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Polymer 40 (1999) 4387–4398

polymer

Synthesis and properties of phosphorus containing polyarylates derived from 2-(6-oxido-6H-dibenz ⟨c,e⟩⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene

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Received 3 April 1998; received in revised form 3 August 1998; accepted 17 September 1998

Abstract

A series of flame-retardant wholly aromatic polyesters was synthesized by high temperature solution polycondensation of 2-(6-oxido-6H-dibenz ⟨c,e⟩⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (**I**) with various aromatic acid chlorides in *o*-dichlorobenzene. These polyesters have good mechanical properties (G':10^8–10^9Pa) up to 180°C and good thermal and flame retardant properties. The glass transition temperatures of these polyesters are in the range of 198.1°C–220.3°C. The degradation temperatures (T_d 5%) in nitrogen ranged from 460°C to 495°C and char yields at 800°C are 34%–47%. The degradation temperatures (T_d 5%) in air ranged from 450°C to 472°C and char yields at 800°C are 21%–32%. The activation energies of degradation ranged from 177.4 KJ/mol to 238.8 KJ/mol. The limiting oxygen indexes (LOIs) of these polyesters are in the range of 37–48. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyarylate; DOPO; Flame retardancy

1. Introduction

Considerable attention was paid in the last three decades in controlling the inherent flammability of common organic polymers by incorporation of fire retardant additives. Commercial fire retardant polymers generally contain elements such as phosphorus, nitrogen, and halogen. These elements may be added in the form of additives to the substrate polymers or incorporated into the structure of the polymer itself; the latter approach is sometimes preferred. As phosphorus containing polymers give off non-toxic combustion products, they are getting more popular [1–18]. Some literatures [1–12] have developed flame retardant polyesters which exhibit high flame retardancy but with low thermal stability. Their degradation temperatures are low, ranged from 180°C to 350°C.

Polyesters are well known as high performance engineering thermoplastics because of their good thermal stability, chemical resistance, and excellent mechanical properties. However, like other organic polymeric materials, the flammability of polyesters is a shortcoming in some applications. In our previous article [18], we have synthesized a phosphorus containing poly(ethylene naphthalate) (PEN) and poly(butylene naphthalate) (PBN) copolyesters derived from a aliphatic phosphorus containing diol, 2-(9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-1,4-bis(2-hydroxyethoxy), with bis (2-hydroxyethyl) naphthalate (BHEN) or bis (4-hydroxybutyl) naphthalate (BHBN), respectively and proved they are more thermally stable flame retardant then PEN and PBN. As our continuous effort on searching high thermally stable flame retardant polyesters, a series of wholly aromatic polyesters based on an aromatic phosphorus-containing diol, 2-(6-oxido-6H-dibenz ⟨c,e⟩⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene (**I**), was synthesized and characterized in this work. The thermal stabilities of these polyesters were also evaluated by DSC, TGA, DMA and LOI.

2. Experimental

2.1. Materials

9, 10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) (from TCI), 2,6-*p*-benzoquinone (from Acros), 2-ethoxyethanol (from Acros) were used without further purification. 4,4′-Biphenyldicarbonyl chloride ($\mathbf{II}_f$) (from TCI), terephthaloyl chloride ($\mathbf{II}_a$) and isophthaloyl chloride ($\mathbf{II}_b$) (both from TCI) were recrystallized from toluene before use. *o*-Dichlorobenzene was purified by distillation under

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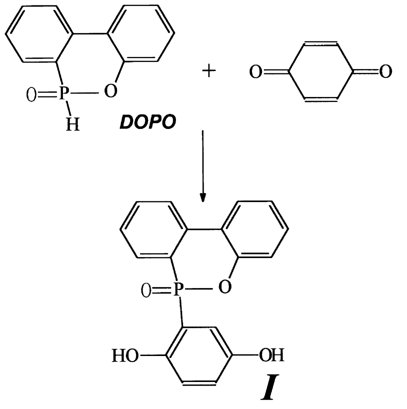
PII: S0032-3861(98)00680-6



Scheme 1.

reduced pressure over calcium hydride (from Acros) and stored over molecular sieves. Other solvents used for solubility test were obtained from various commercial sources and used without further purification. 4,4′-Sulfonyldibenzoyl chloride (**II**$_c$), 4,4′-oxydibenzoyl chloride (**II**$_d$), 2,6-naphthalenedicarbonyl chloride (**II**$_e$) and 4,4′-carbonyldibenzoyl chloride (**II**$_g$) were prepared by reacting the corresponding dicarboxylic acids with thionyl chloride in toluene using a few drops of dimethylformamide (DMF) as a catalyst [19–20] followed by recrystallization from toluene.

*2.2. Synthesis of 2-(6-oxido-6H-dibenz ⟨c,e⟩⟨1,2⟩ oxaphosphorin-6-yl)-1,4-dihydroxy phenylene [21] (**I**)*

1.25 mol of 9, 10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO), 1.125 mol of *p*-benzoquinone

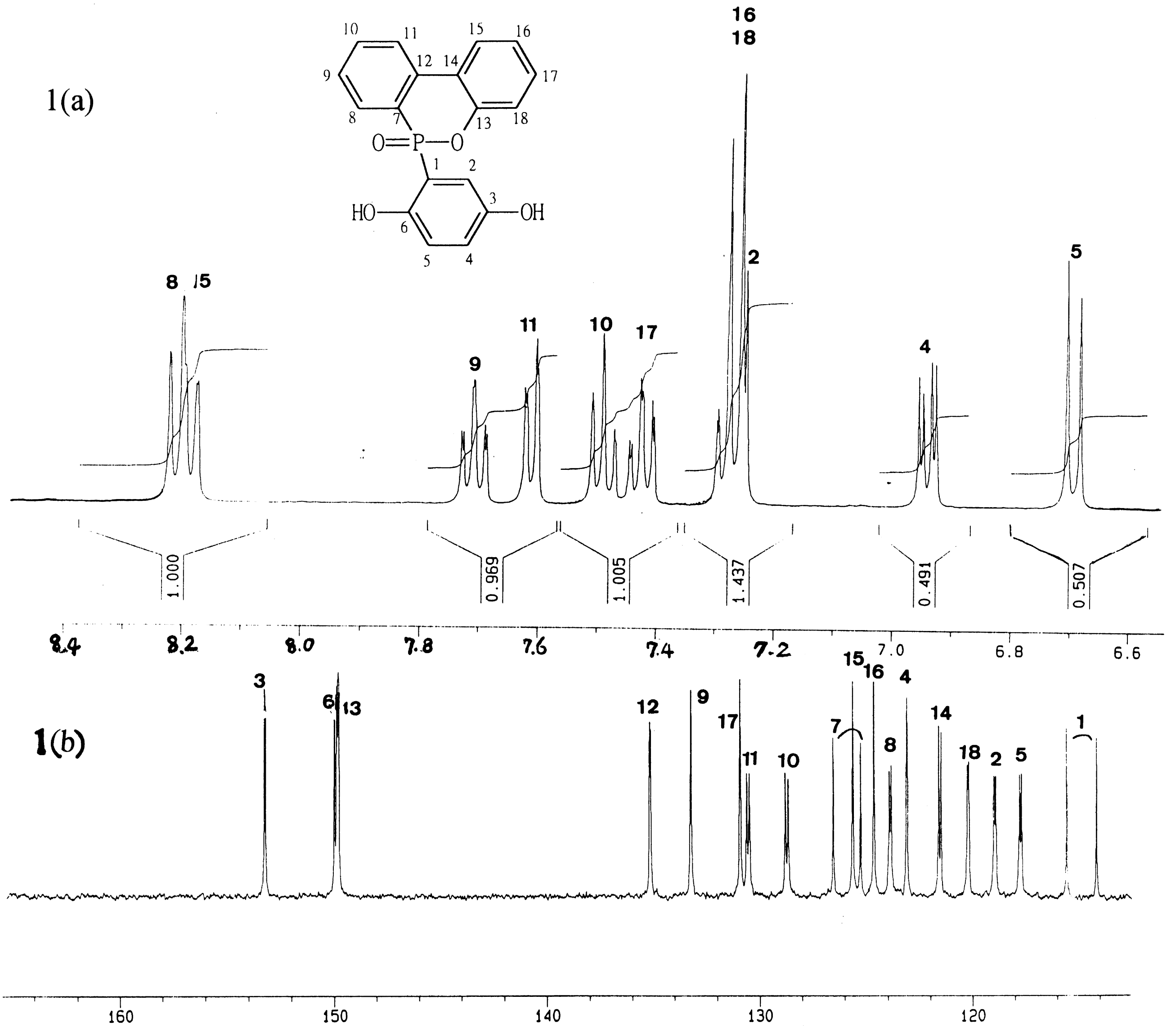


Fig. 1. (a) ^{1}H-NMR, (b) ^{13}C-NMR, (c) ^{1}H-^{1}H-NMR and (d) ^{1}H–^{13}C-NMR spectra of **I**.

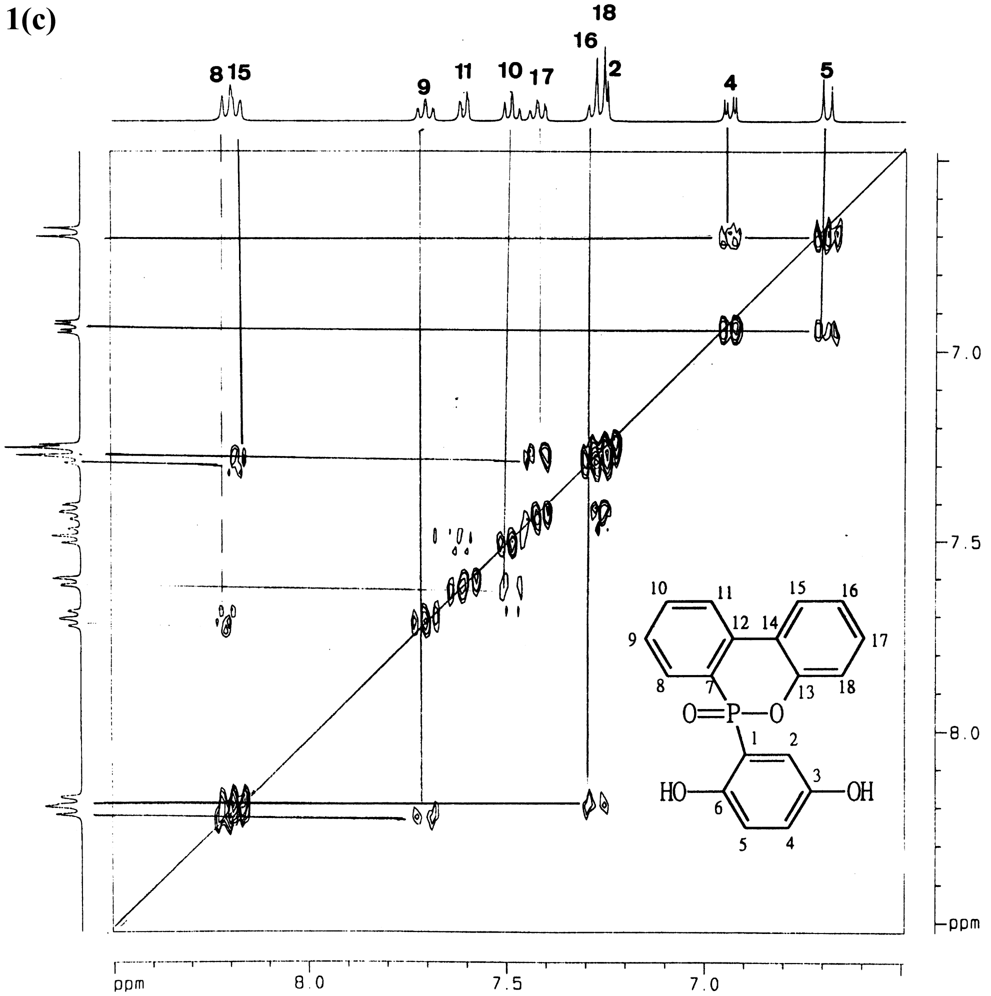


Fig. 1. (*continued*)

and 500 g 2-ethoxyethanol were introduced into a round bottom 1000 ml glass flask equipped with a nitrogen inlet, a condenser and a mechanical stirrer. The flask was heated to 125°C and maintained at that temperature for 4 h. The reaction product was filtered after cooling to room temperature and washed with 2-ethoxyethanol and methanol. It was further recrystallized from 2-ethoxyethanol and then dried in a vacuum oven at 100°C for 8 h. Off-white crystals (m.p. 255°C–256°C, 93% yield) of **I** were obtained. Mass (FAB) (m/e, relative intensity): 325 (M $+$ 1$^+$ 100), 215 ((M-109)$^-$ α cleavage of O $=$ P–Ar, 52). Elemental analysis for $C_{18}H_{13}O_4$ (324): Calcd. %: C, 66.67; H, 4.04; Found %: C, 66.57; H, 4.10. ^{31}P-NMR: 21.52 (s).

2.3. Polymerization

A typical example of the polycondensation is given below and the reaction is shown in Scheme 2.

*2.4. Polyester **III**$_c$ prepared from **I** and **II**$_c$*

A mixture of 20 mmol of **I** and 20 mmol of **II**$_c$ in 50 ml of *o*-dichlorobenzene were heated with stirring at reflux temperature for 20 h under nitrogen. The viscous solution thus obtained was poured into 400 ml of methanol with stirring, giving rise to a precipitate, which was filtered, washed thoroughly with hot methanol, and dried at 100°C under vacuum. The yield was almost quantitative. The inherent viscosity of the polymer in DMAc was 0.61 dl/g measured at a concentration of 0.5 g/dl at 30°C. Elemental analysis for polyester **III**$_c$: Calcd. %: C, 64.65; H, 3.22; Found %: C, 64.01; H, 3.28.

Other polyesters were synthesized by the similar procedure as described above.

2.5. Characterization

Elemental analyses were performed by a Heraeus CHN-Rapid element analyzer. The IR spectra were measured with a Nicolet 520 spectrometer. Inherent viscosities were measured at 30°C at a concentration of 0.5 g/dl in DMAc using an Ubbelohde capillary viscometer (Schott-AVS310). DSC data were obtained using 5–6 mg samples in a nitrogen

1(d)

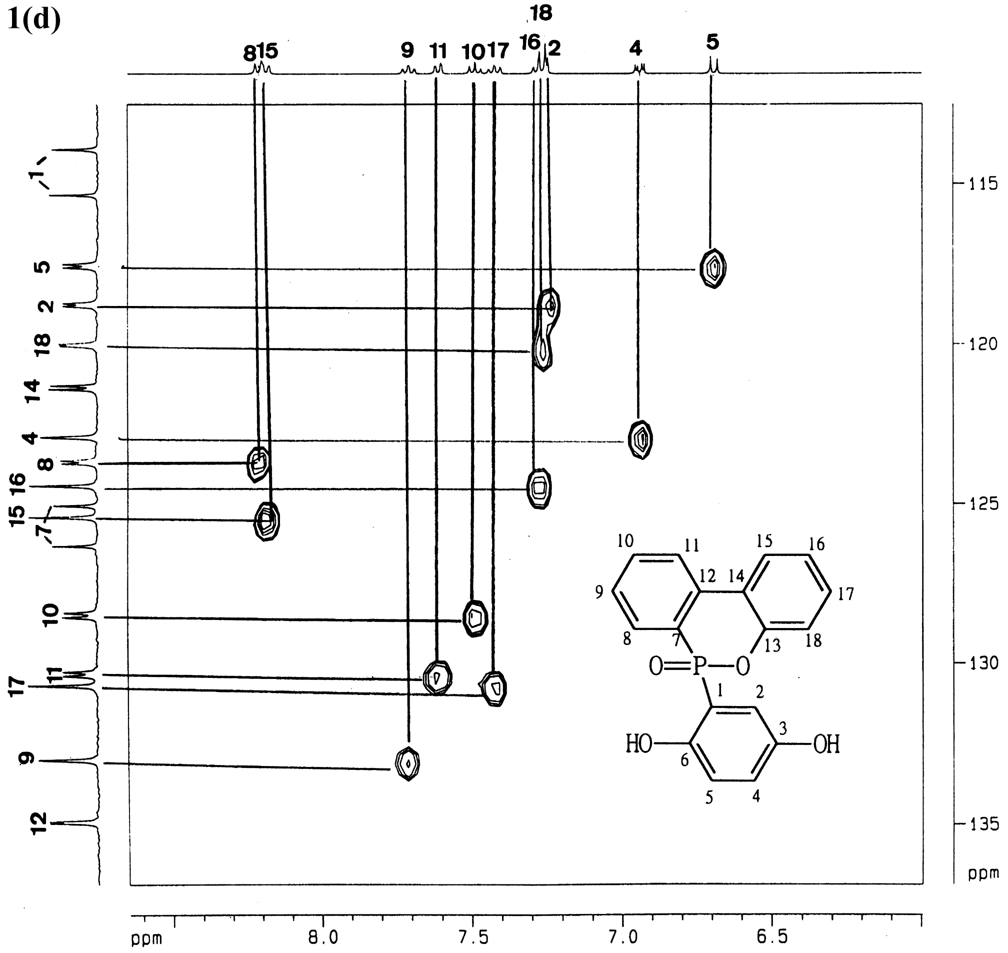


Fig. 1. (*continued*)

atmosphere at a 20°C min^{-1} heating rate using a Perkin–Elmer DSC7. Thermal gravimetric analysis was employed with a Perkin–Elmer TGA7 at a heating rate of 20°C min^{-1} in a nitrogen atmosphere from 30°C to 700°C. TGA kinetics were obtained by a heating rate of 10°C, 20°C, 30°C and 40°C min^{-1} with the sample weight of 5.0 ± 0.3 mg. ^{1}H-NMR and ^{31}P-NMR spectra were obtained with a Bruker AMX-400 using DMSO-d$_6$ as a solvent with TMS and H_3PO_3 as internal standard, respectively. Qualitative solubility was determined using 0.1 g of polymer in 2 ml of solvent. The LOI was determined with an Atlas Limiting Oxygen Index Chamber according to the published literature [3]. The wide angle X-ray diffraction measurements were performed at room temperature with a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni filtered Cu K α-radiation. The scanning rate was 4° min^{-1}. Dynamic mechanical analysis (DMA) was made with a Perkin–Elmer DMA 7e. The storage modulus G' and tan δ were studied when the sample was subjected to temperature scan mode at a programmed heating rate of 10°C min^{-1} from ambient temperature to 300°C at a frequency of 1 Hz. A sample of 6 mm in length, 2 mm in width, and approximately 0.2 mm in thickness was used.

3. Results and discussion

3.1. Monomer synthesis

I was synthesized from 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and *p*-benzoquinone (Scheme 1) and traced by LC. Some by-products were found during the reaction, but these by-products can be removed easily by recrystallization from 2-ethoxyethanol. Fig.1(a) –(d) show the enlargement of ^{1}H-NMR (6.5–8.5 ppm), the enlargement of ^{13}C-NMR (110–160 ppm), 2D ^{1}H–^{1}H COSY and 2D ^{1}H–^{13}C HMQC NMR spectra of **I** respectively. Coupling of ^{31}P with H (P–H, J1–J4 coupling), makes the spectrum so complex that it is difficult to assign an NMR peak. Thus, ‘‘^{31}P decoupling’’ is necessary. The assignment of ^{1}H and ^{13}C-NMR spectra shown in Fig. 1(a) and (b) was performed by COSY (Fig. 1(c)), HMQC (Fig. 1(d)), HMBC, HOHAHA and NOESY (HMBC, HOHAHA and NOESY were not shown in this article) and was consistent with the structure of **I**.

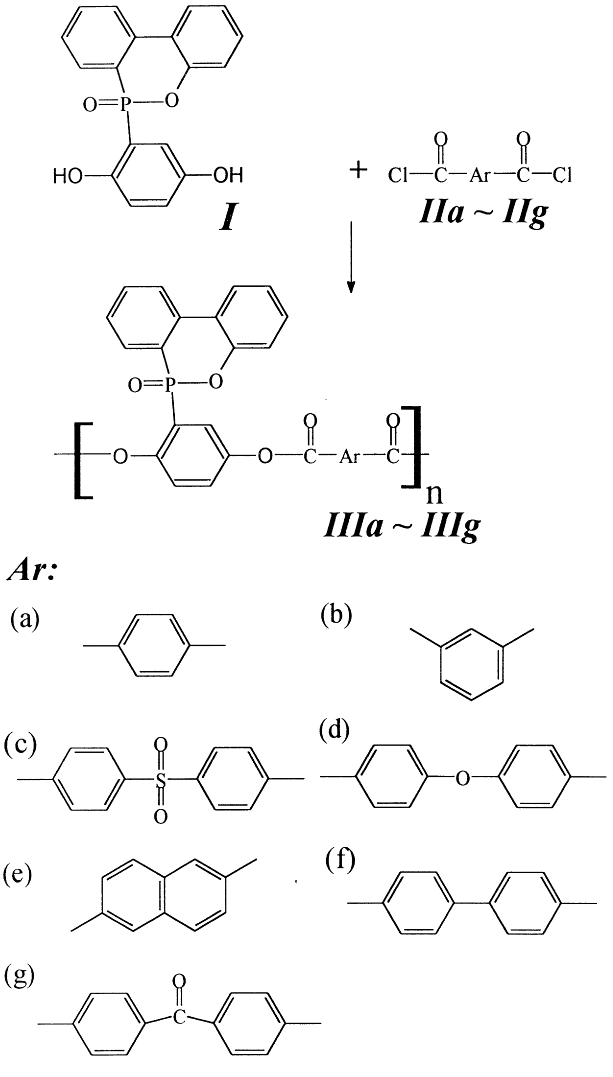
Table 1
Effect of monomer concentration on polymerization[a]

Concentration. of monomer (M)	Yield (%)	η_{inh} (dl g^{-1})[b]	Remark [c]
0.1	94	0.26	S
0.2	96	0.34	S
0.3	96	0.56	S
0.4	97	0.61	S
0.5	98	0.53	P
0.6	97	0.36	P

[a] Polymerization conditions $[\mathbf{I}] = [\mathbf{II}_c]$ 200°C, 20 h.

[b] Measured at 30°C at a concentration of 0.5 g dl^{-1} in DMAc.

[c] Appearance of the polymerization system: S, homogeneous solution; P, partial polymer gel precipitation.



Scheme 2.

3.2. Effect of reaction conditions on the inherent viscosity

Generally, the molecular weight of the polyesters obtained by high temperature solution polycondensation is highly dependent on the monomer concentration, reaction temperature, and reaction time. The best reaction conditions for high temperature solution polycondensation reported by Iami et al. [22] are: monomer concentration = 0.375 mol l^{-1}, reaction temperature = 200°C, reaction time = 20 h, by Chern [23] are: monomer concentration = 0.5 mol l^{-1}, reaction temperature = 200°C, reaction time = 20 h; by Wang [24] et al. are: monomer concentration = 0.6 mol l^{-1}, reaction temperature = 200°C, reaction time = 20 h. The main difference is in the monomer concentration, so the effect of monomer concentration was studied to find out an optimum concentration for the preparation of high molecular weight polyesters. Table 1 indicates that the inherent viscosity of polyester $\mathbf{III}_c$ increases with increasing monomer concentrations up to 0.4 mol l^{-1}. This may be attributed to the higher collisions between reactants in a concentrated solution than a diluted one. However, the effect levels off after the concentration of the monomer exceeded 0.4 mol l^{-1}. Higher concentrations led to a highly viscous state and to a swollen gel at the concentrations above 0.4 mol l^{-1}. This causes a decrease in the inherent viscosities of the polyesters.

3.3. Synthesis of polymers

A series of various polyesters was synthesized from **I** with various acid chlorides ($\mathbf{II}_a$–$\mathbf{II}_g$) by the high temperature solution polymerization in *o*-dichlorobenzene. The reactions are shown in Scheme 2. All polyesters were obtained in almost quantitative yields. The inherent viscosities of these polyesters are summarized in Table 2. The polyesters have inherent viscosities in the range of 0.38–0.61 dl g^{-1}. The highest inherent viscosity of $\mathbf{III}_c$ obtained from 4,4′-sulfonyldibenzoyl chloride ($\mathbf{II}_c$) might be explained by the higher electron affinity owing to the presence of the electron withdrawing sulfonyl (SO_2) group.

3.4. Characterization of polymers

Fig. 2 shows FTIR spectrum of polyester, $\mathbf{III}_d$. The characteristic peaks are at 1176 (P–O–Ar), 1230 (Ar–O–), 1480 (P–Ar), and 1741 cm^{-1} (C=O). Table 3 shows elemental analyses and IR characteristic peaks of polyesters $\mathbf{III}_a$–$\mathbf{III}_g$. Elemental analyses of polyesters shown in Table 3 are in good agreement with the calculated values based on the polymers. The elemental analyses and characteristic bands in the IR spectra correlate sufficiently well with the proposed structures of polyesters.

Table 2
η_{inh} of polyesters $\mathbf{III}_a$–$\mathbf{III}_g$[a]

Polyesters	Yield (%)	η_{inh} (dl g^{-1})[b]	Remark[c]
$\mathbf{III}_a$	93	–[d]	P
$\mathbf{III}_b$	96	–[d]	P
$\mathbf{III}_c$	97	0.61	S
$\mathbf{III}_d$	94	0.38	S
$\mathbf{III}_e$	92	–[d]	P
$\mathbf{III}_f$	95	0.48	S
$\mathbf{III}_g$	97	0.43	S

[a] Polymerization conditions [**I**] = [**II**] = 0.4 mol l^{-1}, 200°C, 20 h.

[b] Measured at 30°C at a concentration of 0.5 g dl^{-1} in DMAc.

[c] Appearance of the polymerization system: S, homogeneous solution; P, partial polymer gel precipitation.

[d] Insoluble in DMAc.

Table 3
Elemental analyses and IR characteristic peaks of polyesters $\mathbf{III}_a$–$\mathbf{III}_g$

Polyster	IR (KBr) P–O–Ar	Elemental analyses Calculated		Found	
		C%	H%	C%	H%
$\mathbf{III}_a$	1172	68.73	3.33	67.92	3.40
$\mathbf{III}_b$	1170	68.73	3.33	68.05	3.41
$\mathbf{III}_c$	1172	64.65	3.22	64.01	3.28
$\mathbf{III}_d$	1176	70.33	3.50	69.70	3.59
$\mathbf{III}_e$	1175	71.43	3.40	70.45	3.47
$\mathbf{III}_f$	1177	72.45	3.61	71.86	3.71
$\mathbf{III}_g$	1174	70.97	3.43	70.11	3.50

3.5. Properties of polymers

The solubility of these polyesters was tested in various solvents, and the results are summarized in Table 4. The polyesters $\mathbf{III}_a$, $\mathbf{III}_b$ and $\mathbf{III}_g$ are insoluble in DMF, DMAc, NMP, *o*-dichlorobenzene and DMSO at room temperature or on heating. This may be attributed to the rigid structure of phenylene and naphthalene group in $\mathbf{II}_a$, $\mathbf{II}_b$ and $\mathbf{II}_e$ respectively. $\mathbf{III}_c$, $\mathbf{III}_d$ and $\mathbf{III}_g$ containing ether, sulfone and carbonyl group respectively exhibit better solubility than other polyesters. However, all polymers were entirely insoluble in THF, acetone and methanol. The X-ray diffraction patterns in Fig. 3 exhibited that most polyesters have an amorphous pattern except polyester $\mathbf{III}_a$ and $\mathbf{III}_e$. This may be another reason why that $\mathbf{III}_a$ and $\mathbf{III}_e$ are insoluble in common organic solvents. Polymer $\mathbf{III}_a$ showed sharp diffraction peaks at $2\theta = \backsim 10^\circ$, 14°, 19° and 23°. Additional work is required to characterize the structure more accurately.

The glass transition temperature, T_g, one of the important parameters, can be obtained from the DSC thermogram. Being a second order thermal transition, T_g provides information regarding softening of the amorphous portion of a polymer as the temperature is elevated. As the residual

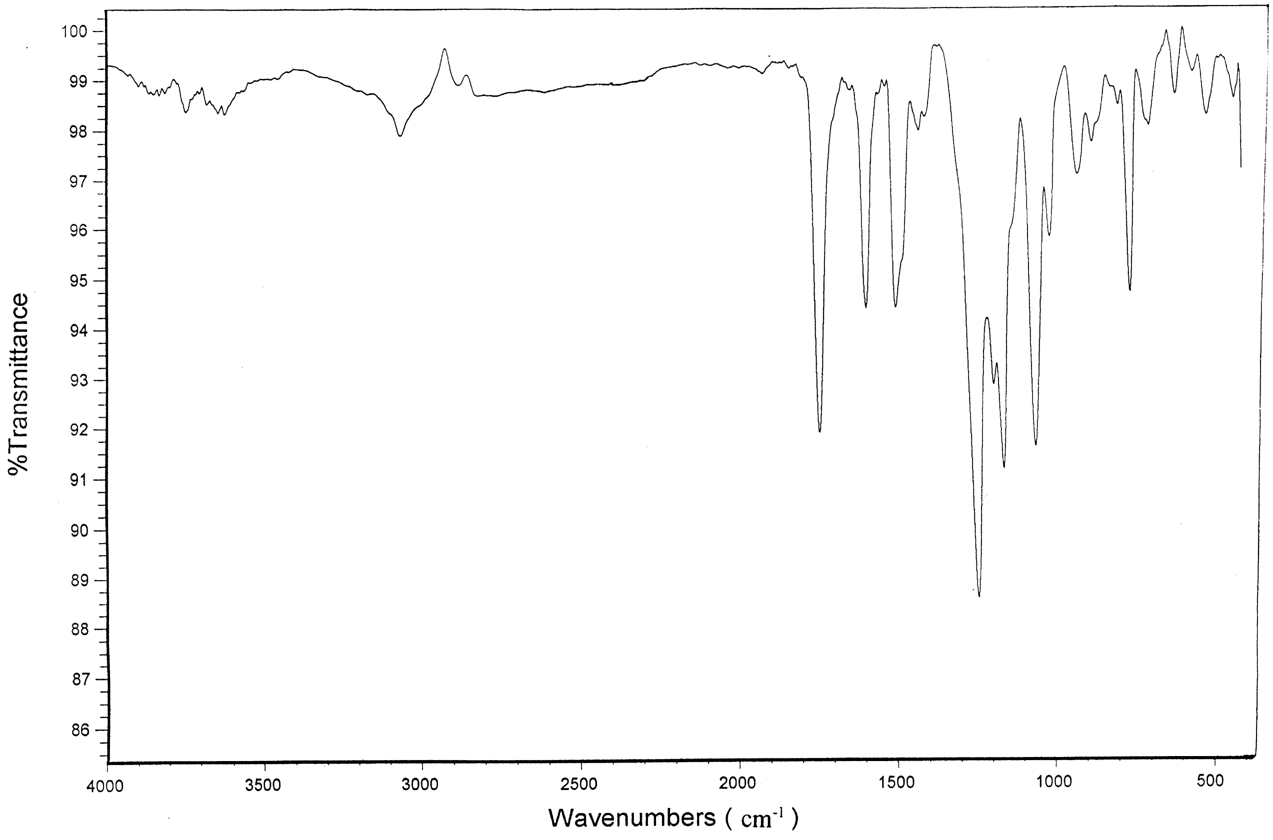


Fig. 2. FTIR spectrum of polyester $\mathbf{III}_d$.

Table 4
Solubility of polyesters **III**$_a$–**III**$_g$ [a] (Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMF, *N*, N- dimethylformamide; DMAc, *N*, N-dimethylacetamide; DMSO, dimethyl sulfoxide; OCP *o*-chlorophenol; ODB, *o*-dichlorobenzene)

	DMF	DMAc	NMP	m-Cresol	OCP	ODB	DMSO	THF	Methanol
III$_a$	–	– –	– –	– –	– –	– –	– –	– –	– –
III$_b$	– –	– –	– –	– –	– –	– –	– –	– –	– –
III$_c$	+ +	+ +	+ +	+ h	+ h	+ h	+ h	– –	– –
III$_d$	+ +	+ +	+ +	+ h	+ h	+ h	+ h	– –	– –
III$_e$	– –	– –	– –	– –	– –	– –	– –	– –	– –
III$_f$	+ h	+ h	+ h	+ h	+ h	+ h	+ h	– –	– –
III$_g$	+ +	+ +	+ +	+ h	+ h	+ h	+ h	– –	– –

[a] Solubility: + + , soluble at room temperature; + h, soluble on heating; – – , insoluble on heating.

water or solvent and the history of thermal annealing may sometimes influence the first heating run of DSC, samples were at first heated to 150°C and the T_gs were determined by the second heating. Fig. 4 shows DSC thermograms of **III**$_b$, **III**$_c$ and **III**$_d$. **III**$_b$, **III**$_c$ and **III**$_d$ show a second order transition at 204.4°C, 198.1°C and 220.3°C, respectively. The other results of DSC traces are listed in Table 5. T_gs polyesters were ranged from 198.1°C to 220.3°C. The polyester (**III**$_d$) containing flexible ether linkage derived from 4,4'-oxydibenzoyl chloride (**II**$_d$) shows the lowest T_g, and the polyester (**III**$_c$) derived from 4,4'-sulfonyldibenzoyl chloride (**II**$_c$) shows the highest T_g. However, polymers **III**$_e$ and **III**$_f$ show rather featureless DSC traces starting from 50°C to 380°C, so that the T_gs of **III**$_g$ and **III**$_f$ can not be detected by DSC scan.

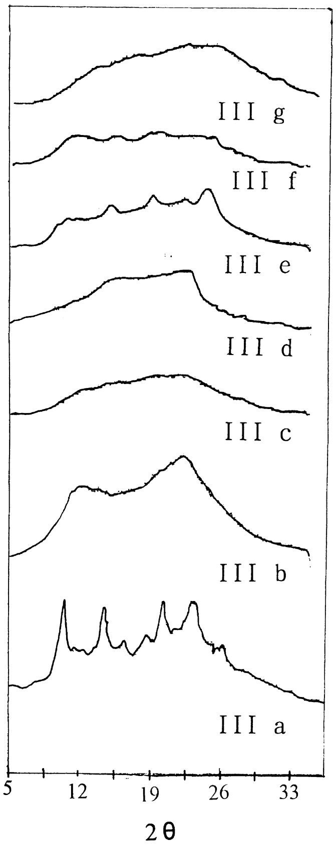


Fig. 3. X-ray diffraction of polyesters **III**$_a$–**III**$_g$.

TGA traces of these polyesters provide additional information regarding their thermal stability and thermal degradation behavior. Fig. 5 shows the thermal degradation (under nitrogen atmosphere) and thermooxidative degradation (under air atmosphere) curves of **III**$_c$ and **III**$_d$. Thermooxidative degradation reveals two decomposition steps because of the oxidative degradation of the carbonaceous residues formed in the first step. This may be why the char yields under the thermooxidative degradation are lower than that of thermal degradation. The decomposition temperatures of **III**$_c$ and **III**$_d$ under air or nitrogen are very close, which implies these polyesters have good resistance to thermooxidative degradation. The other results of TGA traces are listed in Table 5. Their degradation temperatures (T_d 5%) in nitrogen ranged from 460°C to 495°C, and the char yields at 800°C ranged from 34%–47%. Their degradation temperatures (T_d 5%) in air ranged from 450°C to 472°C, and the char yields at 800°C ranged from 21%–32%. These degradation temperatures are unusually high compared to the results reported in literatures [1–4] which has O=P–O bond in the main chain. Fig. 6 shows the decomposition profile of **III**$_a$ and **III'**$_a$ (derived from **II**$_a$ and hydroquinone according to the procedure of **III**$_c$) which has no O=P–O in the pendant group. It is easy to find that the incorporation of bulky O=P–O containing pendant group decreases the thermal decomposition temperature, however, the char yields have increased drastically, which indicates that the incorporation of phosphorus group in the side chain have increased the flame retardancy without sacrificing drastically the thermal stabilities greatly. Hsiue et al. [25] had synthesized phosphorus containing polymers with O=P–O in the main chain and studied their mechanisms of thermal degradation by a TG-FTIR analyzer. They reported that the P–O–C chain scission occurred at 300°C. However, Fig. 6 shows **III**$_a$ and **III**$_a{}'$ have the same thermal behavior below 455°C, indicating P–O–C chain in **III**$_a$ do not break below 455°C. Once the degradation of pendent phosphorus-containing group occurs at around 455°C, the phosphorus moiety in the polymer plays an important role in protecting

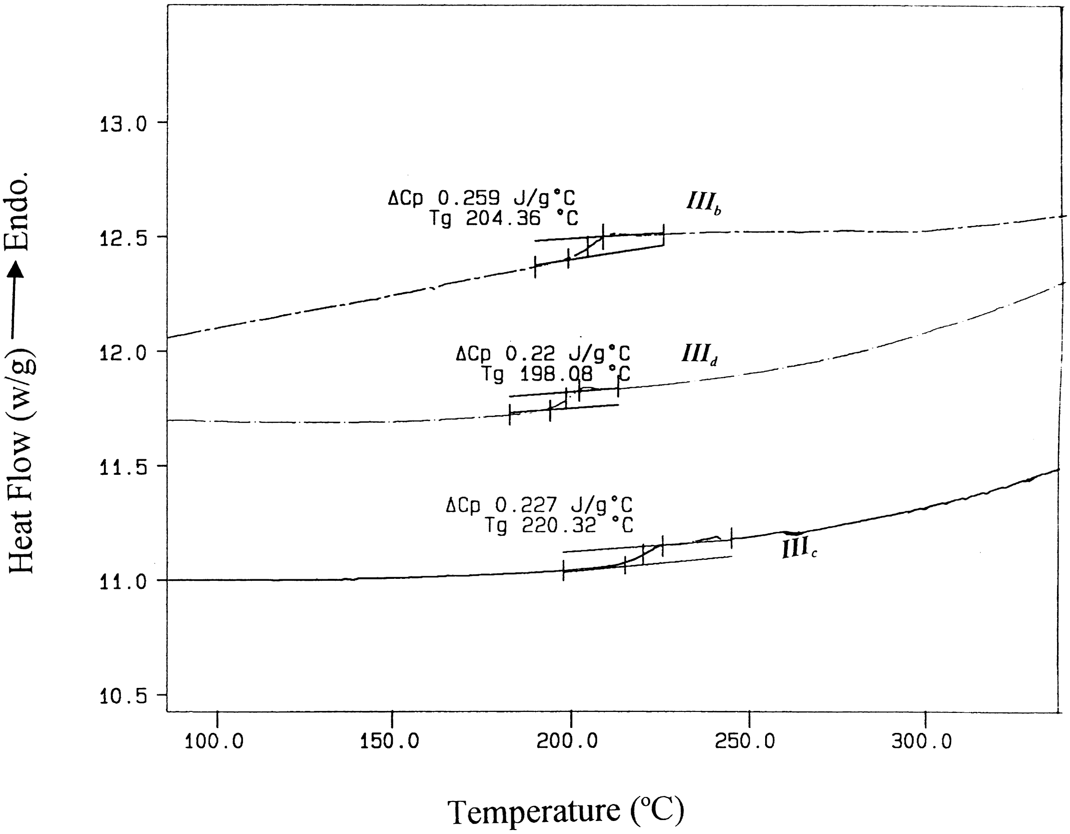


Fig. 4. DSC thermogram of $\mathbf{III_b}$, $\mathbf{III_c}$ and $\mathbf{III_d}$.

the polymer $\mathbf{III_a}$ and results in higher char yield than $\mathbf{III_a}'$. van Krevelen [26] had proposed that the char residue on pyrolysis is linearly proportional to the oxygen index of halogen-free polymers. Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction and the thermal conductivity of the burning materials, and consequently limit the flammability of the materials. Thus, incorporation of monomer **I** into polyesters is beneficial to the flame retardancy. The reason for the unusually highly thermal stabilities for polymers, $\mathbf{III_a}$–$\mathbf{III_g}$ may be attributed to the O=P–O group being protected by three phenylene groups. Other reason may be attributed to the fact that the close O=P–O chain is thermally stable than open O=P–O chain [13–17] that is, introduction of double-stranded units into the backbone will enhance their thermal stability [13–17]. Thus, these polyesters have an outstanding high temperature performance rather than other phosphorus containing polyesters [1–12]. However, it is recognized that additional work is needed to characterize the mechanism of degradation for polyesters $\mathbf{III_a}$–$\mathbf{III_g}$ more specifically.

Table 5

T_gs, degradation temperatures (T_d 5%), char yields at 800°C and LOIs of polyesters $\mathbf{III_a}$–$\mathbf{III_g}$

Polymer code	T_g (°C)	T_d (5%) (°C)		Char yield at 800°C		LOI
		In N_2	In air	In N_2	In air	
III_a	212.6	476	472	47	31	48
III_b	204.4	460	450	34	21	37
III_c	220.3	473	464	41	22	39
III_d	198.1	460	467	44	32	32
III_e	Not found	475	467	44	29	46
III_f	Not found	495	464	46	27	48
III_g	215.9	461	457	42	24	39

The activation energy of degradation is determined by Ozawa's method [27] for a given value of weight fraction (wt.%). He reported the following equation:

$$\log\beta = \frac{1}{2.303}\ln\beta = -0.4567\frac{E}{RT} + \left(\log\frac{AE}{R} - \log F(x) - 2.315\right),$$

where β is the heating rate, E the activation energy, R the ideal gas constant and $F(X)$ the conversion dependent term.

Thus, at the same conversion, a plot of $\ln(\beta)$ versus T^{-1} should be a straight line with a slope of $(2.303 \times 0.4567)E/R$. Therefore, in dynamic experiments, the activation energy may be obtained as a function of conversion. The results are shown in Fig. 7. Straight lines are drawn according to the method of least squares (Fig. 8). From these lines the

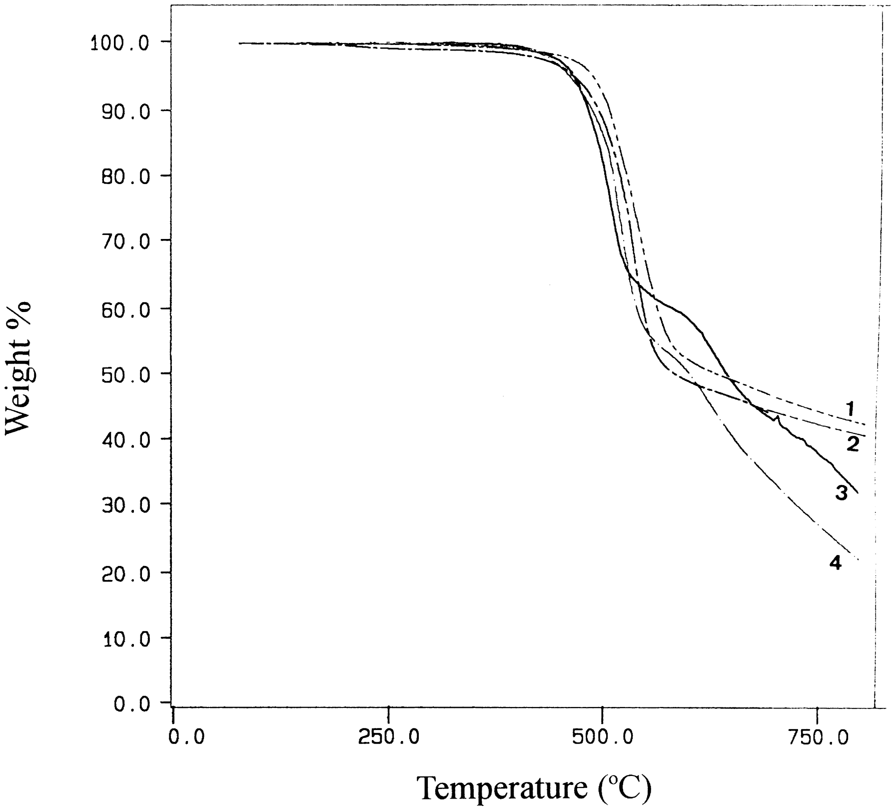


Fig. 5. TGA curves of polyesters $\mathbf{III}_d$ and $\mathbf{III}_c$. (1) $\mathbf{III}_d$ under N_2, (2) $\mathbf{III}_c$ under N_2, (3) $\mathbf{III}_d$ under air, (4) $\mathbf{III}_c$ under air.

activation energies at various conversions in nitrogen are determined and listed in Table 6. Similarly, the degradation activation energies at 10% weight loss for other polyesters are determined and listed in Table 7. The polyester $\mathbf{III}_f$ containing rigid b-phenylene linkage showed the highest activation energy while the polyester $\mathbf{III}_d$ containing flexible ether linkage showed the lowest activation energy. The reason for polymer $\mathbf{III}_f$ having a higher activation energy of degradation than that of $\mathbf{III}_a$ may be attributed to that $\mathbf{III}_f$ have a higher molecular weight than $\mathbf{III}_a$ because $\mathbf{III}_a$ precipitated during reaction and have no chance to grow into high molecular weight. The LOIs of polyesters shown in Table 5 were ranged from 37 to 48, indicating a high flame retardant properties.

Flexible films of polyesters $\mathbf{III}_c$, $\mathbf{III}_d$ and $\mathbf{III}_g$ could be obtained by casting from their DMAc solutions. Fig. 9 shows the dynamic mechanical analysis curves of polyarylate $\mathbf{III}_d$ film at a heating rate of 10°C min^{-1}. The main

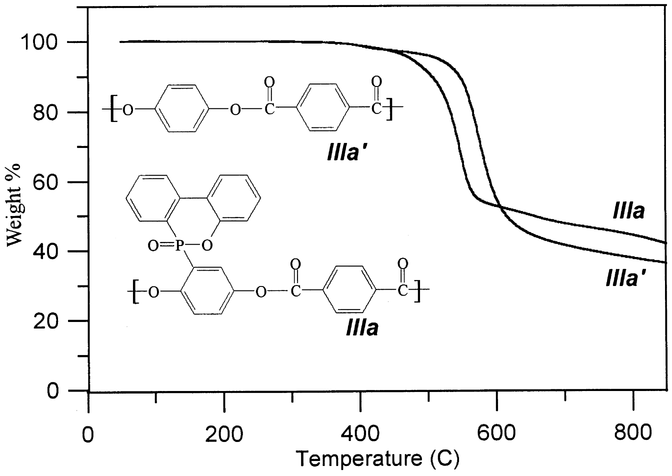


Fig. 6. TGA curves of polyester $\mathbf{III}_a$ and polyester $\mathbf{III}_a'$.

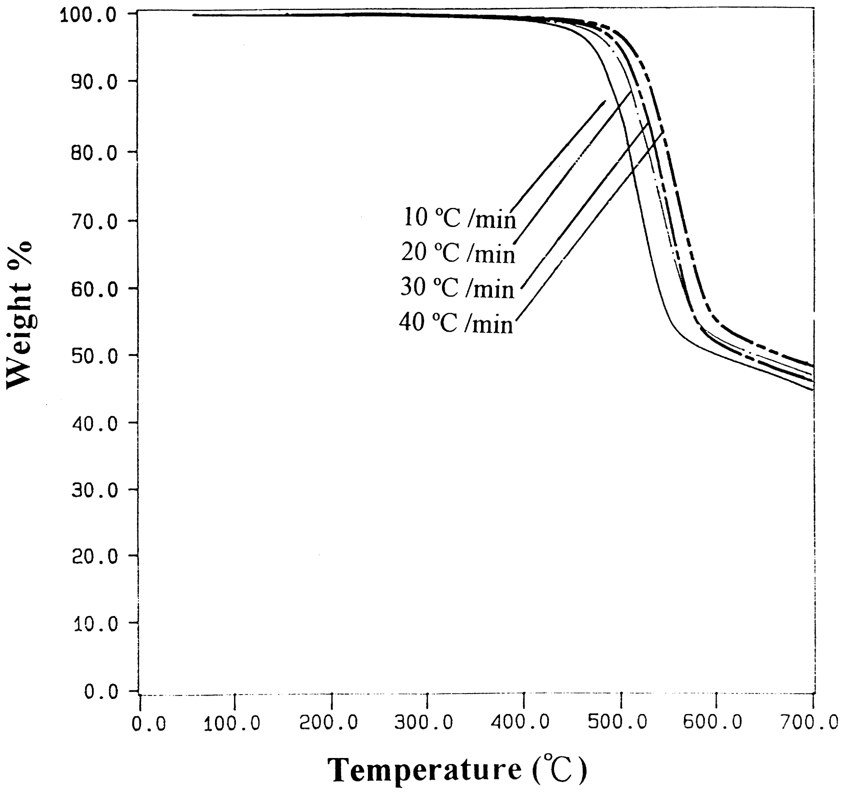


Fig. 7. TGA curves of $\mathbf{III}_d$ at various heating rates in nitrogen (10°C, 20°C, 30°C, 40°C min^{-1}).

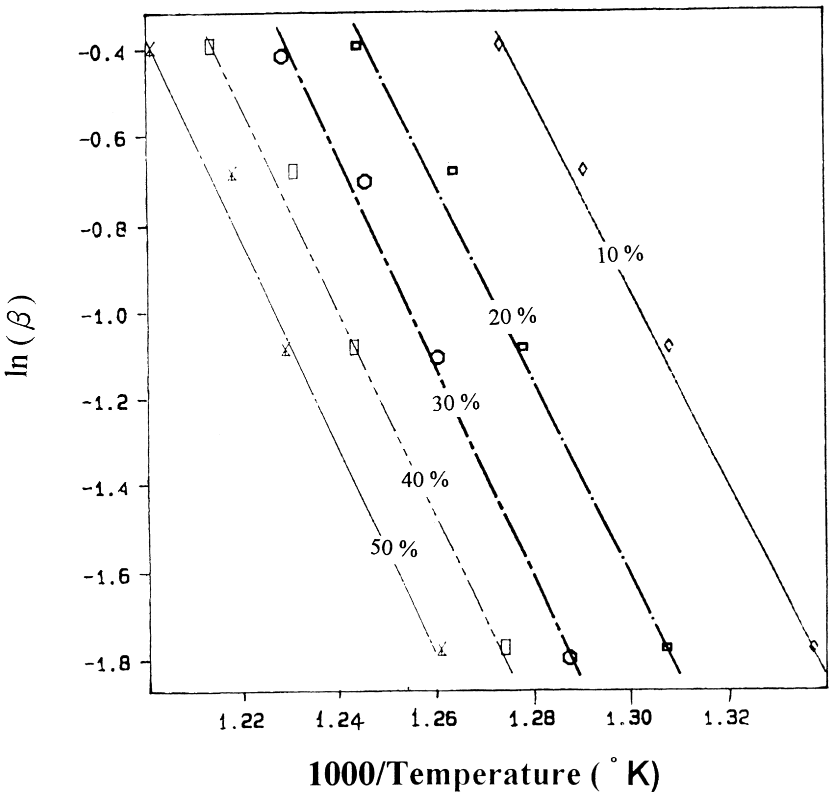


Fig. 8. Ln(β) vs. T^{-1} plots of polyester $\mathbf{III}_d$ at various conversions (10%, 20%, 30%, 40%, 50%).

Table 6
Preexponential factors and activation energies of degradation for **III**$_d$ at various conversions (10%, 20%, 30%, 40%, 50%)

Conversion	Preexponential factor ln Z (1 s^{-1})	Activation energy Ea (KJ mol^{-1})
10%	20.2	170.4
20%	21.0	175.2
30%	23.3	189.2
40%	24.2	184.1
50%	23.2	186.8

Table 7
Activation energies of degradation and degradation order for polyesters **III**$_a$–**III**$_g$ at 10% conversion

Polymer code	Activation energy (KJ mol^{-1})	Degradation order
III$_a$	189.8	1
III$_c$	187.5	1
III$_d$	170.4	1
III$_f$	238.8	1

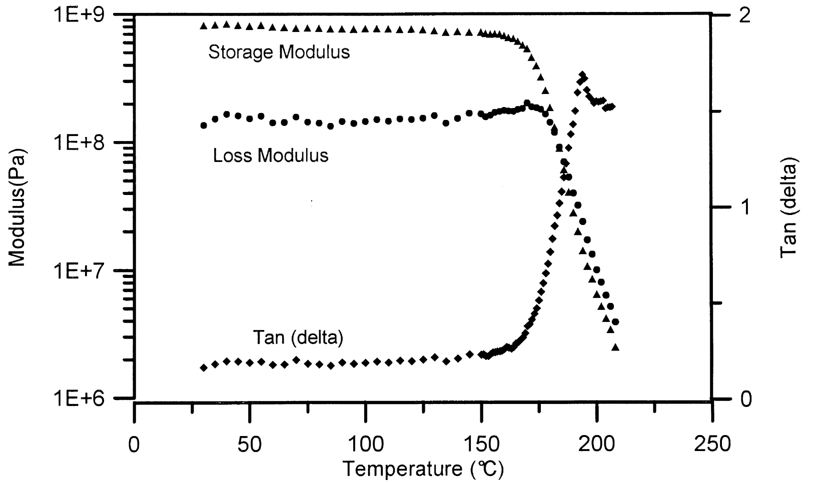


Fig. 9. Dynamic mechanical analysis of polymer **III**$_d$ at a heating rate of 10°C min^{-1}.

transition at around 195°C is associated with approximately a two order of magnitude decrease in *G*‘. This transition could be indicative of either a glass or a melting transition. Moreover, a endothermic transition was observed by DSC at about the same temperature, a fact that supports the glass transition temperature. **III**$_d$ exhibited a rather high initial *G*‘ value ($\backsim 10^8$ Pa) and about 10^9 Pa up to 180°C. The other polyesters (**III**$_c$ and **III**$_g$) showed similar dynamic mechanical behavior and have good mechanical properties (*G*‘: 10^8-10^9 Pa) by the dynamic mechanical analyses.

4. Conclusion

I was synthesized from DOPO and *p*-benzoquinone in 2-ethoxyethanol and its structure was confirmed by IR, MASS, EA, ^{1}H-NMR and ^{13}C-NMR. Phosphorus containing flame retardant polyarylates with highly thermal and flame retardant properties were obtained from **I** and various acid chlorides by high temperature solution polycondensation under a optimum reaction condition. These polyesters have good mechanical properties (G': 10^8–10^9 Pa) up to 180°C temperature and good thermal and flame retardant properties. The glass transition temperatures of these polyesters are in the range of 198.1°C to 220.3°C. The degradation temperatures (T_d 5%) in nitrogen ranged from 460°C to 495°C and char yields at 800°C are 34%–47%. The degradation temperatures (T_d 5%) in air ranged from 450°C to 472°C and char yields at 800°C were 21%–32%. The activation energies of degradation ranged from 177.4 to 238.8 KJ mol^{-1}. The LOIs of these polyesters are in the range of 37–48. These properties should make these polyesters attractive for practical applications such as flame retardant high performance engineering plastics.

Acknowledgements

Financial support of this work by the National Science Council of Republic of China is gratefully appreciated (NSC86-2622-E-006-001)

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