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Synthesis and characterization of new polyesters derived from 1,6- or 4,9-diamantanedicarboxylic acyl chlorides with aryl ether diols

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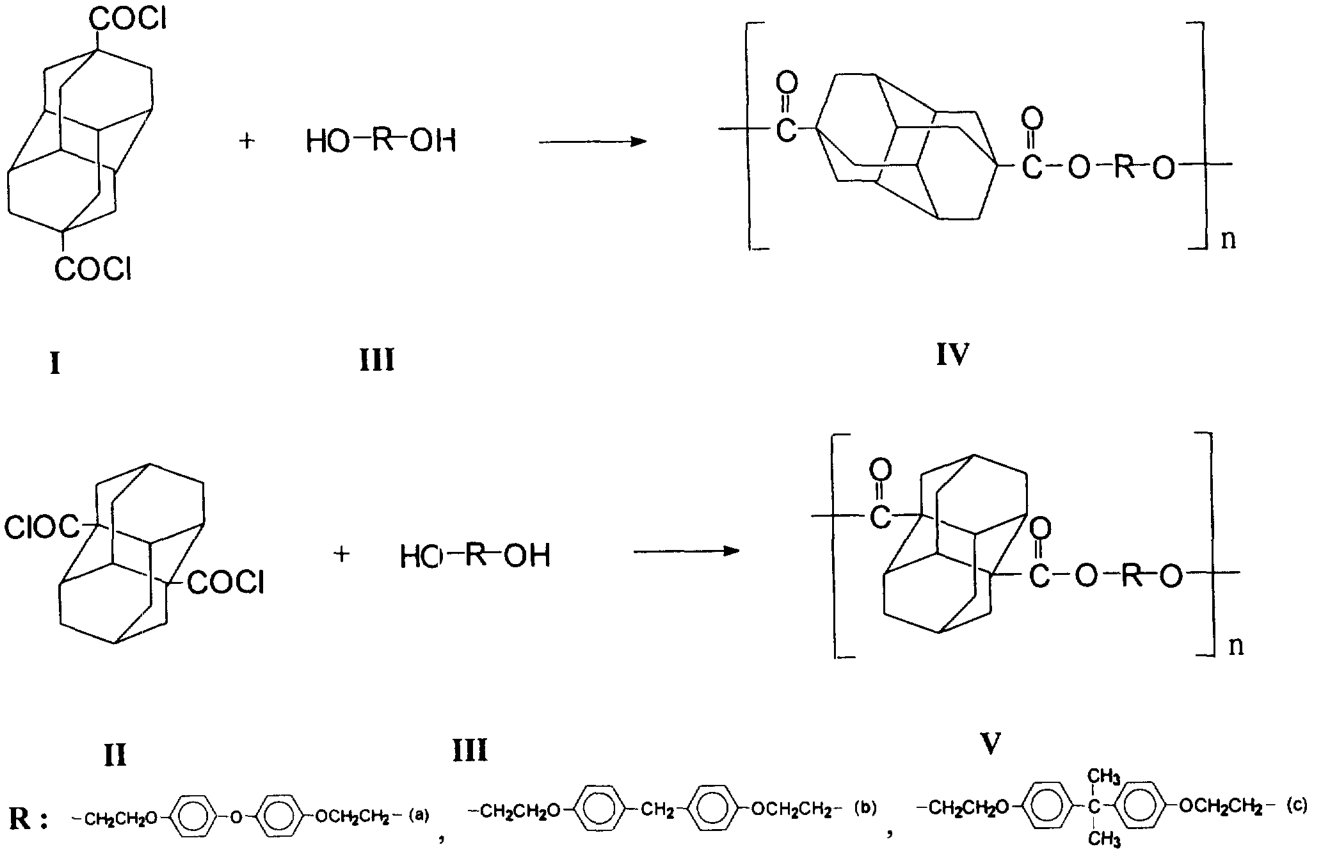
A series of new polyesters was synthesized by high-temperature solution polycondensation of 1,6- or 4,9-diamantanedicarboxylic acyl chlorides with aryl ether diols. All polyesters had good solubilities and could be soluble in chloroform, nitrobenzene, *o*-chlorophenol, *N*-dimethylformamide (DMF), and *o*-dichlorobenzene. Number-average molecular weights (M_n) of polyesters **IV** and **V** were 40 000~280 000 and 48 000~150 000, respectively. The glass transition temperatures of polyesters were 90–108°C and 102–132°C, as determined by differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (DMA), respectively. The temperatures at 5% weight loss of polyesters ranged from 338 to 395°C in air and from 385 to 403°C in N_2 atmosphere. Polyesters had tensile strengths of 34.9~45.5 MPa, elongation to breakage values of 3.5~4.6%, and initial moduli of 1.4~1.6 GPa. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyesters; diamantane; synthesis)



Scheme 1

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INTRODUCTION

Polyarylates have good thermal stability, solvent resistance, and good mechanical properties, and are therefore applied widely in the aviation, automobile, and electronic industries. However, most polyarylates encounter processing difficulty due to their high glass transition or melting temperatures, coupled with insolubility in common organic solvents[1]. Copolymerization and utilization of unsymmetrically substituted monomers are the two most commonly used synthetic approaches in obtaining compositions whose transition temperatures lie in a managable temperature range either for processing or for characterization[2]. In other methods for improving their solubilities, several approaches have been taken: replacing the conventional monomers with ones containing pendant groups[3–10], or introducing kinks of flexible units in the main chain[11–13].

Diamantane is a cycloaliphatic-cage hydrocarbon containing an 'extended-cage' adamantane structure[14,15]. Although diamantane has been investigated for many years, only a few examples of the polymers based on diamantane are known[16–22]. Recently, we reported that incorporation of diamantyl units into poly(amide-imide)s and polyamides had good thermal stability, good mechanical properties at temperatures well above 350°C, and high glass transition temperatures[20–22]. With respect to the incorporation of diamantane into polyester, we only recently reported that incorporation of 1,6-diamantyl groups into polyesters has good thermal stabilities, good mechanical properties at temperatures well above 350°C, and high glass transition temperatures[19]. Preparing diamantane-based polymers has received considerable attention owing to their unique physical properties.

Herein, we describe the synthesis of a new soluble polyester from 4,9- or 1,6-diamantanedicarboxylic acyl chlorides and various aryl ether diols (**III**) by the high-temperature solution method (*Scheme 1*). The polyesters' solubilities can be enhanced by incorporating the ethylene ether linkage into their backbones. In addition, the solubilities, dynamic mechanical properties, and thermal properties of polyesters were investigated.

EXPERIMENTAL

Materials

o-Dichlorobenzene was purified by distillation under reduced pressure over calcium hydride. 1,6-Diamantanedicarboxylic acyl chloride (**II**) and 4,9-diamantanedicarboxylic acid were synthesized in our previous research[19,21]. Bis(4-(2-hydroxyethoxy)phenyl)ether ($\mathbf{III}_a$), bis(4-(2-hydroxyethoxy)phenyl)methane ($\mathbf{III}_b$) and 2,2-bis(4-(2-hydroxyethoxy)phenyl)propane ($\mathbf{III}_c$) were synthesized from the corresponding phenols and ethylene carbonate by a previous method[23,24].

Bis(4-(2-hydroxyethoxy)phenyl)ether (III_a): mp 134–136°C (lit.[24] 119~121°C); i.r. (KBr) 3500, 3080, 2950, 1600, 1247 $\mathrm{cm^{-1}}$; MS (EI) m/z 290 (M^+, 100); ^{1}H n.m.r. (400 MHz, acetone-d_6) δ 3.79 (t, 4H, CH_2), 3.99 (t, 4H, CH_2), 6.86 (m, 8H, ArH); ^{13}C n.m.r. (100 MHz, acetone-d_6) δ 61.47 (t), 71.24 (t), 116.65 (d, Ar), 120.45 (d, Ar), 152.73 (s, Ar), 156.11 (s, Ar).

Bis(4-(2-hydroxyethoxy)phenyl)methane (III_b): mp 104~106°C (lit.[24] 109~110°C); i.r. (KBr) 3450, 3050, 2895, 1600, 1242 $\mathrm{cm^{-1}}$; MS (EI) m/z 288 (M^+, 100); ^{1}H n.m.r. (400 MHz, acetone-d_6) δ 3.79 (m, 6H, CH_2), 3.85 (t, 2H, OH), 3.97 (t, 4H, CH_2), 6.80 (d, 4H, ArH), 7.05 (d, 4H, ArH); ^{13}C n.m.r. (100 MHz acetone-d_6) δ 41.13 (t), 61.88 (t), 70.99 (t), 115.80 (d, Ar), 130.94 (d, Ar), 135.29 (s, Ar), 158.87 (s, Ar).

2,2-Bis(4-(2-hydroxyethoxy)phenyl)propane (III_c): mp 112–114°C (lit.[24] 110~111°C); i.r. (KBr) 3450, 3050, 2989, 1600, 1244 $\mathrm{cm^{-1}}$; MS (EI) m/z 316 (M^+, 38), 301 (100); ^{1}H n.m.r. (400 MHz, acetone-d_6) δ 1.56 (s, 6H, CH_3), 3.79 (m, 4H, CH_2), 3.86 (t, 2H, OH), 3.97 (t, 4H, CH_2), 6.78 (d, 4H, ArH), 7.08 (d, 4H, ArH); ^{13}C n.m.r. (100 MHz, acetone-d_6) δ 31.34 (q), 42.16 (s), 61.37 (t), 70.40 (t), 114.69 (d, Ar), 128.37 (d, Ar), 143.83 (s, Ar), 157.83 (s, Ar).

Synthesis of 4,9-diamantanedicarboxylic acid chloride (I)

4,9-Diamantanedicarboxylic acid (4.20 g, 15.2 mmol) was refluxed in 80 mL of thionyl chloride in a nitrogen atmosphere for 8 h. The thionyl chloride was removed under reduced pressure, and the residual crude product purified by vacuum sublimation. White crystals (4.16 g, 87% yield) of **I** were obtained. Compound **I**: mp 234–236°C; i.r. (KBr) 2914, 2856, 1781, 1125, 984 $\mathrm{cm^{-1}}$; MS (EI) m/z 312 (M^+, 10), 249 (100); ^{1}H n.m.r. (400 MHz, DMSO-d_6) δ 1.76 (m, 18H, hydrogen of diamantane); ^{13}C n.m.r. (100 MHz, DMSO-d_6) δ 35.56 (C-1,2,6,7,11,12), 37.69 (C-4,9), 38.35 (C-3,5,8,10,13,14), 178.47 (C=O); anal. calc. for $C_{16}H_{18}O_2Cl_2$: C, 61.34; H, 5.75. Found: C, 61.61; H, 5.85.

Characterization

A Bio-Rad FTS-40 *FT*i.r. spectrophotometer was used to record i.r. spectra (KBr pellets). In a typical experiment, an average of 20 scans per sample was made. MS spectra were obtained by using a JEOL JMS-D300 mass spectrometer. ^{1}H and ^{13}C n.m.r. spectra were recorded on Bruker AM-300WB or AM-400 Fourier transform nuclear magnetic resonance spectrometers using tetramethyl silane (TMS) as the internal standard. A Perkin-Elmer 240C elemental analyzer was used for elemental analysis. The melting points were obtained by a standard capillary melting point apparatus. Inherent viscosities of all polymers were determined at 0.5 g $\mathrm{dL^{-1}}$ concentration using an Ubbelohde viscometer. Gel permeation chromatography (GPC) on soluble polymers was performed on an Applied Biosystem at 70°C with two PLgel 5 μm mixed-C columns in the NMP solvent system. The flow rate was 0.5 mL $\mathrm{min^{-1}}$, detection was by u.v., calibration was based on polystyrene standards. Qualitative solubility was determined using 0.01 g of polymer in 2 ml of solvent. A Du Pont 9900 differential scanning calorimeter (d.s.c.) and a Du Pont 9900 thermogravimetric analyzer were then employed to study the transition data and thermal decomposition temperature of all the polymers. The d.s.c. was run under a nitrogen stream at a flow rate of 30 cc $\mathrm{min^{-1}}$ and a heating rate of 20°C $\mathrm{min^{-1}}$. Thermogravimetric analysis (TGA) was carried out under a nitrogen flow of 50 cc $\mathrm{min^{-1}}$ with a heating rate of 20°C $\mathrm{min^{-1}}$. Dynamic mechanical analysis (DMA) was performed on a Du Pont 9900 thermal analyzer system. A sample 10 mm in length, 2 mm in width and approximately 0.08 mm in thickness was used. The dynamic shear modulus was measured at a resonance mode. The wide angle X-ray diffraction measurements were performed on a Philips PW 1730-10 X-ray diffractometer using CuKα radiation.

Tensile properties were determined from stress–strain curves with a Toyo Baldwin Instron UTM-III-500 with a load cell of 10 kg at a drawing speed of 5 cm $\mathrm{min^{-1}}$. Next, measurements were performed at 28°C with film specimens (about 0.1 mm thick, 1.0 cm wide and 5 cm long) and an average of at least five individual determinations was used.

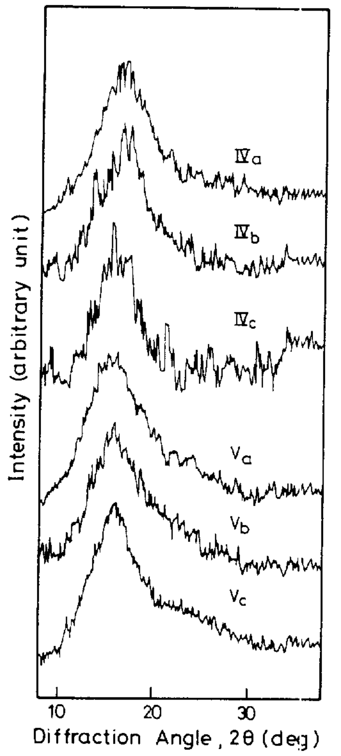

Figure 1 Wide-angle X-ray diffraction curves of polyesters

Polymerization

A typical example of polycondensation is given below.

Polyester IV_a from I and III_a. A mixture of 0.563 g (1.8 mmol) of **I** and 0.522 g (1.8 mmol) of $\mathbf{III_a}$ in 6 mL of *o*-dichlorobenzene was heated and stirred at 200°C for 20 h under nitrogen. The viscous solution thus obtained was poured into 500 mL of methanol. The precipitated polymer was collected by filtration, thoroughly washed with hot methanol, and dried at 100°C in a vacuum oven. The yield was nearly quantitative. The inherent viscosity and M_n of polyester $\mathbf{IV_a}$ were 0.84 dL g^{-1} and 280 000, respectively. The i.r. spectrum of polyester film $\mathbf{IV_a}$ contained absorption peak at 1723 cm^{-1} (C=O str), i.e. characteristic of the ester group.

RESULTS AND DISCUSSION

Monomer synthesis

4,9-Diamantanedicarboxylic acyl chloride (**I**) was prepared from 4,9-diamantanedicarboxylic acid with thionyl chloride in 87% yield (*Figure 1*). In the elemental analysis data, characteristic peaks in the n.m.r. spectra and characteristic bands in the i.r. spectrum correlated well with 4,9-diamantanedicarboxylic acyl chloride (**I**).

Effect of the reaction parameters on the inherent viscosities of IV_a

Part I of *Table 1* reveals that the inherent viscosities of polyester $\mathbf{IV_a}$ increased with increasing monomer concentration up to 0.30 M. Higher concentrations of monomer had

Table 1 Effect of reaction parameters on polymerization[a] of $\mathbf{IV_a}$

	Reaction conditions		Polymer		
Part	Monomer (mol L^{-1})	Reaction temp. (°C)	Yield (%)	η_{inh}^{b} (dL g^{-1})	Remark[c]
I	0.10	200	96.3	0.49	S
	0.30	200	98.2	0.84	S
	0.50	200	98.6	0.83	S
	0.30	150	97.5	0.46	S
II	0.30	180	97.2	0.60	S
	0.30	200	98.2	0.84	S
	0.30	220	97.2	0.50	S

[a] Polymerization conditions [**I**] = [$\mathbf{III_a}$], 20 h
[b] Measured at 30°C at a concentration of 0.5 g dL^{-1} in 1,4-dioxane
[c] Appearance of the polymerization system: S, homogeneous solution

Table 2 Synthesis of polyesters[a]

Polymer	Yield (%)	η_{inh}^{b} (dL g^{-1})	$M_n^c \times 10^{-4}$	M_w/M_n	Remark[d]
$\mathbf{IV_a}$	98.2	0.84	28.78	1.36	S
$\mathbf{IV_b}$	96.4	0.41	4.08	1.70	S
$\mathbf{IV_c}$	96.1	0.33	5.01	1.51	S
$\mathbf{V_a}$	98.0	0.75	15.37	2.66	S
$\mathbf{V_b}$	96.7	0.40	8.14	1.46	S
$\mathbf{V_c}$	94.2	0.27	4.87	1.46	S

[a] Polymerization was carried out with 0.3 M of each monomer in *o*-dichlorobenzene at 200°C for 20 h
[b] Measured at 30°C at a concentration of 0.5 g dL^{-1} in 1,4-dioxane
[c] By GPC (relative to polystyrene)
[d] Appearance of the polymerization system: S, homogeneous solution

Table 3 Solubilities of polyesters[a]

Solvent	Polymer IV_a	IV_b	IV_c	V_a	V_b	V_c
o-Chlorophenol	++	++	++	+	+	++
o-Dichlorobenzene	++	++	++	+	++	++
Chloroform	++	++	++	++	++	++
DMF	−	++	−	−	++	−
NMP	++	++	++	++	++	++
Nitrobenzene	++	++	++	++	++	++

[a] Solubility: ++, soluble at room temperature; +, soluble on heating at 60°C; −, insoluble on heating at 60°C. Abbreviation: NMP, *N*-methyl-2-pyrrolidone; DMF, *N*,*N*-dimethylformamide

an adverse effect on the solubility of polyester IV_a. This caused a decrease of the inherent viscosity of the polyester. Part II of *Table 1* also indicates that the inherent viscosities of polyester IV_a increased with reaction temperature. However, a decreased inherent viscosity of 0.50 dL g^{-1} was obtained when the reaction was performed at 220°C. This decrease in viscosity is attributed to an increase in side reactions at an excessively high temperature. From the above results we can infer that the most favourable conditions for this system are a monomer concentration of 0.30 M and reaction temperature of 200°C.

Table 4 Tensile properties of polymer films[a]

Polymer	Strength to break (MPa)	Elongation to break (%)	Initial modulus (GPa)
IV_a	45.5	4.4	1.4
IV_b^b	42.5	4.1	1.5
IV_c	36.3	3.5	1.6
V_a	41.3	4.3	1.4
V_b^b	41.6	4.6	1.5
V_c	34.9	4.3	1.5

[a] Films were cast from polymer solution of *o*-dichlorobenzene
[b] Films were cast from polymer solution of dichloromethane

Synthesis of polyesters IV and V

Various new polyesters were prepared from **I** or **II** with the corresponding aryl ether diols **III** by using the most favourable conditions for the reaction with diol III_a. The results of the polycondensation are listed in *Table 2*. All the polyesters were obtained in nearly quantitative yield. Polyesters **IV** and **V** had inherent viscosities of 0.33~0.84 dL g^{-1} and 0.27–0.75 dL g^{-1}, respectively. According to GPC data, polyesters **IV** and **V** had medium and high molecular weights. *Table 2* also indicates that inherent viscosities of polyesters derived from III_c were lower than those of polyesters derived from the other diols **III**. This lower viscosity is possibly attributed to the fact that III_c has the highest steric hindrance among all three diols. The steric hindrance retarded further polycondensation. Therefore, the inherent viscosities of IV_c and V_c were lower. The i.r. spectroscopy confirmed the formation of polyesters. *FT*i.r. spectra of the polyesters detected characteristics of ester bands appearing at around 1725 cm^{-1} (C=O str).

Characterization of polyesters

The solubilities of these polymers was tested in various solvents. *Table 3* summarizes the results. Owing to the flexible ethylene ether element, these polyesters were amorphous and soluble in a number of common organic solvents, e.g. chloroform, nitrobenzene, *o*-chlorophenol, DMF, and *o*-dichlorobenzene. The structural characterization was first made by X-ray methods with polyesters **IV** and **V**. Owing to the incorporation of bulky diamantyl elements and flexible ether groups into the polyesters, both polyesters **IV** and **V** had nearly the same amorphous patterns with broad peaks appearing (2θ) at around 16°, as shown in *Figure 1*.

Tough and colourless films of all polyesters were obtained by casting from their *o*-dichlorobenzene or dichloromethane solutions. The mechanical properties were determined via an instron machine. *Table 4* summarizes the polyesters' tensile properties. Polyesters **IV** and **V** had medium tensile strengths of 36.3~45.5 MPa and 34.9~41.6 MPa, respectively. Owing to the rigid diamantyl element, all polyesters were fractured in a brittle manner under the tensile test. Therefore, the elongation to breakage values of polyesters **IV** and **V** were low.

Thermal analysis was performed by means of d.s.c.,

Table 5 Thermal properties of polyesters

Polymer	T_g^a	T_g^b	T_5^c (°C) In N_2	T_5^c (°C) In air	T_d^d (°C) In N_2	T_d^d (°C) In air
IV_a	108	130	394	338	447	412
IV_b	96	128	403	395	443	453
IV_c	100	116	394	376	451	458
V_a	96	110	386	361	446	453
V_b	90	132	397	387	445	449
V_c	99	102	385	359	461	453

[a] Glass transition measured by d.s.c.
[b] Glass transition measured by DMA
[c] Temperature at which 5% weight loss recorded by TGA at a heating rate of 20°C min^{-1}
[d] Maximum decomposition temperature of polymer films recorded by TGA at a heating rate of 20°C min^{-1}

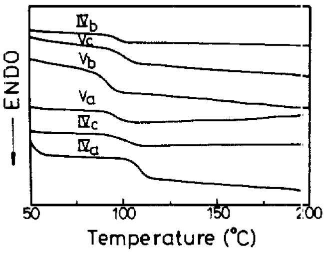

Figure 2 D.s.c. thermograms of the studied polymers at a heating rate of 20°C min^{-1} in nitrogen atmosphere

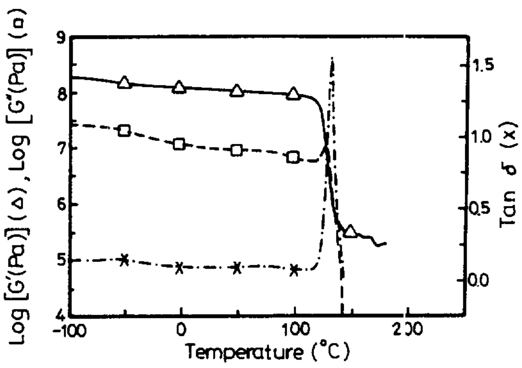

Figure 3 Dynamic mechanical analysis curves (G' (shear storage modulus Δ), G'' (shear loss modulus, □) and tan δ (X)) for **IV**$_a$ at a heating rate of 5°C min^{-1}

DMA and TGA. *Table 5* summarizes the results. The temperatures of polyesters at a 5% weight loss ranged from 338 to 395°C in air and from 385 to 403°C in N_2 atmosphere. As regards the d.s.c. experiment, initial heating of the samples was curtailed at 150°C. In addition, glass transition temperatures (T_g) and other thermal properties were evaluated according to the d.s.c. charts of the second heating. According to *Figure 2*, all polyesters displayed typical T_g values. Owing to the flexible ethylene ether element, the T_g values of all polyesters were medium at around 95°C.

The mechanical relaxation spectra of polyester **IV**$_a$ are shown in *Figure 3*. Based on tan δ and G'' peaks, two relaxations appeared at *ca.* −50 and 130°C. The low-temperature transition, termed γ (*ca.* −50°C), is a typical relaxation for polyesters. This relaxation is attributed to the reorientation of the carbonyl groups[3,25]. The glass relaxation process of **IV**$_a$ was observed at around 130°C in G'' and tan δ. This relaxation is associated with a two order step decrease in G'. *Table 5* summarizes the T_g values of all polyesters **IV** and **V**. The T_g values of both types of polyesters **IV** and **V** are close. This is attributed to the fact that the two types of polyesters have similar chemical structures in their backbones.

CONCLUSIONS

According to the results presented herein, introducing diamantane and ethylene ether elements into the polyester backbones yielded polyesters with good solubility, good thermal stability, and medium glass transition temperature. The M_n values of polyesters **IV** and **V** were 40 000~280 000 and 48 000~15 0000, respectively. All polyesters had good solubilities and were soluble in chloroform, nitrobenzene, *o*-chlorophenol, DMF, and *o*-dichlorobenzene. These polyesters had tensile strengths of 34.9~45.5 MPa, elongation to breakage values of 3.5~4.6%, and initial moduli of 1.4~1.6 GPa. The temperatures of polyesters at 5% weight loss ranged from 338 to 395°C in air and from 385 to 403°C in N_2 atmosphere. The glass transition temperatures of polyesters were 90~108°C and 102~132°C by means of d.s.c. and DMA, respectively.

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