S0032-3861(96)00236-4

Polymer Vol. 37 No. 19, pp. 4397–4402, 1996
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0032-3861/96/$15.00 + 0.00

Synthesis and characterization of aromatic liquid crystalline poly(ester–imide)s derived from an imidodicarboxylic acid

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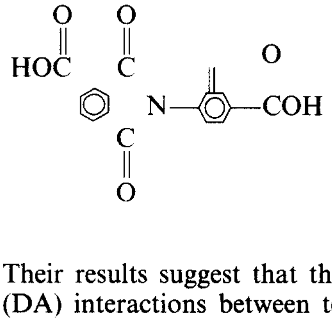
(Received 6 April 1994; revised 26 June 1995)

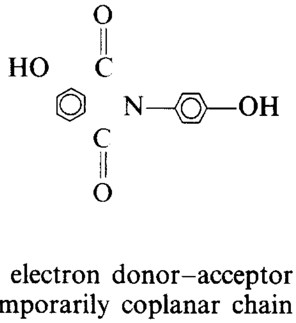
A new class of liquid crystalline poly(ester–imide)s was synthesized by melt polycondensation. The basic physical properties of the resulting polymers were investigated by differential scanning calorimetry (d.s.c.), wide-angle X-ray diffraction (WAXD), polarized light microscopy, scanning electron microscopy (SEM), thermogravimetric analysis (t.g.a.), and rheological and mechanical testing. All of these poly(ester–imide)s were amorphous, as reflected by the results obtained from the WAXD and d.s.c. studies. Characterization and comparison of these poly(ester–imide)s with the corresponding polyesters suggested that the introduction of imide groups into the polyester chain is favourable for the formation of liquid crystalline phases. These results, together with the rheological studies, suggested that there existed a form of strong inter- or intramolecular electron donor–acceptor interaction which played a significant role in the liquid crystalline properties of the poly(ester–imide)s. The polymer products thus obtained exhibited good mechanical properties, with flexural strengths and moduli as high as 174 MPa and 6.9 GPa, respectively. The morphology of the fracture surfaces of extruded rod samples showed a sheet-like structure which consisted of ribbons and fibres oriented along the flow direction. The glass transition temperatures and thermal stabilities of the polymers were improved by the incorporation of imide groups. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystalline polymer; poly(ester–imide)s; imidodicarboxylic acid)

INTRODUCTION

The study of the structure–property relationships of liquid crystalline polymers has been a popular research subject in recent years[1–4]. In order to obtain a thermotropic liquid crystalline polymer (TLCP) which is melt processible, various approaches have been tried for reducing the melting temperature of the polymer, with the most often used techniques involving incorporation of kink structures and asymmetrically substituted monomers or flexible spacers, or by a multicopolymerization method[4]. Although the introduction of kink structures is believed to be a very effective way of reducing the melting points of the TLCPs[5,6], it inevitably leads to poorer mechanical properties and a loss of liquid crystallinity at a certain critical composition[7]. In addition, the glass transition temperatures of the TLCPs are not very high, usually occurring at around 150°C which will limit the service temperatures when they are used as structural materials or blended with high-performance plastics with high glass transition temperatures (T_gs) for preparing so-called *in situ* composites[8]. Recently the thermotropic liquid crystalline behaviour of poly(ester–imide)s was reported, with studies being carried out by a number of researchers[9–14]. Kricheldorf and coworkers[12–14] have studied the structure–property relationships of two series of poly(ester–imide)s derived from the following two monomers:





Their results suggest that the electron donor–acceptor (DA) interactions between temporarily coplanar chain segments play a significant role in the stabilization of the nematic phase, whereas geometrical factors such as chain stiffness and linear conformation play only a minor role. From a practical point of view, this might mean that the excellent performances of both polyimides and TLCPs can be combined by the synthesis of liquid crystalline poly(ester–imide)s, thus imparting unusual physical properties to the resulting polymers.

The purpose of the present paper is to investigate the structure–property relationships of various poly(ester-imide)s derived from another imidodicarboxylic acid,

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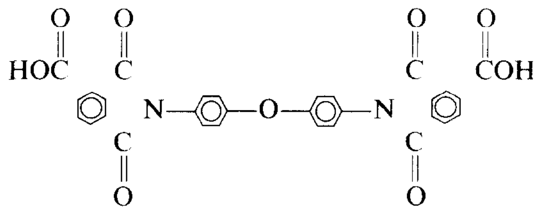
namely 4,4′-diaminodiphenylether bistrimellitimide:



EXPERIMENTAL

Materials

Hydroquinone, resorcinal and 4,4′-dihydroxydiphenyl sulfone were purchased from the Shanghai Third Chemical Reagent Factory, 4-hydroxybenzoic acid and 4,4′-oxydianiline were purchased from the Peking Chemical Factory, 4,4′-dihydroxydiphenyl propane was purchased from the Shanghai First Chemical Reagent Factory, and terephthalic acid and trimellitic anhydride were obtained from the Merk-Schuchardt Co., Germany. All of these materials were used without further purification.

Preparation of the imidodicarboxylic acid

4,4′-Diaminodiphenylether bistrimellitimide (DAEB) was prepared according to the literature procedure[15]. A 1 l round-bottomed flask, fitted with a mechanical stirrer, a thermometer, and a reflux condenser, was charged with a solution of 50 g (0.25 mol) of 4,4′-oxydianiline and 200 ml of *N*,*N*-dimethylformamide (DMF). Trimellitic anhydride (96 g, 0.50 mol) was then slowly added to the solution with stirring, with the system being kept below 40°C by using a cold water bath during the addition, and the solution was stirred for an additional 24 h at room temperature. Acetic anhydride (60 ml), followed by pyridine (15 ml), was then added. A greenish precipitate formed over a period of several hours. The mixture was then heated (by means of an oil bath) at 150°C for 6 h to complete the reaction. The orange solid, which formed on cooling, was filtered, washed with acetone, and recrystallized from DMF to give 95 g (70% yield) of the orange-coloured diacid (m.p. 374°C). Elemental analysis (%): found C 65.21, H 2.86, N 4.97; calculated C 65.96, H 2.94, N 5.11. I.r. (KBr) cm^{-1}: 3110–2850 (0–H stretch), 1721, 1694 (imide C–O), 1220 (Ph–O–Ph stretch), and 1118 (imide structure).

Polycondensation

A general method was employed for the synthesis of the poly(ester–imide)s. As an example, the synthesis of a typical polymer (TA-5) is described here. In this procedure, 10 mmol of the DAEB diacid, 5 mmol of hydroquinone, 5 mmol of resorcinol, 20 mmol of 4-hydroxybenzoic acid and 15 g of acetic anhydride were placed in a cylindrical glass reactor fitted with a stirrer and gas inlet and outlet tubes. The reactor was then heated by means of a metal bath at 150°C for 1 h under a flow of N_2 to achieve acetylation of the mixture. The temperature was then raised to 250°C over a period of 1 h in order to remove any excess acetic anhydride. The polycondensation reaction was then slowly started: the temperature was raised to 325°C, in 25°C steps, over a period of 2 h, followed by the application of a vacuum, after which the reactor was heated to 350°C over a period of a further 1 h. After cooling, the product was collected and powdered. Because the resultant polymers were insoluble in common solvents, further structural characterization was not carried out.

Characterization

Intrinsic viscosities were measured with an Ubbelohde-type viscometer at concentrations of 0.5 g dl^{-1} in

Table 1 Composition and properties of the poly(ester–imide)s

	Monomer feedstock[a]							
Polymer system	DAEB/TA	HQ/RES	HBA	Yield (%)	$[\eta]$[b] (dl g^{-1})	T_f[c] (°C)	T_g[d] (°C)	T_i[e,i] (°C)
RES-1	1/0	0.75/0.25	2.5	93	Insoluble	>400	171	>480 (dec)
RES-2	1/0	0.5/0.5	2.5	93	1.02	320	162	>460 (dec)
RES-3	1/0	0.25/0.75	2.5	93	0.83	315	170	440–460
RES-4	1/0	0/1	2.5	96	1.07	330	169	420–450
PAB-1	1/0	0/1	1.5	97	0.70	315	168	360–370
PAB-2	1/0	0/1	1	90	0.66	320	177	By shear
PAB-3	1/0	0/1	0.6	98	0.41	340	191	Isotropic
TA-1	0.75/0.25	0/1	2.5	92	0.76	295	157	450–460
TA-2	0.5/0.5	0/1	2.5	91	0.51	285	138	>440
TA-3	0.25/0.75	0/1	2.5	90	0.53	285	131	380–400
TA-4[f]	0/1	0/1	2.5	–	–	–	145	By shear
TA-5	1/0	0.5/0.5	2	97	1.41	315	166	>460 (dec)
TA-6	0.75/0.25	0.5/0.5	2	95	1.22	300	158	>460 (dec)
TA-7	0.5/0.5	0.5/0.5	2	92	1.03	295	149	>450 (dec)
TA-8	0.25/0.75	0.5/0.5	2	89	0.66	285	147	>430 (dec)
TA-9	0/1	0.5/0.5	2	88	0.41	240	111	>400 (dec)
DP-S	1/0	0.5/0.5[g]	2	95	Insoluble	350	199	>460 (dec)
DP-A	1/0	0.5/0.5[h]	2	93	Insoluble	315	190	>450 (dec)

[a] DAEB, 4,4′-diaminodiphenylether bistrimellitimide; TA, terephthalic acid; HQ, hydroquinone; RES, resorcinol; HBA, 4-hydroxybenzoic acid

[b] Measured at 30°C, at concentration of 0.5 g dl^{-1}, in *p*-chlorophenol/1,1,2,2-tetrachloroethane (40/60 by weight)

[c] Flow temperatures obtained from optical microscopy studies at a heating rate of 5°C min^{-1}

[d] Glass transition temperature obtained from d.s.c. measurements at a heating rate of 20°C min^{-1}

[e] Dec, decomposition takes place

[f] Results obtained from ref. 4

[g] Polymer synthesized by using 4,4′-dihydroxydiphenyl sulfone instead of resorcinol

[h] Polymer synthesized by using 4,4′-dihydroxydiphenyl propane instead of resorcinol

[i] Isotropization temperature obtained from polarized optical microscopy

mixed solutions of *p*-chlorophenol and 1,1,2,2-tetrachloroethane 40/60 by weight at 30°C d.s.c. thermograms were recorded on a Perkin-Elmer DSC-7 calorimeter, using a heating rate of 20°C min^{-1}, under nitrogen. T.g.a. thermograms were obtained on a TGS-2 (Perkin–Elmer) thermogravimetric analysis system using a heating rate of 10°C min^{-1}. WAXD patterns were taken on a Rigaku-2028 X-ray diffractometer, using CuKα radiation with a graphite crystal monochromator and continuous scanning at 2° min^{-1}. SEM (JEOL JXA-840) was used to analyse the morphology of the fracture surfaces of extruded rod specimens. Tensile properties were measured by an Instron Model-1121 tensile tester, using a gauge length of 20 mm and a strain rate of 10 mm min^{-1} at room temperature. Melt rheology measurements were carried out by using Contraves CP-400 cone plate rheometer.

RESULTS AND DISCUSSION

Liquid crystalline behaviour

The d.s.c. curves of all of these poly(ester–imide)s show only a distinct glass transition point. It can therefore be preliminary deduced that they are amorphous materials. The glass transition temperature (T_g) reaches 90°C or higher for polymers synthesized when using 4,4′-dihydroxydiphenyl propane or 4,4′-dihydroxydiphenyl sulfone as the comonomers (see polymers DP-S and DP-A in *Table 1*), which is 40–50°C higher than that of the corresponding polyesters. It is also observed that the shapes and positions of the T_g line shift on the d.s.c. curves are related to the polymerization time, e.g. two T_g steps clearly appear when the polymerization time is short, as in the case of 15 min under vacuum for polymer TA-5, where values of 147 and 237°C are found (*Figure 1*). These two steps move closer and closer together on continuation of the reaction at high temperatures, with finally only one T_g step showing up on the d.s.c. curve, which lies between the two points at e.g. 166°C for the final product TA-5. These multiple T_g steps might result from the multiplicity of the chain segments, with the lower T_g (which is very close to that of the copolyester TA-4 (*Table 1*)) being more likely related to the chain segments that are rich in ester groups, while the higher one can be ascribed to the segments which are rich in imide groups.

Most of the resultant polymers show a distinct birefringence under the polarized optical microscope (*Figure 2*) after shear, and the band texture can be clearly seen (*Figure 2B*). It is worth indicating here that the liquid crystallinity is still retained when the HBA mole content is reduced to 33% for the DAEB/RES/HBA terpolymers. When compared with the TA/RES/HBA terpolyesters, for which a minimum HBA mole content of 50% is needed to retain the liquid crystallinity[16], it is evident that DAEB is a more favourable candidate for obtaining liquid crystalline behaviour. However, from a molecular structure point of view, DAEB should be less favourable than TA for mesophase formation, as its ether bond will introduce a kink structure into the polymer chain, thus reducing its linearity and rigidity. Nevertheless, if there exist special strong interactions such as intermolecular hydrogen bonding[17,18], complexing[19], ionic interactions[20,21], and electron donor–acceptor interactions[22,23], the liquid crystallinities might be caused or induced in some cases by the orientational action of these special interactions. In our present case, we have a strong electron acceptor in DAEB which might form a type of electron donor–acceptor (DA) interaction with an electron donor such as phenylenedioxide. As a result, the melt viscosities of the poly(ester–imide)s are almost ten times as high as those of the corresponding polyesters (*Figure 3*).

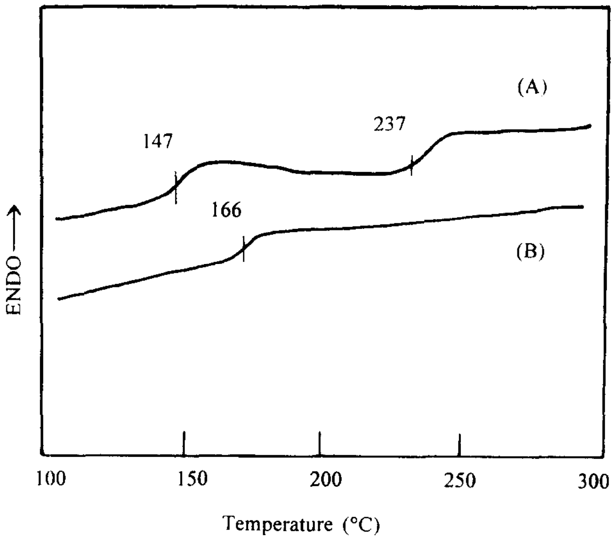


Figure 1 D.s.c. heating curves of TA-5 with different polymerization times at vacuum applied period: (A) 15 min; (B) 45 min

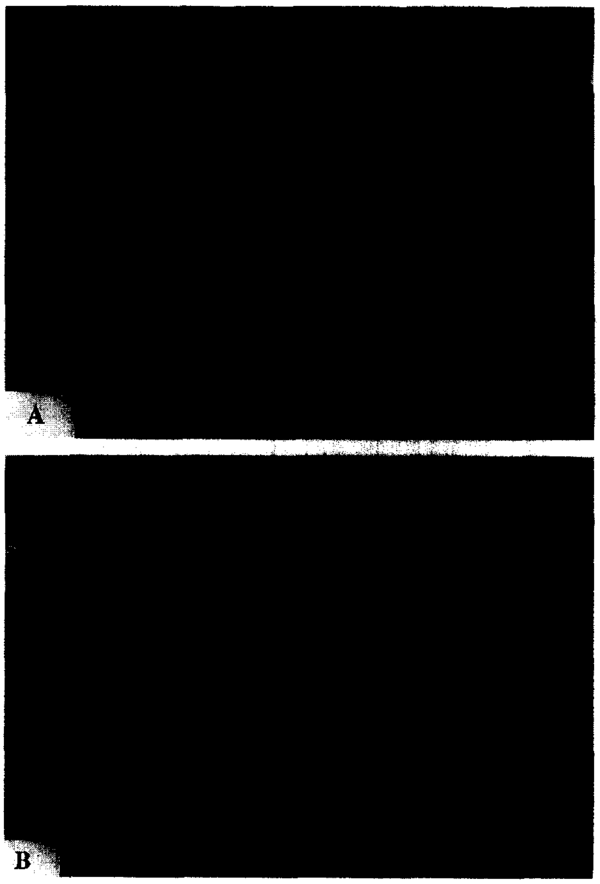


Figure 2 Polarized micrographs of RES-2 (A), TA-3 (B) at 330 and 320°C, respectively

The WAXD powder patterns of these poly(ester–imide)s only show a diffused peak at ca. $2\theta = 20°$, which is characteristic of amorphous polymers (*Figure 4*). After the fibre is annealed at elevated temperatures, only two diffused diffraction spots appear on the X-ray diagram (*Figure 5*), thus suggesting that they are non-crystalline materials. The amorphous structure can be the result of the random structure of the polymer chain and the strong electron DA interactions which hinder the packing of the chain to form crystallites. However, it should be mentioned here that these samples have at least the nematic order retained from the nematic melt, which means that the solid structure can more appropriately be described as a nematic glass.

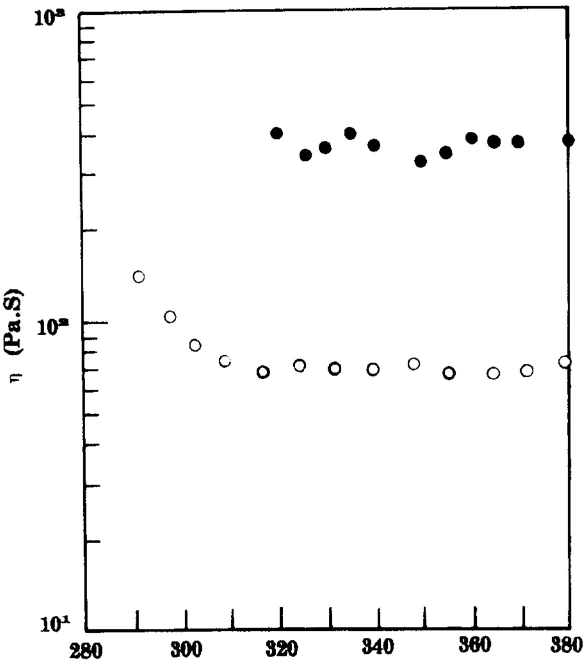


Figure 3 Melt viscosity of TA-8 (●), TA-9 (○) *versus* temperature at the shear rate of $10\,s^{-1}$, the inherent viscosities of TA-8 and TA-9 here are 0.66 and $0.64\,dl\,g^{-1}$, respectively

Mechanical properties and morphology

The polymer TA-5 was extruded at 340°C in a mini-extruder and then melt drawn into rods with different diameters. The mechanical properties of TA-5 showed the characteristics of liquid crystalline polymers, e.g. high strength and modulus, and low elongation at break. Furthermore, its strength and modulus both show a great dependence on the draw ratios (*Table 2*).

It is worth indicating here that the flexural strength and modulus reach 174.22 MPa and 6.96 Pa, respectively, which are very close to those of typical commercial

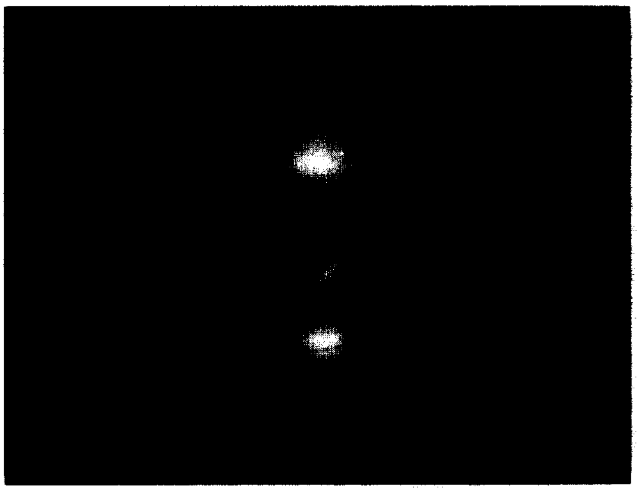


Figure 5 X-ray fibre pattern for TA-8 after annealing at 200°C for 2 h

Table 2 Mechanical properties of the poly(ester–imide) TA-5[a]

Draw ratio	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
1	109.21	3.59	5.5
1.28	172.70	4.97	4.5
1.71	227.90	6.45	4.4
Injection moulded sample	97.61	4.03	3.3

[a] Flexural strength, 174.22 MPa; flexural modulus, 6.96 GPa

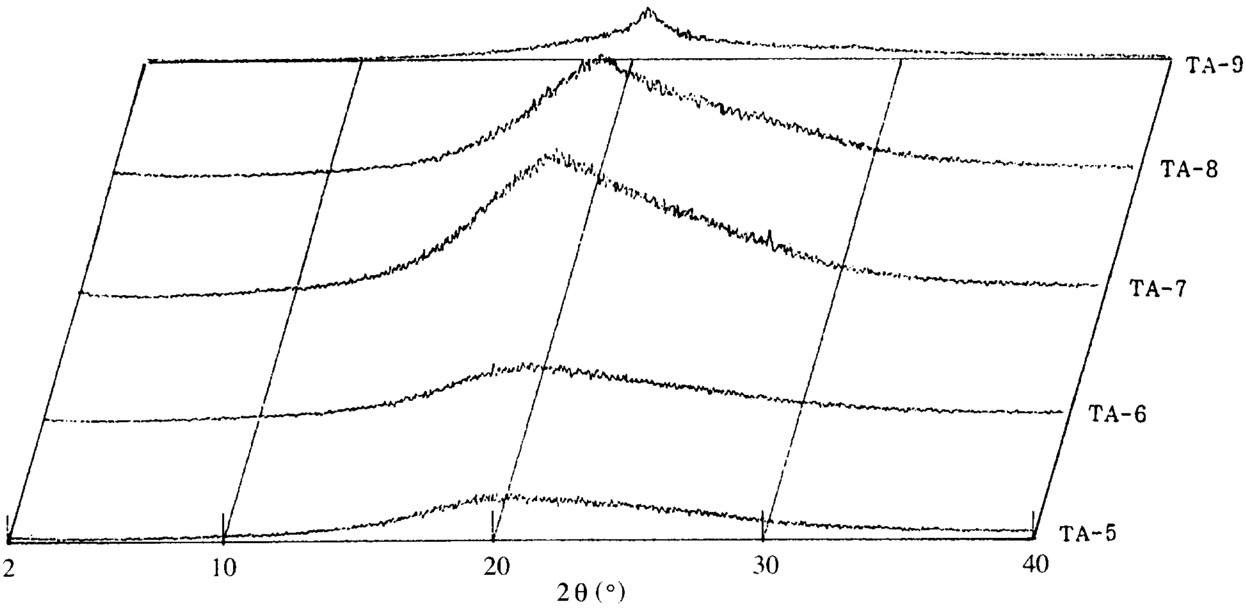


Figure 4 WAXD powder patterns of TA-5 to TA-9

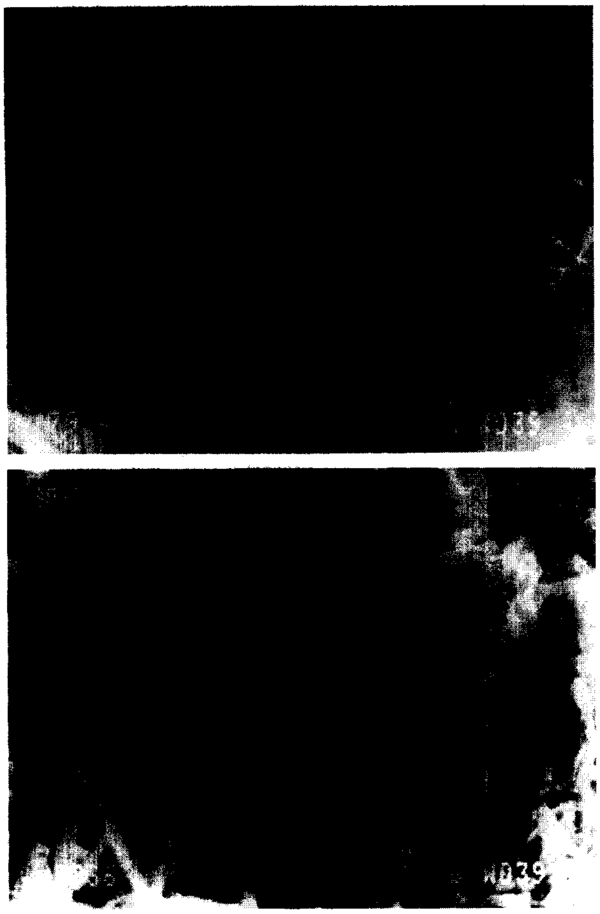


Figure 6 SEM microphotographs for fracture surface of extruded rod of TA-5. (A) An overall view of the fracture surface; (B) sheet-like structure along the radial direction of extruded rod

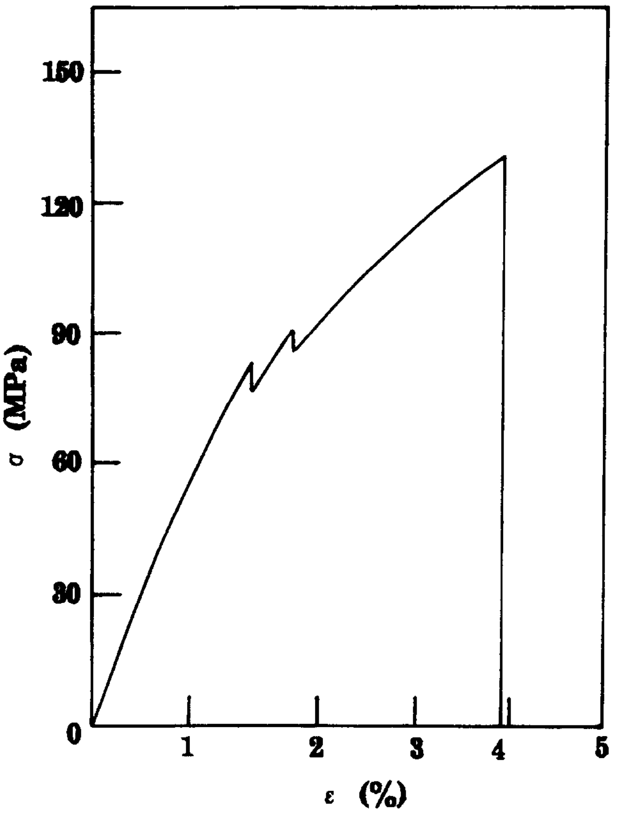


Figure 7 Stress–strain curve for the extruded rod of TA-5

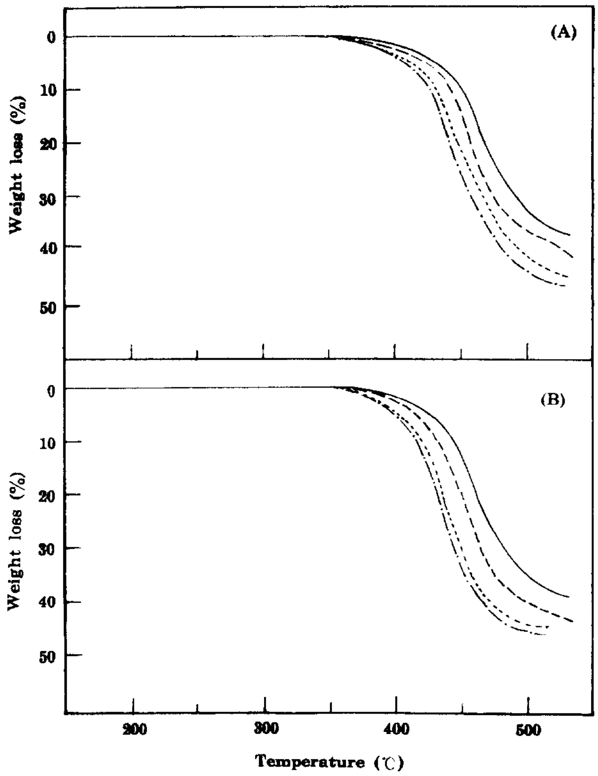


Figure 8 T.g.a. thermograms of RES-4 (——), TA-1 (— — —), TA-2 (· · ·), TA-3 (—·—). (A) In air; (B) in nitrogen

aromatic TLCPs. The fracture surface of an undrawn sample resembles a series of sheet-like structures which lie in the radial direction and orient along the flow direction (*Figure 6*). The shell is much more oriented than the core, with the strain being concentrated on the shell during drawing, thus leading to breaking occurring from the outside to the inside of the specimen. As a result of this, the stress–strain curve resembles a zigzag (*Figure 7*).

Thermostability

Thermogravimetric analyses of the polymers RES-4, and TA-1–3 were carried out at a heating rate of 10°C min^{-1} in both air and nitrogen (*Figure 8*). It can be seen that below 400°C, the weight loss of these polymers is less than 5% in both nitrogen and air, thus providing a broad range of processing temperatures (a processing window) for the resulting polymers. Moreover, the thermostability is somewhat enhanced with an increase in the DAEB diacid content.

CONCLUSIONS

1. The poly(ester–imide)s synthesized from the imido-dicarboxylic acid, 4,4-diaminodiphenylether bistrimellitimide, were shown to be amorphous, even when using high HBA levels in the monomer feedstocks. The amorphous character could be the result of a random distribution of chemical units and the highly restricted mobility of the chain segments due to electron donor–acceptor (DA) interactions. The solid structure can be described as a nematic glass.
2. The strong electron DA interactions in the poly(ester–imide)s were responsible for the liquid crystalline properties and the high melt viscosities of these polymers.

3. The polymers exhibited good mechanical properties, with tensile strengths and moduli as high as 97.61 MPa and 4.03 GPa, respectively. The results are related to the domain deformation and molecular orientation along the flow direction.
4. The glass transition temperatures and thermal stabilities were improved to some extent by the introduction of imide groups into the polyester chains. The results suggested that a combination of the excellent performances of polyimides and TLCPs can be expected by the synthesis of thermotropic poly(ester–imide)s. Furthermore, we would expect that the poor melt processibility of polyimides can be improved to a certain extent by blending thermotropic poly(ester–imide)s or by imparting liquid crystallinity to the polyimide.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China.

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