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Synthesis and Properties of New Polycyclic Polyesters from 1,6-Diamantanedicarboxylic Acyl Chloride and Aromatic Diols

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ABSTRACT: A series of new polyesters was synthesized by high-temperature solution condensation of 1,6-diamantanedicarboxylic acyl chloride with aromatic diols in *o*-dichlorobenzene. The polyesters had inherent viscosities of 0.20−1.50 dL/g and were obtained in high yield. Diamantane-containing polyesters IIIa, IIIb, and IIIc show secondary transitions at low temperatures and a mainly melting transition at around 375 °C over a range of −100 to +400 °C, but no glass transition was observed by DMA. Particularly, a step in modulus at the β transition at around 60 °C was also observed in diamantyl-containing polyesters. In all cases, these polyesters show a rather high G' value (about 10^8 Pa) up to 350 °C. The 5% weight loss temperatures of these polyesters were in the range 403−451 °C in nitrogen. The melting temperatures of polymers IIId, IIIe, and IIIf were 429, 369, and 395 °C, respectively. The glass transition temperature of IIId was 267 °C. Polymers IIIa, IIIb, and IIIc were soluble in *o*-chlorophenol and could be cast into transparent, tough, and flexible films. Their cast films had a tensile strength at break up to 80.5 MPa, an elongation to break up to 15.1%, and an initial modulus up to 1.6 GPa. The dielectric constants of polyesters IIIa, IIIb, and IIIc ranged from 1.3 to 1.9.

Introduction

Because polyarylates have good thermal stability, solvent resistance, and good mechanical properties, they are applied to many industries. However, most of these polymers have a drawback in processing owing 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 popular synthetic approaches in obtaining compositions whose transition temperatures lie in a manageable temperature range either for processing or for characterization.[2] Two approaches have been taken to improve their solubility: replacing the conventional monomers with ones containing pendant groups,[3−16] and introducing kinks of flexible units in the main chain.[17−20]

Diamantane is a cycloaliphatic cage hydrocarbon containing an "extended cage" adamantane structure.[21,22] Although diamantane has been investigated for many years,[23−26] its use in polymers is limited.[27,28] There has been one report indicating that the thermoset resins prepared from diethynyldiamantane are stable to 518 °C in air.[28] This unusually high thermal stability for an aliphatic hydrocarbon polymer presumably results from the presence of diamantane units in the polymer backbone, which due to their "diamond-like" structure retard degradation reactions resulting from nucleophilic attack, electrophilic attack, or elimination reaction.[21,29] Recently, we reported that a series of novel polyamides had been synthesized by direct polycondensation of 1,6-diamantanedicarboxylic acid with various aromatic diamines. Colorless polyamide films were obtained with good mechanical properties up to temperatures well above 350 °C.[30] From these results, 1,6-diamantanedicarboxylic acyl chloride would be a potential monomer for the preparation of colorless and transparent polyester films. In this article, we describe a successful synthesis of novel soluble polyesters from 1,6-diamantanedicarboxylic acyl chloride (I) and various aromatic diols by the high-temperature solution method (Scheme 1). The polymers obtained were studied by differential scanning calorimetry, thermogravimetric analysis, thermomechanical analysis, X-ray diffraction, and dynamic mechanical analysis.

Experimental Section

Materials. 2,2-Bis(4-hydroxyphenyl)propane (IIa), 4,4′-dihydroxydiphenylmethane (IIb), 4,4′-dihydroxydiphenyl ether (IIc), hydroquinone (IId), and 4,4′-bis(4-hydroxyphenyl) sulfone (IIf) were purified by vacuum sublimation. Biphenyl-4,4′-diol (IIe) was purified by recrystallization. *o*-Dichlorobenzene was purified by distillation under reduced pressure over calcium hydride. Diamantane was prepared by a previous method from norbonadiene in three steps.[31,32] 1,6-Diamantanedicarboxylic acid was prepared from diamantane in two steps. Diamantane was reacted with dry bromine to give 1,6-dibromodiamantane, and then Koch−Haaf carboxylation was carried out to obtain 1,6-diamantanedicarboxylic acid. The detailed procedure for synthesis of 1,6-diamantanedicarboxylic acid has been shown in our previous research.[30]

Synthesis of 1,6-Diamantanedicarboxylic Acyl Chloride (I). 1,6-Diamantanedicarboxylic acid (4.2 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 residue crude product was purified by vacuum sublimation. White crystals (4.3 g, 90% yield) of I were obtained. Its properties are as follows: mp 227−229 °C; IR (KBr) 1781 (C=O), 1125 (C−O), 984 cm^{-1} (COCl). EIMS *m/z* (%) 312 (M^+, 1), 277 (2), 276 (4), 249 (100); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.65 (4H, m, J = 13.3 Hz, H-3a,8a,10a,14a), 1.89 (8H, m, J = 14.3 Hz, H-3b,5,8b,10b,13,14b), 2.03 (2H, m, H-4,9), 2.37 (4H, s, H-2,7,11,12) (Figure 2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 25.28 (C-4,9), 33.64 (C-3,8,10,14), 38.61 (C-2,7,11,12), 40.21 (C-5,13), 56.78 (C-1,6), 178.67 (COCl) (Figure 1). Anal. Calcd for $C_{16}H_{18}O_2Cl_2$: C, 61.34; H, 5.75. Found: C, 61.38; H, 5.90.

Polymerization. A typical example of polycondensation is given below.

Polyester IIIc from I and IIc. A mixture of 1.565 g (5.0 mmol) of I and 1.01 g (5.0 mmol) of IIc in 10 mL of *o*-dichlorobenzene was heated with stirring 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, washed thoroughly with hot methanol, and dried at 100 °C in a vacuum oven. The polymer weighed 2.16 g (98%) and had an inherent viscosity of 1.50

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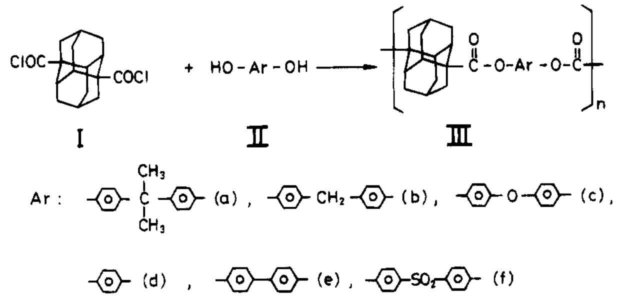
Scheme 1



dL/g, measured at a concentration of 0.5 g/dL in *o*-chlorophenol at 30 °C. The IR spectrum (film) exhibited absorption at 1745 cm^{-1} (C=O). Anal. Calcd for $(C_{28}H_{26}O_5)_n$: C, 76.02; H. 5.88. Found: C, 75.17; H, 5.01.

Characterization. A Bio-Rad FTS-40 FTIR spectrophotometer was used to record spectra of the KBr pellets. In a typical experiment, an average of 20 scans per sample was made. MS spectra were obtained using a JEOL JMS-D300 mass spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM-300 WB Fourier transform nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as the internal standard. A Perkin-Elmer 240C elemental analyzer was used for elemental analysis. Inherent viscosities of all polymers were determined at 0.5 g/dL concentration in *o*-chlorophenol at 30 °C using an Ubbelohde viscometer. Qualitative solubility was determined using 0.01 g of polymer in 2 mL of solvent. A Du Pont 9900 differential scanning calorimeter (DSC) and a Du Pont 9900 thermogravimetric analyzer (TG) were employed to study the transition data and thermal decomposition temperatures of all the polymers. The glass transition temperature, T_g, was estimated from the inflection point on the thermogram, and the melting temperature, T_m, was taken from the endothermic peaks. Thermomechanical analysis (TMA) was carried out with a Du Pont 9900 thermal analyzer system. TMA was recorded under a fixed load (2 g) at a heating rate of 10 °C/min. The softening temperature, T_s, was estimated from the inflection point on the displacement. Dynamic mechanical analysis (DMA) was performed on a Du Pont 9900 thermal analyzer system. A sample 10 mm in length, 3 mm in width, and approximately 0.05 mm in thickness was used. The dynamic shear modulus was measured at a frequency of 1 Hz and an amplitude of 0.2 mm. The wide-angle X-ray diffraction measurements were performed on a Philips PW 1730-10 X-ray diffractometer using Cu Kα 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/min. Next, measurements were performed at 25 °C with film specimens (approximately 0.06 mm in thickness, 1.0 cm in width, and 5 cm in length), and an average of at least five individual determinations was used. Dielectric constants were measured by the parallel-plate capacitor method using a dielectric analyzer (TA Instruments DEA 2970) in the frequency range 10-0.1 MHz on thin (about 40-50 μm) films. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by measuring at 25 °C in a sealed humidity chamber at 0% relative humidity.

Results and Discussion

Monomer Synthesis. 1,6-Diamantanedicarboxylic acyl chloride (I) was prepared from 1,6-diamantanedicarboxylic acid with thionyl chloride in 90% yield. On the basis of the shielding effect of carbon, the positions of the chemical shifts for carbons were readily assigned in Figure 1. The 2D ^{1}H-^{13}C COSY spectrum of I is shown in Figure 2. With the aid of the carbon spectrum assignments, the positions of the chemical shifts for protons were readily assigned in Figure 2. The singlet H_2O proton peak was also observed in this figure at 1.57 ppm, with a trace amount of moisture associated with the solvent. This was probably due to the fact that the water was added to the chloroform solution containing I, which was only slightly hydrolyzed at room temperature. The reason for the effect toward the hydrolytic stability of I remains unclear. In the elemental analysis, characteristic peaks in the NMR spectra and characteristic bands in the IR spectrum correlated well with 1,6-diamantanedicarboxylic acyl chloride (I).

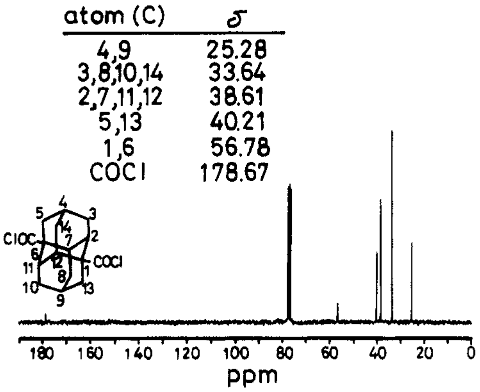


Figure 1. ^{13}C-NMR (75 MHz, $CDCl_3$) of I.

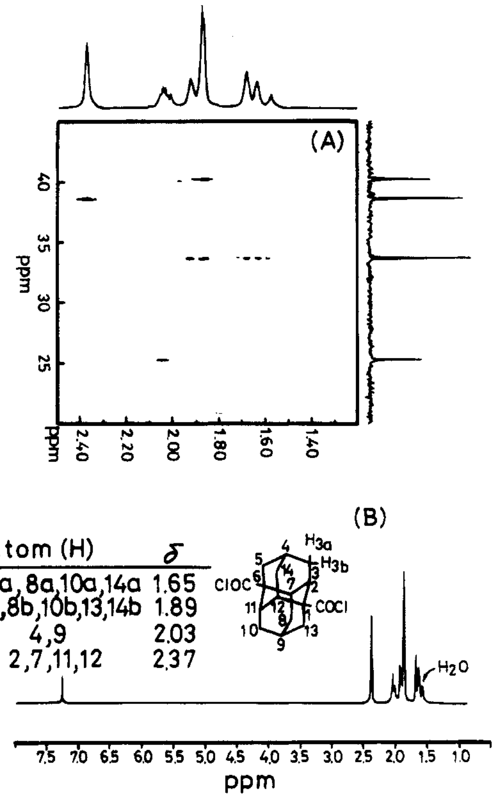


Figure 2. ^{1}H-NMR (300 MHz, $CDCl_3$) of I: (A) ^{1}H, ^{13}C-COSY; (B) ^{1}H-NMR.

Synthesis of Polymers. Generally, the molecular weight of the polyesters obtained from high-temperature solution condensation is highly dependent on the monomer concentration, reaction temperature, and reaction time. Hence, the effect of monomer concentration was first studied to find out a suitable concentration for the preparation of high-molecular-weight polyester IIIa (Table 1). Table 1 indicates that the inherent viscosity of polyester IIIa increased with increasing monomer concentrations up to 0.5 mol/L. Higher concentrations led to a highly viscous state and to a swollen gel for concentrations above 0.6 mol/L. This caused a decrease of the inherent viscosities of the polyesters.

Table 1. Effect of Monomer Concentration on Polymerization[a]

concn of monomer (M)	yield (%)	η_{inh}[b] (dL/g)	remark[c]
0.20	95.3	0.30	S
0.30	96.1	0.37	S
0.35	96.5	0.40	S
0.40	98.6	0.44	S
0.50	98.3	0.65	S
0.60	97.6	0.52	P
0.70	98.2	0.47	P
0.80	98.4	0.43	P

[a] Polymerization conditions: [I] = [IIa], 200 °C, 20 h. [b] Measured at 30 °C at a concentration of 0.5 d/gL in *o*-chlorophenol. [c] Appearance of the polymerization system: S, homogeneous solution; P, partial polymer gel precipitation.

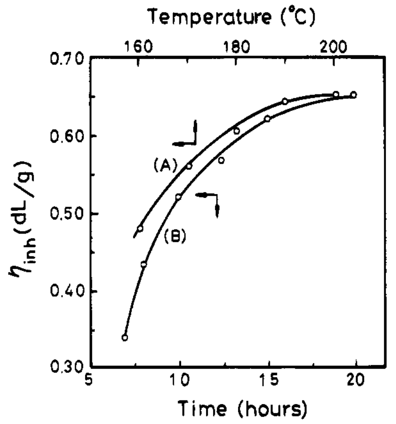


Figure 3. Effect of reaction conditions on inherent viscosity of polymer IIIa formed during the polycondensation at a monomer concentration of 0.5 M in *o*-dichlorobenzene: (A) effect of reaction temperature, at 20 h; (B) effect of reaction time, at 200 °C.

Table 2. Synthesis of Polyesters[a]

polymer	yield (%)	η_{inh}[b] (dL/g)	remark[c]
IIIa	98	0.65	S
IIIb	97	1.01	S
IIIc	98	1.50	S
IIId	93	0.20	P
IIIe	94	0.23	P
IIIf	92	0.21	S

[a] Polymerization was carried out with 0.5 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 in *o*-chlorophenol. [c] Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation.

Figure 3 shows inherent viscosities of polyesters prepared from diol IIa and I at various temperatures ranging from 160 to 200 °C. At the same reaction time of 20 h, a higher inherent viscosity of 0.65 dL/g was obtained at 200 °C. Figure 3 also shows inherent viscosities of polyesters IIIa at various times of reaction. A reaction temperature of 200 °C for 20 h, with a monomer concentration of 0.5 mol/L, was found to be suitable for preparing polymer IIIa with a high inherent viscosity.

Various polyesters III were prepared from I with the corresponding aromatic diols II by using the most favorable conditions for the reaction with diol IIa. The results of the polycondensation are listed in Table 2. All the polyesters were obtained in almost quantitative yield. The polyesters had inherent viscosities ranging from 0.20 to 1.50 dL/g. The inherent viscosities of polyesters IIId, IIIe, and IIIf were low. This was probably due to the fact that the poor solubility of polyesters IIId and IIIe resulted in an early precipitation of the reaction medium, which retarded further polymerization. The unsatisfactory results obtained from 4,4′-bis(4-hydroxyphenyl) sulfone (IIf) might be explained by its lower nucleophilicity owing to the presence of the electron-withdrawing sulfonyl group. The formation of polyesters III was confirmed by IR spectroscopy and elemental analysis. The elemental analyses of polyesters III were in good agreement with the calculated values for the proposed structures. FTIR spectra of all the polyesters showed characteristics of ester bands at around 1741 cm^{-1}. A representative FTIR spectrum of IIIc is shown in Figure 4.

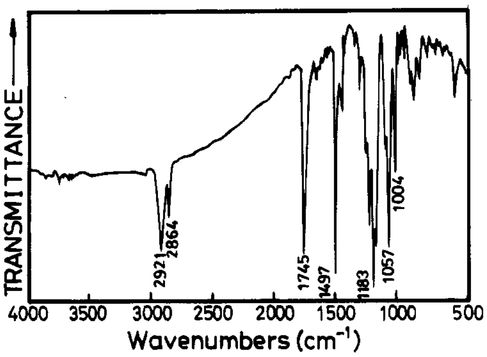


Figure 4. FTIR spectrum of polymer IIIc (film).

Table 3. Solubility of Polyesters[a]

	polymer					
solvent	IIIa	IIIb	IIIc	IIId	IIIe	IIIf
o-chlorophenol	++	++	++	+	+	++
o-dichlorobenzene	++	++	++	+	+	++
chloroform	++	+−	+−	−	−	++
DMF	+−	+−	+−	+−	+−	++
NMP	+−	+−	+−	+−	+−	++
DMSO	+−	+−	+−	+−	+−	++
nitrobenzene	+−	+−	+−	+−	+−	++

[a] Solubility: ++, soluble at room temperature; +, soluble on heating; +−, partial soluble; −, insoluble. Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide.

Table 4. Mechanical Properties and Dielectric Constants of Polyester Films[a]

polymer	strength to break (MPa)	elongation to break (%)	initial modulus (GPa)	dielectric constant (dry, 0.1 MHz)
IIIa	63.2	6.2	1.6	1.9
IIIb	65.3	8.1	1.4	1.3
IIIc	80.5	15.1	1.1	1.5

[a] Films were cast from a polyester solution of *o*-chlorophenol.

Characterization of Polyesters. The solubility of these polymers was tested in various solvents, and those results are summarized in Table 3. All the polyesters were soluble in *o*-chlorophenol and *o*-dichlorobenzene at room temperature or on heating. Polymer IIIf containing the flexible sulfone group showed excellent solubility in all the tested solvents, even in chloroform. Polymer IIIa was also soluble in chloroform. Transparent and colorless films for polyesters IIIa and IIIc and a light yellow film for polyester IIIb could be cast onto glass plates from their *o*-chlorophenol or *o*-dichlorobenzene solutions. All three polyester films were tough. The dielectric constants of the three polyesters are summarized in Table 4. The dielectric constants of diamantane-based polyesters were notably low, ranging from 1.3 to 1.9. The mechanical properties were determined with an Instron machine. All the tensile properties are also summarized in Table 4. All polyesters

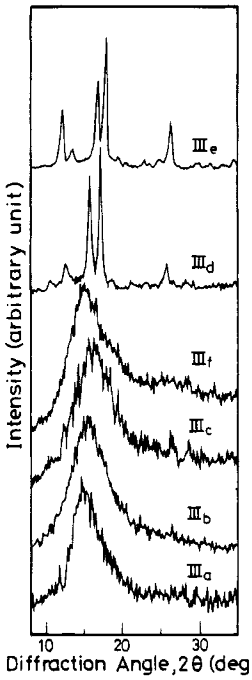


Figure 5. Wide-angle X-ray diffraction curves for the synthesized polyesters III (sample appearance: films, IIIa, IIIb, IIIc; powders, IIId, IIIe, IIIf).

exhibited high tensile strengths at break of 63.2–80.5 MPa. The polymer film of IIIc exhibited the highest tensile strength among the three (80.5 MPa); this was primarily due to the fact that IIIc had the highest inherent viscosity. The polymer film of IIIc contained a flexible ether segment; therefore, the elongation at break of IIIc was also greater. Polyester IIIf could also be cast into a film but was quite brittle.

The structural characterization was made first by X-ray methods with the "as-prepared" powders or films. Polymers IIId and IIIe show sharp diffraction peaks which indicate the presence of a high degree of crystallinity, as shown in Figure 5. Since the diffraction patterns of IIId and IIIe are rather similar in the positions of their peak angles, similarity in lattice parameters for both polymers is expected. The other polyesters have nearly the same semicrystalline patterns and exhibit crystalline peaks appearing (2θ) at around 15°. Additional work is required to characterize the structures more accurately.

Thermal analysis was made by means of DSC, TMA, DMA, and TG. The thermal properties of the polymers are summarized in Table 5. Representative TG curves for these polymers are shown in Figure 6. Their temperatures at a 5% weight loss ranged from 403 to 451 °C in nitrogen and from 383 to 433 °C in air. The reasons for the unusually high thermal stability for aliphatic hydrocarbon polyesters III are similar to those of the adamantane-based polymer.[29]

Table 5. Thermal Properties of Polyesters

	DSC[a]		TMA[b]	DMA[c]			decomp temp[d] (°C)	
polymer	T_g (°C)	T_m (°C)	T_s (°C)	T_α (°C)	T_β (°C)	T_γ (°C)	in air	in N_2
IIIa	*e*		350	380	60	−50	383	405
IIIb			330	376	60	−80	405	434
IIIc			380	370	70	−50	395	420
IIId	267	429					431	450
IIIe		369					433	451
IIIf		395					388	403

[a] Glass transition temperature (T_g) and melting transition temperature measured by DSC at a heating rate of 20 °C/min in nitrogen. [b] Softening temperature (T_s) measured by TMA at a heating rate of 10 °C/min. [c] α, β, and γ transitions measured by DMA using the shear mode at a heating rate of 5 °C/min. [d] Temperature at which 5% weight loss occurred as recorded by TG at a heating rate of 20 °C/min. [e] Not found.

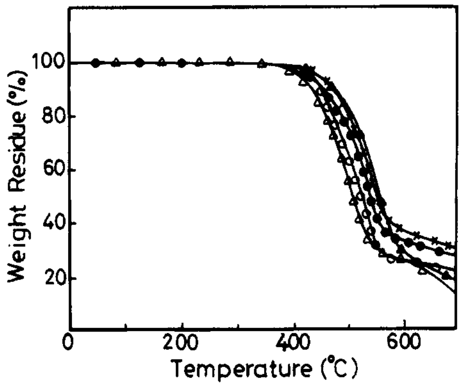


Figure 6. TG curves for polyesters III at a heating rate of 20 °C/min in nitrogen: (△) IIIa; (○) IIIb; (●) IIIc; (▲) IIId; (×) IIIe.

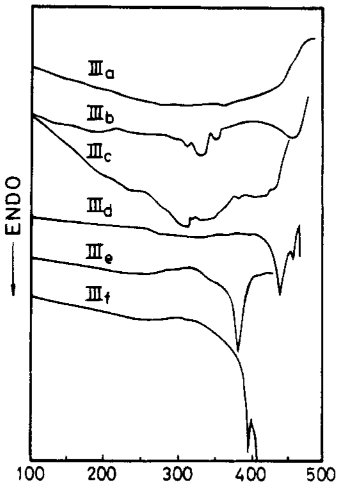


Figure 7. DSC curves of polyesters in a nitrogen atmosphere at a heating rate of 20 °C/min.

The influences of residual water or solvent and history of thermal annealing were sometimes observed in the first DSC heating run. Therefore, the first heating of the samples was curtailed at 250 °C; in addition, T_g and other thermal properties were evaluated according to the DSC charts of the second heating. The DSC curves are shown in Figure 7. Polymer IIIa exhibited a featureless trace up to a temperature of around 365 °C followed by the onset of an exothermic process toward higher temperature up to 480 °C, interpreted here as a thermal decomposition process. Polymer IIIb exhibited a weak exothermic process at around 210 °C, interpreted here as a recrystallization process followed by a melt transition with a broad endothermic peak appearing at around 327 °C. Polymer IIIc exhibited a very broad endothermic process which started at around 260 °C. In this temperature range, it was interpreted as a melting process followed by a thermal decomposition well above 400 °C. Polymer IIId showed a classical glass transition at 267 °C. At around 325 °C, a broad exothermic process started to take place in this temperature range, interpreted here as a recrystallization process followed by a melt transition with a sharp endothermic peak appearing at 429 °C. In polymer IIIe,

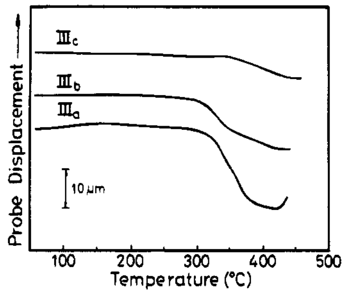


Figure 8. TMA curves of polyester films.

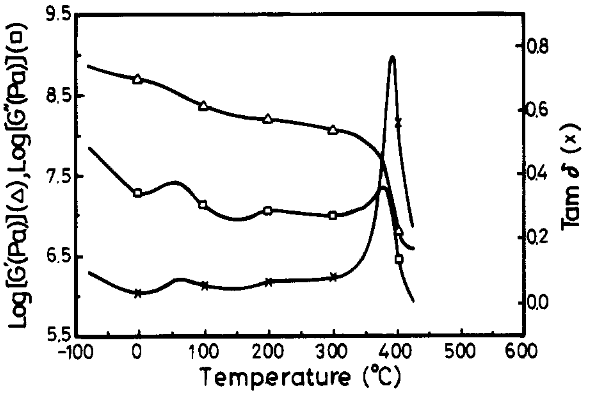


Figure 9. Mechanical-dynamical spectra of polyester IIIb.

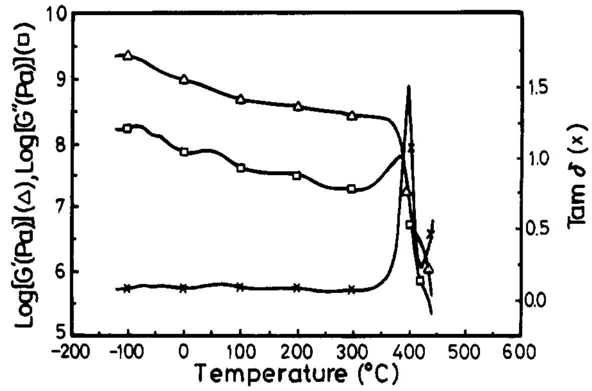


Figure 10. Mechanical-dynamical spectra of polyester IIIa.

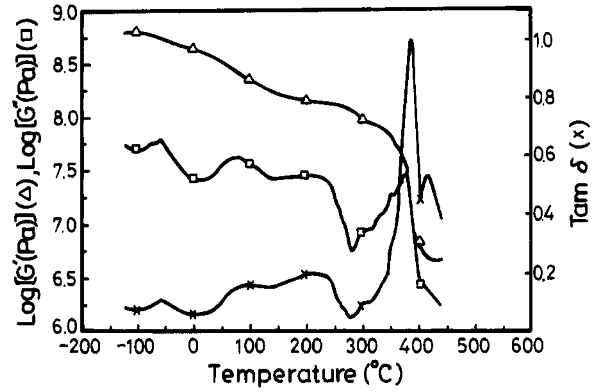


Figure 11. Mechanical-dynamical spectra of polyester IIIc.

the transition from an ordered solid to an isotropic melt gave rise to quite sharp endothermic peaks appearing at 369 °C. The transition behavior was consistent with the results of X-ray diffraction studies, indicating that polymers IIId and IIIe had a large fraction of crystallinity. Polymer IIIf exhibited a very broad exothermic process which started at around 250 °C; taking place in this temperature range, it was interpreted here as a recrystallization process followed by a melt transition with a sharp endothermic peak appearing at around 395 °C. Again, the onset of thermal decomposition was well above 400 °C. Samples subjected to DSC analysis gave rise to thermograms which showed little information related to the glass transition. There was no evidence of a glass transition in the conventional sense in all the samples, except polymer IIId.

Thermal properties of IIIa, IIIb, and IIIc measured by TMA are shown in Figure 8. When the temperature reaches 330 °C, the film of IIIb softens and displays a softening transition temperature (T_s). The appearance of a softening transition at 330 °C is in very good agreement with the melting endothermic peak, as obtained by DSC. Polymers IIIa and IIIc also show softening transition temperatures at 350 and 380 °C, respectively.

More detailed information can be obtained from the dynamic mechanical behavior measurements taken of the film as a function of temperature. Films of about 50 μm thickness were prepared by casting from *o*-chlorophenol solutions. The mechanical relaxation spectra of polymer IIIb are shown in Figure 9. Three relaxations are observed at ca. −80, 60, and 376 °C, based on tan δ and G'' peaks. The relaxation process can be approached by verifying results obtained for other related polymers.[3,8,33,34] The low-temperature transition named γ (ca. −80 °C) is a typical relaxation for polyesters. This relaxation is attributed to the reorientation of the carbonyl groups. The second transition, at 60 °C, is associated with a step decrease in G'. Such a transition was also observed in the case of polyesters with an aliphatic side chain, while aromatic polyesters without an aliphatic side chain had no such transition at 60 °C.[3,8] Thus, this transition is believed to correlate with the presence of the aliphatic moiety of diamantane. A shoulder is observed at 200 °C without any effect on the G' value. The main transition at around 376 °C is associated with approximately a one order of magnitude decrease in G'. This transition could be indicative of either a glass or a melting transition. At the temperature, the polymer particles softened and coalesed. Moreover, a broad endothermic peak was observed by DSC, a fact which supports the melting transition. Such a transition has been observed in other aromatic polyesters at 350 °C.[3]

The mechanical relaxation spectra of polymers IIIa and IIIc are shown in Figures 10 and 11. Three relaxation transitions are also observed in both cases on the temperature scale between −100 and +400 °C. The low-temperature transition is shifted to −50 °C in both cases, which fits much more the γ-relaxation process observed in polyesters. The second transition of IIIa and IIIc appears at 60 and 70 °C, respectively. A shoulder in tan δ and G'' is observed at around 200 °C in both cases, without any effect on the G' value. The main transition of IIIa and IIIc appears at 380 and 370 °C, respectively. For the same reasons, this transition is believed to be due to the melting transition.

These samples show a rather high G' value (about 10^8 Pa) up to 350 °C. The partial crystallization of the present type of polyesters would be one of the reasons for making polyesters with good mechanical properties at high temperatures. A comparison of the mechanical behavior of the systems studied here with that of other polyesters, studied by Wrasidlo,[35] showed that the main difference was the observation of a β transition. In the polyesters without aliphatic side chains, no β transition is observed, and the high-modulus region extends to temperatures close to the α transition (usually higher than 300 °C).[35] However, for polyesters with aliphatic side chains, a step in the modulus at the β transition is observed.[3] Nevertheless, in our system with no aliphatic side chains attached to the polyesters, there was a step in the modulus at the β transition. Thus, there is a close correlation between the β transition and the presence of diamantane in the system studied here. It is recognized that additional work is needed to characterize the mechanism of motion for the β transition more specifically.

Conclusion

Diamantane-containing polyesters with high inherent viscosities can be obtained by high-temperature solution condensation. The introduction of the diamantyl unit into the polyester backbone resulted in polyesters with high T_g's and high thermal stability. The melting temperatures of polymers IIId, IIIe, and IIIf were 429, 369, and 395 °C, respectively. The crystallinity of polyesters III varies significantly, depending on the main-chain moiety from the diols. Transparent and colorless films could be cast with polyesters IIIa and IIIc, while the film of IIIb is transparent and light yellow. Polyesters IIIa, IIIb, and IIIc display good mechanical properties and low dielectric constants. Polyesters IIIa, IIIb, and IIIc show secondary transitions at low temperatures and a mainly melting transition without a glass transition by DMA. Particularly, a step in the modulus at the β transition at about 60 °C is also observed in diamantane-containing polyesters. In all cases, these samples show a rather high G' value (about 10^8 Pa) up to 350 °C.

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