New polymer syntheses: 62. Thermotropic aromatic polyesters containing phosphate or phosphonate groups

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Numerous phosphorus-containing aromatic polyesters were prepared by polycondensation of silylated diphenols with dicarboxylic or phosphoric acid dichlorides. Phenyl phosphate and naphthyl phosphate, phenyl- or methylphosphonate groups were incorporated into poly (phenylhydroquinone terephthalate). Regardless of the substituent attached to the phosphorus atom the nematic phase disappeared when more than 20 mol% of the terephthalic acid was replaced by phosphoric or phosphonic acid units. Furthermore, phenylphosphonic acid was incorporated into various thermotropic copolyesters. It was found in all cases that the stability of the mesophase depends on the percentage of phosphorus and on the length of the repeating unit.

(Keywords: thermotropic behaviour; polyesters; polycondensation)

INTRODUCTION

The incorporation of phosphorus atoms into main chains or side chains of polymers has the general advantage that the flammability is significantly reduced. Low molecular weight additives, such as tricresylphosphate, have the shortcoming that they may be washed out or may slowly evaporate from the polymeric material. In the case of thermotropic engineering plastics, such as aromatic polyesters, incorporation of phosphate or phosphonate groups into the main chain has the disadvantage that the sp^3 hybridized phosphorus destabilizes the mesophase due to the unfavourable bond angle of 109°. The purpose of this work was to study this destabilizing effect in a variety of thermotropic copolyesters. A similar study dealing with a thermotropic poly(ester imide) was published recently[1]. Together with the results of the present work, structure/property relationships of more general validity should be elaborated.

EXPERIMENTAL

Materials

Phenyl dichlorophosphoridate, phenylphosphonic dichloride and methylphosphonic dichloride were purchased from Aldrich (Milwaukee, WI, USA) and distilled prior to use. Hydroquinone, phenylhydroquinone, 4-hydroxybenzoic acid and terephthaloyl chloride were gifts of Bayer AG (Uerdingen, Germany). The diphenols and 4-hydroxybenzoic acid were silylated with hexamethyldisilazane in refluxing toluene and the products were isolated by distillation: bistrimethylsilyl hydroquinone, m.p. = 51°C (literature[2] value 52°C); bistrimethylsilyl phenylhydroquinone, $n_D^{20} = 1.5207$ (literature[3] value 1.520); bistrimethylsilyl 4-hydroxybenzoic acid, $n_D^{20} = 1.4840$ (literature[4] value 1.4843).

4-Trimethylsilyloxybenzoylchloride was prepared as described previously[4], $n_D^{20} = 1.5265$ (literature[4] value 1.5270). α-Naphthyldichlorophosphoridate was prepared as described previously[5], $n_D^{20} = 1.6005$, b.p. = 108°C/0.1 mbar (literature[5] value 138–140°C/0.5 mbar).

Polycondensations

Copolyesters of Tables 1–3. Bistrimethylsilylhydroquinone (40 mmol), a mixture of terephthaloyl chloride and phenylphosphonic dichloride (together 41 mmol) and 10 mg benzyltriethylammoniumchloride were weighed into a cylindrical glass reactor equipped with stirrer, gas inlet and outlet tubes. The reactor was placed into a metal bath preheated to 150 or 160°C where the condensation started slowly. The reaction temperature was gradually raised to 320°C over a period of 3 h. The liberated chlorotrimethylsilane was removed with a slow stream of nitrogen. Finally, vacuum was applied for 0.5 h at 120°C. The cold copolyester was powdered, dissolved in CH_2Cl_2/trifluoroacetic acid (TFA) (4:1 by volume), precipitated into cold methanol, filtered off and dried at 115°C *in vacuo*.

All other copolyesters of *Tables 1–3* were prepared by analogous methods. However, with methane phosphonic dichloride the final reaction temperature was limited to 290°C, and in the case of naphthyl-dichlorophosphoridate to 300°C.

Copolyesters of Tables 4 *and* 5. Bistrimethylsilylhydroquinone (20 mmol), a mixture of phenoxyterephthaloylchloride and phenylphosphonic dichloride (together 20 mmol), 4-trimethylsilyloxybenzoylchloride (20 mmol) and benzyltriethylammoniumchloride (10 mg) were weighed

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Table 1 Yields and properties of copolyesters from terephthaloyl chloride, silylated phenylhydroquinone and methylphosphonylchloride[a]

Polymer	T/P[b]	Yield (%)	η_{inh}[c] (dl g^{-1})	T_g[d] (°C)	T_m[d] (°C)	T_i[e] (°C)	Elemental analyses	C	H	P
1a[f]	100/0	97	1.70[g]	170	346	475				
1b	90/10	98	0.90	130	319–326	420–460	Calcd	74.70	4.19	1.00
							Found	74.78	3.88	0.91
1c	80/20	97	0.80	129	–	380–410	Calcd	73.90	3.94	2.05
							Found	72.46	3.85	2.05
1d	70/30	95	0.78	129	–	–	Calcd	72.81	3.99	2.15
							Found	72.52	3.88	2.81
1e	60/40	95	0.78	131	–	–	Calcd	71.18	4.13	4.37
							Found	71.39	4.06	4.35

[a] All polycondensations were conducted at 160–290°C (3 h)
[b] Molar ratio of terephthalate and phosphonate groups
[c] Measured at 20°C with $c=2\,g\,l^{-1}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1)
[d] From d.s.c. heating curves with a heating rate of 20°C min^{-1}
[e] Isotropization temperature as revealed by optical microscopy
[f] For synthesis and characterization see ref. 10
[g] Measured at 25°C with $c=5\,g\,l^{-1}$ in phenol/4-chlorophenol/tetrachloroethane (25/40/35 wt%)

Table 2 Yields and properties of copolyesters from terephthaloyl chloride, silylated phenylhydroquinone and phenyl phosphonylchloride[a]

Polymer	T/P[b]	Yield (%)	η_{inh}[c] (dl g^{-1})	T_g[d] (°C)	T_i[e] (°C)	Elemental analyses	C	H	P
2a[f]	100/0	97	1.70[g]	170	475				
2b	90/10	98	1.22	144	440–460	Calcd	75.38	3.86	0.98
						Found	74.87	3.79	0.91
2c	80/20	96	1.50	132	390–410	Calcd	74.80	3.91	1.97
						Found	74.85	3.88	1.95
2d	70/30	96	0.62	131	–	Calcd	74.23	3.95	2.96
						Found	74.15	3.93	3.10
2e	60/40	97	0.58	127	–	Calcd	73.65	3.99	3.96
						Found	73.18	3.94	4.00
2f	50/50	96	0.57	128	–	Calcd	73.07	4.04	4.96
						Found	72.92	3.96	4.07

[a] All polycondensations were conducted at 160–320°C (3.5 h)
[b] Molar ratio of terephthalate and phosphonate groups
[c] Measured at 20°C with $c=2\,g\,l^{-1}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1)
[d] From d.s.c. heating curves with a heating rate of 20°C min^{-1}
[e] Isotropization temperature as revealed by optical microscopy
[f] $T_m=346$°C, see ref. 10
[g] Measured at 25°C with $c=5\,g\,l^{-1}$ in phenol/4-chlorophenol/tetrachloroethane (25/40/35 wt%)

into a cylindrical glass reactor equipped with stirrer, gas inlet and gas outlet tubes. The reactor was placed in a metal bath at 130°C and the reaction temperature was gradually raised to 320°C over a period of about 3 h. Finally vacuum was applied and the cold reaction product was reprecipitated as described above. The copolyesters of *Table 4* were prepared analogously in the temperature range 120–280°C.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostatted at 20°C.

The d.s.c. measurements were conducted with a Perkin-Elmer DSC-4 in aluminium pans under nitrogen at a heating rate of 20°C min^{-1}.

The WAXS powder patterns were obtained on a Siemens D-500 powder diffractometer with Ni-filtered CuKα radiation.

The 100 MHz ^{1}H n.m.r. spectra were recorded with a Bruker AM-100 FT n.m.r. spectrometer in 5 mm o.d. sample tubes (tetramethylsilane served as internal standard).

The dynamic mechanical measurements were conducted with a DuPont DMA Md 983 at a heating rate of 2°C min^{-1}.

Thermogravimetric analyses were conducted with a Perkin-Elmer TSG-2 at a heating rate of 10°C min^{-1} in air.

RESULTS AND DISCUSSION

Syntheses of copolyesters

The phosphorus-containing copolyesters synthesized

Table 3 Yields and properties of copolyesters derived from terephthaloyl chloride, silylated hydroquinone and phenyl or α-naphthylphosphate

Polymer	T/P[a]	Reaction temperature (°C)	Yield (dl g^{-1})	η_{inh}[b] (°C)	T_g^c (°C)	T_i^d (°C)	Elemental analyses	C	H	P
3a	90/10	170–320	93	0.68	141	420–460	Calcd	74.99	3.85	0.98
							Found	74.31	3.72	0.70
3b	80/20	170–320	95	0.47	116	400–430	Calcd	74.05	3.87	1.95
							Found	73.62	3.76	1.48
3c	70/30	170–320	87	0.35	112	–	Calcd	73.11	3.89	2.92
							Found	73.60	3.88	2.30
3d	90/10	150–300	93	0.55	125	410–440	Calcd	75.32	3.85	0.96
							Found	74.76	3.82	0.97
3e	80/20	150–300	91	0.30	106	360–400	Calcd	73.99	3.84	1.87
							Found	73.20	3.80	1.86
3f	70/30	150–300	84	0.25	92	–	Calcd	74.14	3.90	2.78
							Found	73.50	3.75	2.65

[a] Molar ratio of terephthalate and phosphate units
[b] Measured at 20°C with $c = 2\,\mathrm{g\,l^{-1}}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1)
[c] From d.s.c. measurements with a heating rate of 20°C min^{-1}
[e] Isotropization temperature as revealed by optical microscopy

Table 4 Yields and properties of copolyesters from terephthaloyl chloride, silylated phenylhydroquinone, 4-trimethylsilyloxybenzoylchloride and phenyl phosphonylchloride[a]

Polymer	T/P[b]	Yield (%)	η_{inh}[c] (dl g^{-1})	T_g^d (°C)	T_i^e (°C)	Elemental analyses	C	H	P
4a	100/00	96	1.32	139	>460	Calcd	73.38	3.62	–
						Found	72.91	3.69	–
4b	75/25	95	1.14	143	>460	Calcd	72.56	3.68	1.40
						Found	71.66	3.70	1.35
4c	50/50	93	0.77	120	410–460	Calcd	71.74	3.74	2.80
						Found	71.24	3.74	2.71
4d	40/60	97	1.04	126	400–450	Calcd	71.41	3.76	3.31
						Found	70.99	3.76	3.24
4e	30/70	98	0.73	126	390–450	Calcd	71.08	3.79	3.94
						Found	70.01	3.82	3.93
4f	20/80	96	0.54	125	–	Calcd	70.07	3.86	5.65
						Found	69.61	3.80	5.90
4g	0/100	98	0.56	123	–	Calcd	70.07	3.86	5.65
						Found	69.45	3.84	6.14

[a] All polycondensations were conducted at 120–280°C (3.5 h)
[b] Molar ratio of terephthalate and phosphonate groups
[c] Measured at 20°C with $c = 2\,\mathrm{g\,l^{-1}}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1)
[d] From d.s.c. heating curves with a heating rate of 20°C min^{-1}
[e] Isotropization temperature as revealed by optical microscopy

in this work can be divided into two groups. The first group are derivatives of poly(phenylhydroquinone terephthalate) (*1a–e*, *2a–f*, *3a–f*). This group was synthesized to study the influence of various substituents attached to the phosphorus. The second group is characterized by longer repeating units (those of the parent homopolyesters *4a* and *5a*) and the phenylphosphonate group as the only kind of phosphorus-containing building block (*4a–f* and *5a–f*).

All copolyesters were synthesized by the 'silyl method' as exemplified by equation (1). As usual, chloride ions served as catalyst. This method has previously demonstrated its usefulness for the preparation of phosphorus-containing copolyesters[1,5]. The copolyesters obtained in this way correspond to the feed ratio. The molar composition was checked by P elemental analyses (*Tables 1–5*) and in the case of copolyesters *1b–e* by ^1H n.m.r. spectroscopy. The ^1H n.m.r. signals of terephthaloyl unit and of the P–CH_3 group allow an easy comparison of the molar ratio (*Figure 1*). The n.m.r. spectroscopic analyses of the isolated copolyesters *2a–e* agreed well with the feed ratio. The triplet-like splitting of the CH_3– signals is the result of the head-to-head, head-to-tail sequence isomerism resulting from the phenyl substituent of hydroquinone. This splitting indicates the expected randomness of the sequences. The doublet splittings result from scalar coupling of the ^1H and ^{31}P nuclei.

The relatively high volatility of the phosphoric and

Table 5 Yields and properties of copolyesters prepared from phenoxyterephthaloyl chloride, silylated hydroquinone, 4-trimethylsilyloxybenzoylchloride and phenylbenzene phosphonylchloride[a]

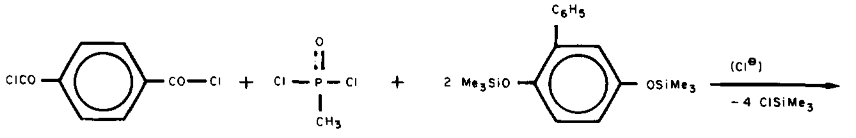
Polymer	T/P[b]	Yield (%)	η_{inh}[c] (dl g^{-1})	T_g[d] (°C)	T_i[e] (°C)	Elemental analyses	C	H	P
5a	100/0	84	1.46	121	>460	Calcd	71.33	3.52	–
						Found	71.28	3.56	–
5b	75/25	89	1.40	128	420–460	Calcd	70.20	3.54	1.41
						Found	69.64	3.53	1.63
5c	50/50	89	0.78	117	400–440	Calcd	68.97	3.57	2.96
						Found	67.63	3.39	2.90
5d	40/60	94	0.94	118	390–440	Calcd	68.44	3.58	3.63
						Found	68.20	3.59	3.55
5e	30/70	97	0.96	122	315–430	Calcd	67.89	3.59	4.31
						Found	67.12	3.48	4.05
5f	20/80	90	0.52	118	–	Calcd	67.32	3.60	5.03
						Found	66.50	3.47	4.89
5g	0/100	87	0.52	125	–	Calcd	66.11	3.63	6.56
						Found	65.30	3.52	6.32

[a] All polycondensations were conducted at 170–320°C (3.5 h)
[b] Molar ratio of terephthalate and phosphonate groups
[c] Measured at 20°C with $c=2\,g\,l^{-1}$ in CH_2Cl_2/trifluoroacetic acid (volume ratio 4:1)
[d] From d.s.c. heating curves with a heating rate of 20°C min^{-1}
[e] Isotropization temperature as revealed by optical microscopy

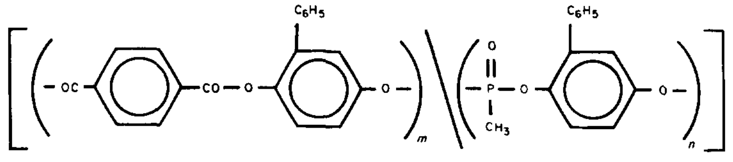
phosphonic dichlorides affected the molecular weights in the small scale experiments of this work. Therefore, the phosphoric and phosphonic dichlorides were added in 1–3 mol% excess. Nonetheless the viscosities listed in *Tables 1–5* show that the viscosities decrease with increasing molar fraction of the phosphorus. Yet previous studies of aromatic polyphosphates[6] and polyphosphonates[7,8] suggest that a greater coil density might contribute to the lower viscosity values.

Thermal properties

D.s.c. measurements of the phosphorus-containing copolyesters were conducted at a heating rate of 20°C min^{-1}. They revealed that both phosphonic acids strongly reduce the crystallinity of the homopolyester *1a* (or *2a*) even at the lowest molar ratio of 90/10. Only a weak, flat endotherm is detectable in the heating curves (*Tables 1* and *2*). Higher molar fractions of phosphonate groups (*1c–e*, *2c–f*) eliminate the crystallinity completely.

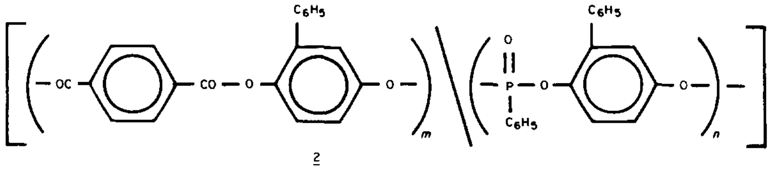


(I)



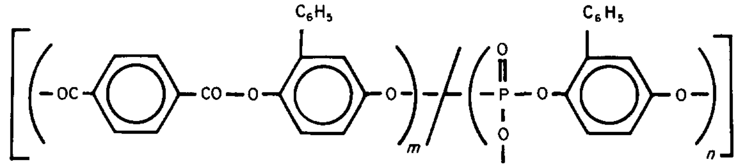
1

a: m/n = 100/0
b: m/n = 90/10
c: m/n = 80/20
d: m/n = 70/30
e: m/n = 60/40



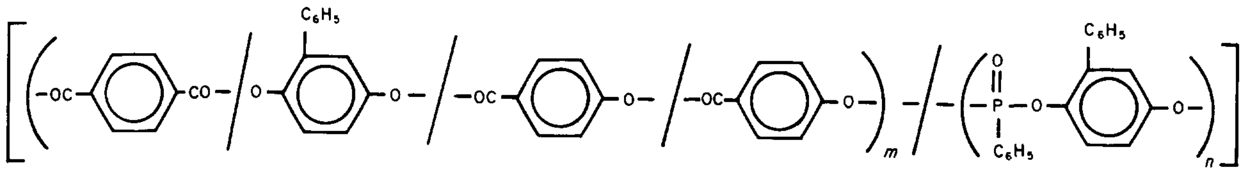
2

a: m/n = 100/0
b: m/n = 90/10
c: m/n = 80/20
d: m/n = 70/30
e: m/n = 60/40
f: m/n = 50/50



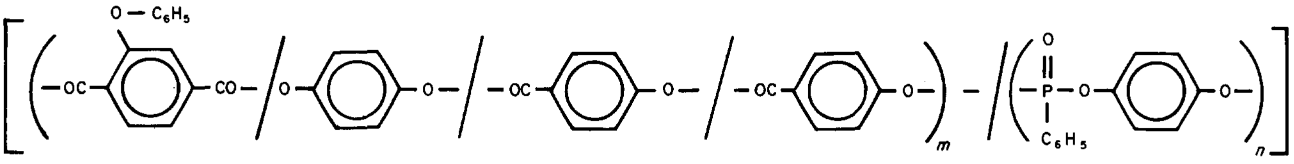
3

a: R = C_6H_5 m/n = 90/10
b: R = C_6H_5 m/n = 80/20
c: R = C_6H_5 m/n = 70/30
d: R = $C_{10}H_7$ m/n = 90/10
e: R = $C_{10}H_7$ m/n = 80/20
f: R = $C_{10}H_7$ m/n = 70/30



4

a: m/n = 100/0
b: m/n = 75/25
c: m/n = 50/50
d: m/n = 40/60
e: $m\ n$ = 30/70
f: m/n = 20/80
g: m/n = 0/100



5

a: m/n = 100/0
b: m/n = 75/25
c: m/n = 50/50
d: m/n = 40/60
e: m/n = 30/70
f: m/n = 20/80
g: m/n = 0/100

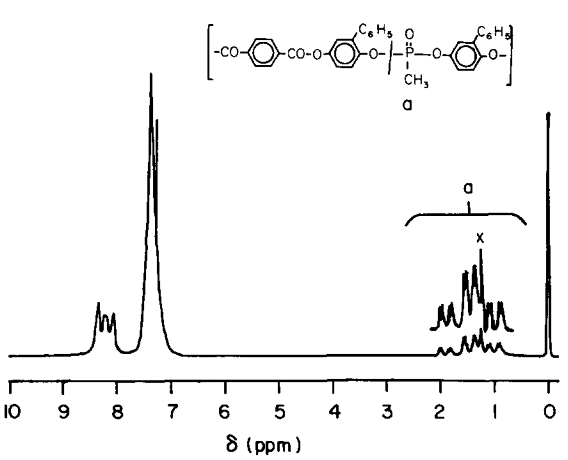


Figure 1 100 MHz ^1H n.m.r. spectrum of copolyester 1 measured in $CDCl_3$/TFA (volume ratio 3:1)

In the case of phenyl or naphthylphosphate groups even 10 mol% suffices to suppress the crystallinity. WAXS powder patterns confirmed this interpretation of the d.s.c. measurements. The solid state of copolyesters forming a nematic melt is a nematic glass, whereas copolyesters with an isotropic melt form, of course, an isotropic glass below T_g.

Methyl or phenylphosphonate groups reduce the T_g of the homopolyester *1a* (= *2a*) to a value around 129 ± 2°C. This value is quite independent of the composition and of the molecular weight within the range of inherent viscosities examined (*Tables 1* and *2*). Lower T_g values were found for the incorporation of phenyl and naphthylphosphate, but in the latter case the lower molecular weights may contribute to the low T_g values. In the case of copolyesters *4a–g* and *5b–g* a systematic influence of the phosphonate groups on the T_g is not detectable (*Tables 4* and *5*).

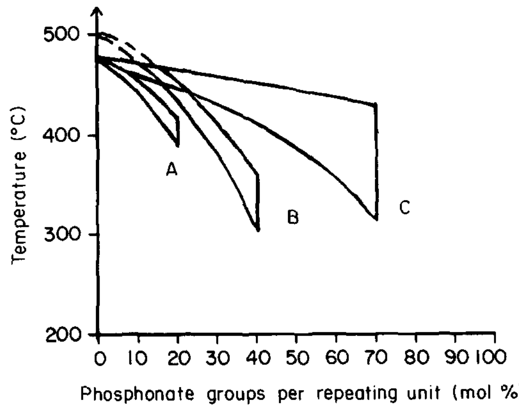


Figure 2 Plot of isotropization temperatures *versus* molar fraction of phenylphosphonate groups (per repeating unit of the parent homopolyester): A, copolyesters *2a–f*; B, poly(ester imide)s *6a–f*; C, copolyesters *5a–g*

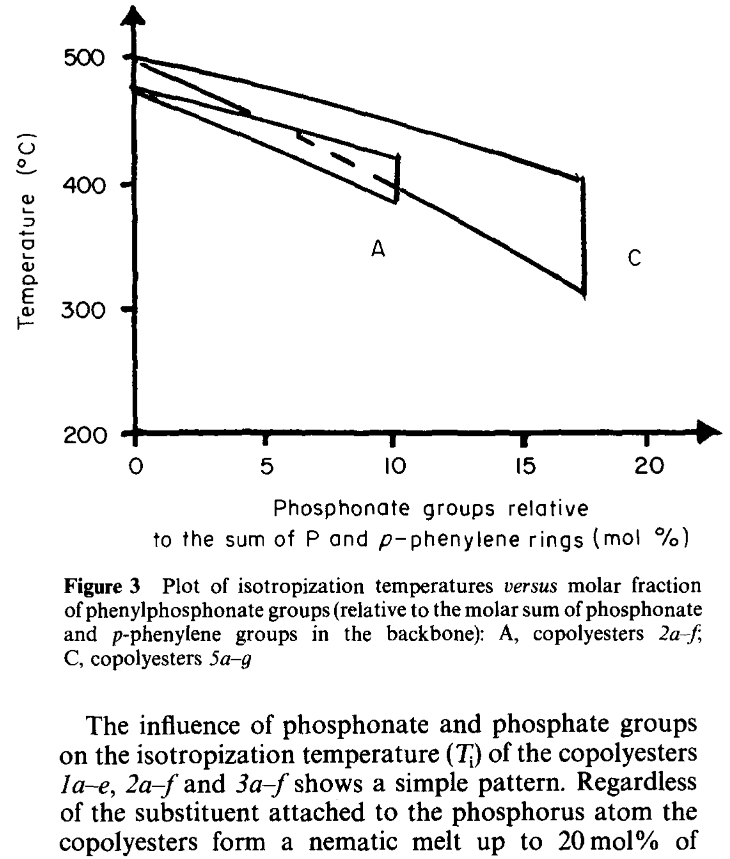


Figure 3 Plot of isotropization temperatures *versus* molar fraction of phenylphosphonate groups (relative to the molar sum of phosphonate and *p*-phenylene groups in the backbone): A, copolyesters *2a–f*; C, copolyesters *5a–g*

The influence of phosphonate and phosphate groups on the isotropization temperature (T_i) of the copolyesters *1a–e*, *2a–f* and *3a–f* shows a simple pattern. Regardless of the substituent attached to the phosphorus atom the copolyesters form a nematic melt up to 20 mol% of phosphorus atoms and turn isotropic with 30 mol% or more phosphonate and phosphate groups. This result agrees with the properties of the phosphorus-containing poly(ester imide)s *6a–f* described previously[1]. The unfavourable bond angle of the sp^3-hybridized phosphorus is the main source of instability for the nematic phase.

In the case of copolyesters *4a–g* and *5a–g* the destabilizing effect of the phosphonate group is considerably reduced, if the longer repeating units of the parent homopolyesters (*4a* and *5a*) are taken as the basis of the consideration. Even when 70 mol% of the terephthaloyl or phenoxyterephthaloyl units are replaced by phenylphosphonate, a nematic melt is still formed. The influence of phenylphosphonate groups on the T_i of three copolyesters with different lengths of the repeating units is illustrated in *Figure 2*.

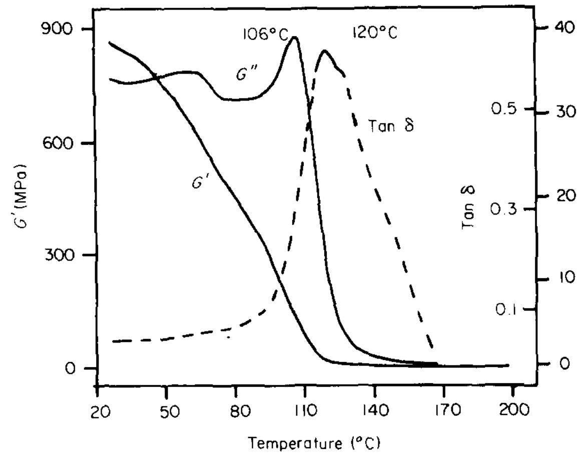
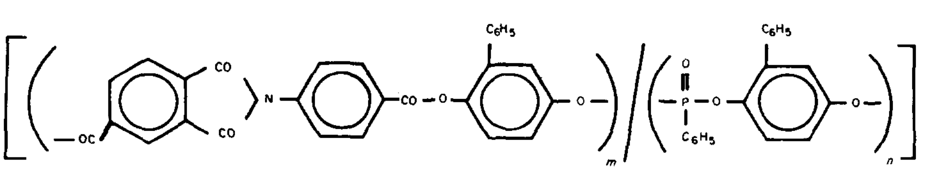


Figure 4 Dynamic mechanical measurements of copolyester conducted at a heating rate of 2°C min^{-1}

In order to avoid misunderstanding the role of the repeating unit in this consideration, it is useful to consider the molar ratio of phosphonate groups and *para*-substituted phenylene rings in the backbones of all copolyesters. In this consideration all *p*-phenylene rings are assumed to stabilize the nematic phase regardless of their substituents. The T_i values plotted *versus* this molar ratio of phosphonate and *p*-phenylene group demonstrates that the destabilizing effect of the phosphonate groups in copolyesters *2a–f*, *4a–f* and *5a–f* is very similar (*Figure 3*). The poly(ester imide)s cannot be included in this type of evaluation, because it is difficult to express the role of the imide structure in an exact number of *p*-phenylene rings.

The continuous decrease of T_i with increasing molar fraction of phosphonate groups in copolyesters *4a–g* and *5a–g* suggests that these materials are homogeneous over the full range of compositions. This property is not trivial, because biphasic materials were obtained when copolyesters were prepared from cyclohexane-1,4-dicarboxylic acid, chloro- or methyl-hydroquinone and benzene phosphonic acid[7,9]. In order to check the homogeneity of copolyesters *4a–g* and *5a–g* by a method which is more sensitive than d.s.c. measurements, films of *4e* and *5e* were subjected to dynamic mechanical measurements. However, as demonstrated by *Figure 4*, tan δ displays only one maximum, thus indicating the existence of only one amorphous phase. However, it should be emphasized that the isotropization temperature



6

a: m/n = 10/0
b: m/n = 9/1
c: m/n = 8/2
d: m/n = 7/3
e: m/n = 6/4
f: m/n = 5/5

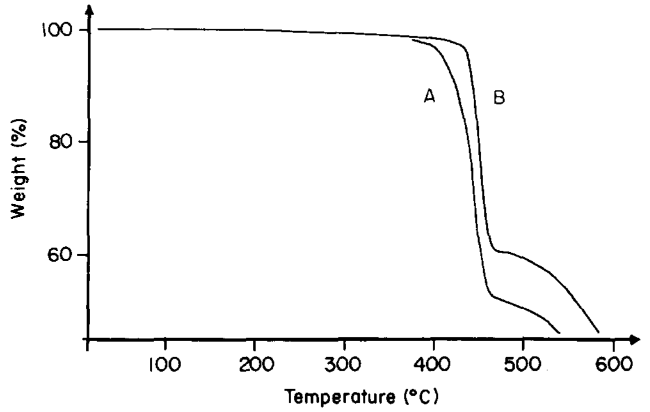


Figure 5 Thermogravimetric analyses conducted at a heating rate of 10°C min^{-1} in air: A, copolyester *5d*; B, copolyester *4d*

is not a sharp point but a temperature range where isotropic and nematic domains coexist. This temperature range broadens with increasing molar fraction of phosphate or phosphonate groups, as demonstrated in *Figures 2* and *3*.

Finally thermogravimetric measurements of some copolyesters were conducted to obtain a crude idea of how phosphonate and phosphate groups influence the thermostability of the copolyesters under investigation. Both phosphate and phosphonate groups slightly reduce the thermostability compared to the parent homopolyesters, but the differences between individual phosphorus-containing copolyesters are small as exemplified by the two typical thermogravimetric curves in *Figure 5*.

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