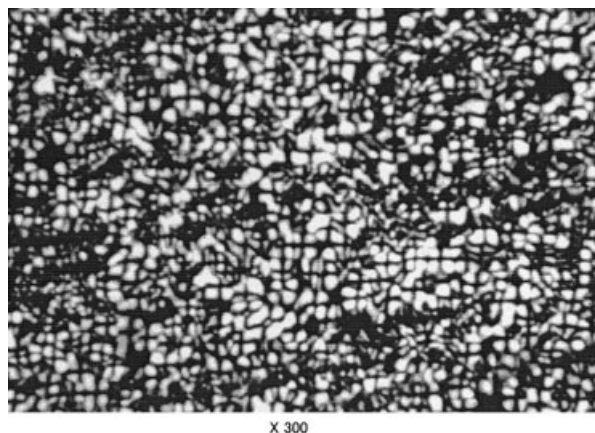


Figure 5 Polarized microscopic images of poly(4,4'-thiodiphenylene pimelate) (run 4).

confirmation of the liquid-crystalline phase. Figure 5 shows polarized microscopic image of poly(4,4'-thiodiphenylene pimelate) (run 4) on cooling from the isotropic state. Unfortunately, the polyesters (runs 3–6) showed only spherical crystals. The narrow angle of the sulfide bond in the diphenylsulfide group is fairly unfavorable for the conformation of a liquid-crystalline phase on these polyesters.

For the existence of two endothermic/exothermic peaks in the DSC curves, Kricheldorf et al. proposed following hypotheses¹²:

1. Bimodal distribution of their molecular weights.
2. Formation of a liquid-crystalline phase.
3. Two populations of crystallites with different sizes or a reversible change of crystal modifications in the solid state.

For first hypothesis, GPC measurement clarified the polyester runs 4 and 6, which dissolve in THF, have no bimodal distribution. Second, it can be hardly expected that the polyesters are liquid-crystalline poly-

mers as mentioned above. In order to confirm the third hypotheses, DSC measurement was performed again. After long annealing between the endothermic peaks, the lower endothermic peak of the polyesters in the DSC curve on heating approximately disappeared. Therefore the existence of two endothermic peaks in the DSC curve would be attributed to the third hypothesis, which was proposed by Kricheldorf et al.

Mechanical property and gas permeability

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

The tensile strengths at the breaking point of the TDP polyesters become weak with an increase of the methylene numbers. The TDP polyesters would soften and the tensile strengths decrease with longer methylene units. The TDP polyesters of runs 7 and 8 easily induce plastic deformation since they have lower T_g s than the testing temperature and, therefore, result in low tensile strengths.

The $\tan \delta$ peaks, which were determined by dynamic mechanical measurement, were matched with their T_g s. They 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 (Fig. 6). At 25°C, the storage moduli were relatively high and showed a similar relationship with the methylene numbers, as did the tensile strength¹².

The oxygen permeabilities of the TDP polyester films were plotted against the methylene numbers, as shown in Figure 7. The gas barrier property of the TDP polyesters against oxygen permeation decreased with the increasing of the methylene numbers. Furthermore, the oxygen permeabilities of the TDP polyesters with even methylene numbers were lower than those of the TDP polyesters with odd numbers. Thus, the

TABLE III
Properties of the Polyesters Derived from TDP and Several Acid Dichlorides

Run	Acid dichloride	Tensile strength at break ^a (MPa)	Tan δ peak ^b (°C)	Storage modulus ^c (GPa)	Oxygen permeability (cm ³ · cm/cm ² · s · Pa)
1	Succinyl	58.5	81.4	3.23	—
2	Glutaryl	30.2	61.7	2.62	2.4×10^{-15}
3	Adipoyl	38.5	52.7	2.19	1.2×10^{-15}
4	Pimeloyl	30.6	40.9	1.80	4.2×10^{-15}
5	Suberoyl	29.7	42.9	1.66	1.8×10^{-15}
6	Azelaoyl	29.1	31.1	1.12	8.0×10^{-15}
7	Sebacoyl	26.8	35.5	0.83	2.2×10^{-15}
8	Dodecanedioyl	17.2	27.4	0.13	4.8×10^{-15}

^a Tensile rate : 5 mm/min.

^b Measured by viscoelastic spectrometer.

^c Determined by viscoelastic spectrometer at 25°C.

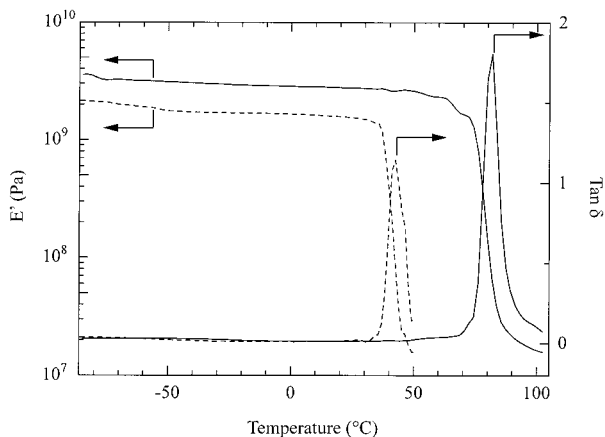


Figure 6 Storage modulus and tanδ of the polyesters.

oxygen permeabilities of the TDP polyesters also exhibited an odd–even effect based on the methylene numbers. In particular, the TDP polyesters of runs 2, 3, 5, and 7 exhibited lower oxygen permeabilities (permeation coefficient, $1.2\text{--}2.4 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$) in comparison with that of PET (40% crystallinity, $2.6 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$).¹³ 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, increasing of crystallinity generally gives an improvement of gas barrier property. As the estimation of crystallinity will be helpful to assess the odd–even effect between properties and number of methylene units, a WAXD was used to determine the crystallinity of the specimens for measurement of oxygen permeability. As shown in Figure 8, the crys-

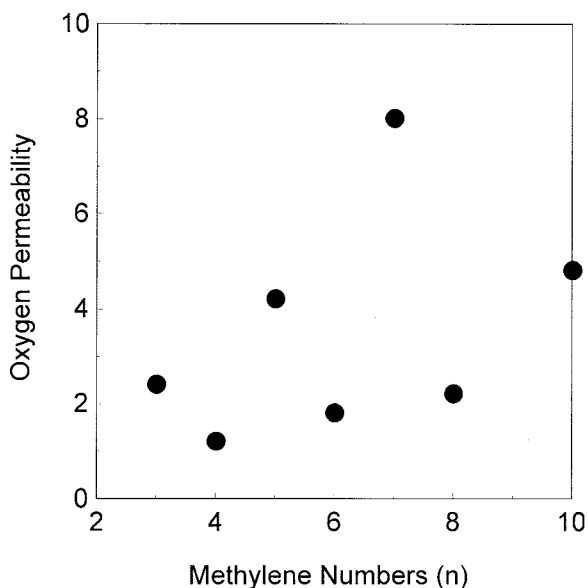


Figure 7 Oxygen permeability of the polyesters.

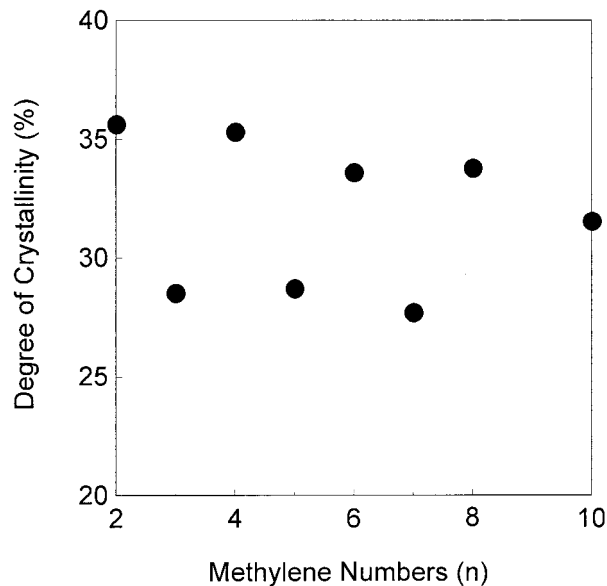


Figure 8 Degree of crystallinity of the polyesters.

tallinity decreases slightly as the methylene numbers of the polyester increase. Furthermore, the crystallinity of the polyesters with even methylene numbers is higher than that with odd methylene numbers. From these results, it was found that the odd–even effect for oxygen permeability of the polyesters exhibited the good correlation with the crystallinity.

CONCLUSION

TDP polyesters were synthesized from bis(4,4'-hydroxyphenyl)sulfide (TDP) and a variety of acid dichlorides by interfacial polycondensation. The structures of the polyesters thus prepared were confirmed by FTIR and ¹H-NMR. It was found that the TDP polyesters have a high molecular weight and high degree of heat resistance.

Some TDP polyesters were observed to have two endothermic peaks on heating in DSC curve. It was clarified that the polyesters with two endothermic peaks contain two populations of crystallites with different sizes or displaying a reversible change of crystal modifications in the solid state.

The TDP polyesters exhibit very high gas barrier properties against oxygen permeation. In particular, the polyesters with 3, 4, 6, and 8 methylene units (runs 2, 3, 5, and 7) have lower oxygen permeabilities than that of PET.

The TDP polyesters with odd methylene numbers show a higher *T_g*, melting point (*T₁*), crystallinity, and gas barrier property against oxygen permeation than do the TDP polyesters with even methylene numbers. In other words, an odd–even effect between the properties and the methylene numbers was observed in these TDP polyesters.

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