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Synthesis, properties and crosslinking of unsaturated cyano-substituted homo- and copolyesters prepared from 1-hydroxy-4-(2-cyano-2-carboxyvinyl)benzene

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4-Hydroxybenzaldehyde or 3-methoxy-4-hydroxybenzaldehyde was condensed with cyanoacetic acid to afford 1-hydroxy-4-(2-cyano-2-carboxyvinyl)benzene (**1**) and 1-hydroxy-2-methoxy-4-(2-cyano-2-carboxyvinyl)benzene (**2**) respectively. They were converted to the corresponding acid chlorides by reacting with thionyl chloride and polycondensed in the presence of pyridine to afford unsaturated cyano-substituted homopolyesters. In addition, various copolyesters were prepared from the acid chlorides of **1** and 4-hydroxybenzoic acid. The polyesters were characterized by Fourier-transform infra-red spectroscopy and differential thermal analysis as well as by inherent viscosity, X-ray and water absorption measurements. They softened between 100 and 200°C, were amorphous and showed higher hydrophilicity and solubility in certain organic solvents than did the reference polyester prepared from 4-hydroxybenzoic acid. The crosslinked polymers obtained by curing at 300°C for 48 h were remarkably more thermally stable than the cured reference polyester. They were stable up to 291–355°C in N_2 or air and afforded anaerobic char yield of 49–68% at 800°C. The thermal stabilities of cured polyesters were correlated with their composition.

(Keywords: cyano-substituted polyesters; thermal stability; crosslinking)

INTRODUCTION

Heat-resistant polyesters have been obtained from the reaction of various bisphenols with aromatic diacid derivatives by the interfacial or bulk polymerization method[1]. However, most of these polyesters have problems in processing owing to high softening temperatures by virtue of their rigid structure. Therefore, many attempts have been made to improve the processability by structural modification and incorporation of flexible moieties in the polymer backbone.

Maleimide, nadimide, acetylenic, biphenylenic and *N*-cyanourea are among the functional groups[2] widely employed for preparation of thermally crosslinkable polymers. The cyano- and dicyanovinyl groups (C=C(CN) and $C=C(CN)_2$) are also thermally curable functions, although their curing mechanism has not been elucidated. It has been reported that poly(enaminonitrile)s[3–8] and poly(enaryloxynitrile)s[9,10] as well as polyarylates containing dicyanovinyl groups[11] are thermally curable, yielding heat-resistant resins.

Certain new cyano-substituted polyesters derived from 2,6-bis(4-hydroxybenzylidene)-1-dicyanomethylenecyclohexane[12] and 1-(2,2-dicyanovinyl)-3,4-dihydroxybenzene[13] have recently been prepared and crosslinked in our laboratory. In addition, the following have been synthesized and thermally crosslinked to afford heat-resistant resins: some polyamides containing enaminonitrile segments[14,15]; *N*-cyano-substituted polyamides[16]; polyamides bearing pendent cyano groups derived from 1,4-bis(2-cyano-2-carboxyvinyl)benzene[17] and 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene[18]; as well as cyano-substituted polyamides and polyimides prepared from 2,6-bis(3-aminobenzylidene)-1-dicyanomethylenecyclohexane[19], 2,7-diamino-9-dicyanomethylenefluorene[20], 1-(2,2-dicyano-1-hydroxyvinyl)-3,5-diaminobenzene sodium salt[21] and diaminomaleonitrile[22].

The present investigation deals with the synthesis, characterization and investigation of the physical, chemical and thermal properties of a new class of unsaturated cyano-substituted polyesters derived from 1-hydroxy-4-(2-cyano-2-carboxyvinyl)benzene or its derivative. Their properties are compared to those of a reference polyester and correlated with their chemical structure. In addition, they are thermally crosslinked without the release of volatile by-products to afford heat-resistant resins that can be used as matrix resins for composites.

EXPERIMENTAL

Instrumentation

Melting temperatures were determined on an electrothermal melting-point apparatus IA6304 and are uncorrected. I.r. spectra were recorded on a Perkin–Elmer 16PC *FT*i.r. spectrometer with KBr pellets. ^1H n.m.r.

spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. D.t.a. and t.g.a. were performed on a DuPont 990 thermal analyser system. D.t.a. measurements were made using a high-temperature (1200°C) cell at a heating rate of $20^{\circ}C\ min^{-1}$ in N_2 atmosphere at a flow rate of $60\ cm^3\ min^{-1}$. Dynamic t.g.a. measurements were made at a heating rate of $20^{\circ}C\ min^{-1}$ in atmospheres of N_2 or air at a flow rate of $60\ cm^3\ min^{-1}$. The inherent viscosities of polyamides were determined for solutions of 0.5 g/100 ml in *N*,*N*-dimethylformamide (DMF) at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyser. The wide-angle X-ray diffraction patterns were obtained for powder specimens on a Philips PW-1840 X-ray diffractometer.

To determine the equilibrium water absorption, powder samples of polymers were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator where 65% r.h. (relative humidity) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20°C, and were periodically weighed.

Reagents and solvents

4-Hydroxybenzaldehyde, 3-methoxy-4-hydroxybenzaldehyde (vanillin) and 4-hydroxybenzoic acid were recrystallized from distilled water. Acetonitrile and thionyl chloride were purified by distillation. *N*,*N*-Dimethylformamide (DMF) was dried by distillation under reduced pressure over calcium hydride. Glacial acetic acid, pyridine and piperidine were used as supplied.

Preparation of starting materials

1-Hydroxy-4-(2-cyano-2-carboxyvinyl)benzene (*1*). A flask equipped with a magnetic stirrer and condenser was charged with a mixture of 4-hydroxybenzaldehyde (4.6894 g, 38.4 mmol), cyanoacetic acid (6.5334 g, 76.8 mmol), acetonitrile (30 ml), glacial acetic acid (2 ml) and a catalytic amount of piperidine. The mixture was stirred and refluxed for 24 h. Upon standing at 0°C, compound **1** precipitated from the reaction solution as a slightly brown solid (6.34 g, 87%). It was purified by recrystallization from a mixture of 1,4-dioxane/water (1:4 v/v) and had m.p. 258–261°C (decomposition).

I.r. (KBr) (cm^{-1}): 3306 (phenolic O–H stretching); 3050–2532 (carboxylic O–H stretching); 2230 (C≡N); 1672 (C=O); 1592 (olefinic bond); 1564, 1510 (aromatic); 1436 (carboxylic C–OH stretching and O–H deformation); 1370 (phenolic O–H deformation); 1288, 1226 (phenolic C–OH stretching); 942 (carboxylic O–H deformation).

^1H n.m.r. (DMSO-d_6) δ (ppm): 10.36 (b, 2H, COOH and OH); 8.02 (s, 1H, olefinic); 7.85–7.73 (m, 2H, aromatic of positions 3 and 5); 6.83–6.70 (m, 2H, other aromatic).

Analysis calculated for $C_{10}H_7NO_3$: C, 63.49%; H, 3.73%; N, 7.40%. Found: C, 63.25%; H, 3.78%; N, 7.36%.

1-Hydroxy-2-methoxy-4-(2-cyano-2-carboxyvinyl)-benzene (*2*). A mixture of 3-methoxy-4-hydroxybenzaldehyde (3.9559 g, 26.0 mmol), cyanoacetic acid (3.3177 g, 39.0 mmol), acetonitrile (20 ml), glacial acetic acid (2 ml) and a few drops of piperidine was stirred and refluxed for 24 h. Compound **2** precipitated as a pale yellow solid upon cooling the reaction solution at 0°C (3.30 g, 58%). It was recrystallized from 25% ethanol (m.p. 218–221°C).

I.r. (KBr) (cm^{-1}): 3474 (phenolic O–H stretching); 3073–2780 (carboxylic O–H stretching); 2222 (C≡N); 1686 (C=O); 1606 (olefinic bond); 1578, 1518 (aromatic); 1454 (carboxylic C–OH stretching and O–H deformation); 1392 (phenolic O–H deformation); 1270, 1210 (phenolic C–OH stretching); 930 (carboxylic O–H deformation).

^1H n.m.r. (DMSO-d_6) δ (ppm): 10.95 (b, 2H, COOH and OH); 7.93 (s, 1H, olefinic); 7.55–7.23 (m, 2H, aromatic of positions 3 and 5); 6.82–6.68 (m, 1H, other aromatic).

Analysis calculated for $C_{11}H_9NO_4$: C, 60.28%; H, 4.14%; N, 6.39%. Found: C, 60.13%; H, 4.17%; N, 6.42%.

Preparation of polyesters

A typical procedure for the preparation of copolyester PE_{25} is as follows: A flask equipped with magnetic stirrer, condenser and gas trap was charged with a mixture of compound **1** (1.4189 g, 7.5 mmol), 4-hydroxybenzoic acid (3.1077 g, 22.5 mmol), excess of thionyl chloride (10 ml) and a few drops of DMF. The mixture was gradually heated and then refluxed for about 2 h with stirring. The excess thionyl chloride was distilled off under reduced pressure. DMF (30 ml) was added to dissolve the acid chloride, and then 4–5 drops of pyridine. The polymerization was continued overnight at 80°C and copolyester PE_{25} was isolated as a brown solid by pouring the reaction solution into water. The solid was filtered off, washed with water and dried (3.46 g, 87%).

The weights of reactants, the reaction yields and the inherent viscosities of all homopolyesters and copolyesters thus prepared are listed in *Table 1*.

Table 1 Quantities of reactants, reaction yields and inherent viscosities of polyesters

Polyester	Quantities of reactants (g(mmol)) Compound **1**	Compound **2**	HBA^a	Yield (%)	$\eta_{inh}{}^b$ ($dl\ g^{-1}$)
PE_0			8.2872 (60.0)	99	0.44
PE_{25}	1.4189 (7.5)		3.1077 (22.5)	87	0.33
PE_{50}	2.8379 (15.0)		2.0718 (15.0)	94	0.32
PE_{75}	4.2568 (22.5)		1.0359 (7.5)	79	0.32
PE_{100}	2.0054 (10.6)			81	0.31
PEV_{100}		2.5649 (11.7)		95	0.30

^{a} HBA = 4-hydroxybenzoic acid
^{b} Inherent viscosities in DMF ($0.5\ g\ dl^{-1}$) at 30°C

Curing of polyesters

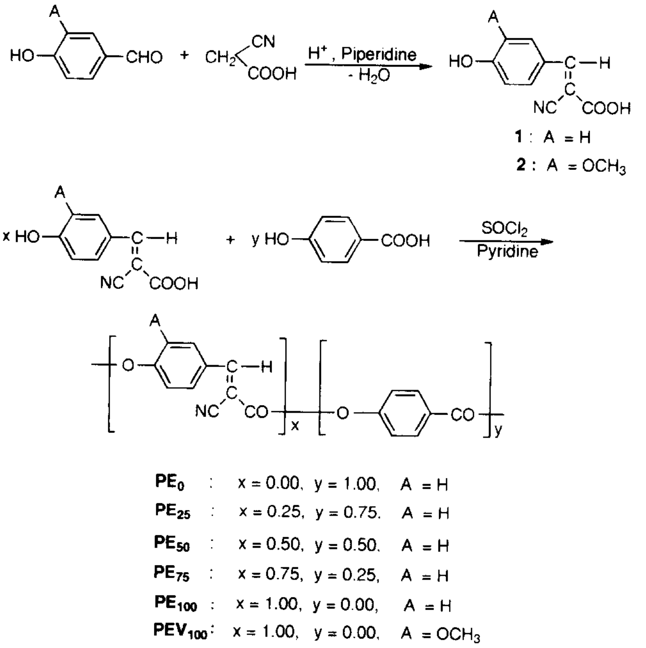
The isolated polyesters were each placed in an aluminium dish and curing was accomplished in static air by heating in an oven at 300°C for 48 h.

RESULTS AND DISCUSSION

4-Hydroxybenzaldehyde or 3-methoxy-4-hydroxybenzaldehyde was condensed with cyanoacetic acid in refluxing acetonitrile in the presence of glacial acetic acid and a catalytic amount of piperidine to afford compounds **1** and **2** respectively (*Scheme 1*). The latter were obtained in satisfactory yields (58–87%) when excess cyanoacetic acid was used. The addition of piperidine as catalyst was necessary, because it raised the reaction yield remarkably. Note that compound **1** was obtained only in 8% yield when the reaction took place under the same conditions but in the absence of piperidine.

Compounds **1** and **2** together with 4-hydroxybenzoic acid were used as starting materials for the preparation of a new series of unsaturated cyano-substituted homopolyesters and copolyesters (*Scheme 1*). They were converted to the corresponding acid chlorides by means of thionyl chloride and a catalytic amount of DMF. The acid chlorides thus prepared were polycondensed without further purification in DMF at 80°C in the presence of pyridine. Under these conditions, the polyesters did not precipitate from the reaction solution and their isolation was accomplished by pouring the solution into a non-solvent.

Homopolyesters PE_{100}, PEV_{100} and PE_0 were prepared from the self-polycondensation of the acid chlorides of compounds **1**, **2** and 4-hydroxybenzoic acid, respectively. Homopolyester PE_0 was prepared for comparative purposes. In addition, random copolyesters PE_{25}, PE_{50} and PE_{75} were prepared by polycondensing mixtures of the acid chlorides of **1** and 4-hydroxybenzoic acid under various molar ratios. The polyesters were prepared in yields of 79–99% and their inherent viscosities (η_{inh}) ranged from 0.30 to 0.44 dl g^{-1} (*Table 1*). The reference polyester PE_0 exhibited the highest values of yield and η_{inh}.



PE_0 : x = 0.00, y = 1.00, A = H
PE_{25} : x = 0.25, y = 0.75, A = H
PE_{50} : x = 0.50, y = 0.50, A = H
PE_{75} : x = 0.75, y = 0.25, A = H
PE_{100} : x = 1.00, y = 0.00, A = H
PEV_{100} : x = 1.00, y = 0.00, A = OCH_3

Scheme 1

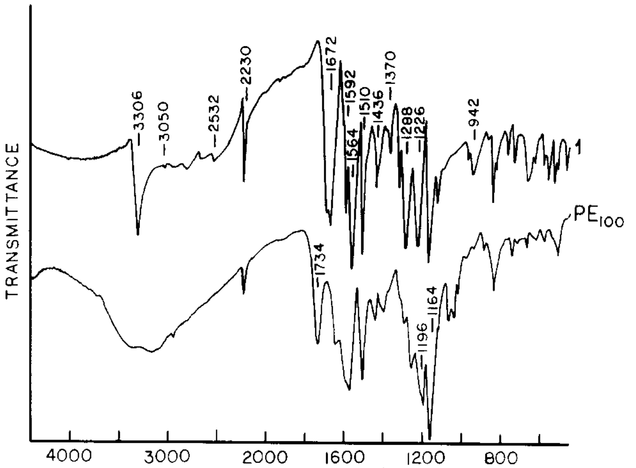


Figure 1 *FT*i.r. spectra of compound **1** and polyester PE_{100}

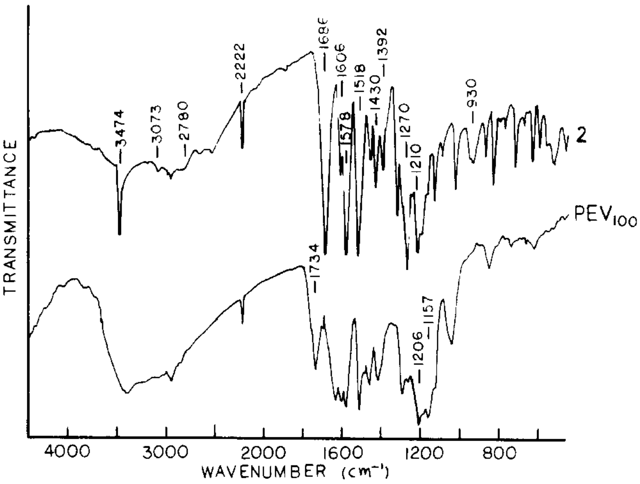


Figure 2 *FT*i.r. spectra of compound **2** and polyester PEV_{100}

Compounds **1** and **2** were characterized by elemental analyses as well as by i.r. and ^1H n.m.r. spectroscopy. Their *FT*i.r. spectra (*Figures 1* and *2*) completely lacked the absorption band of the aldehyde carbonyl of the parent compounds at 1666 cm^{-1} and showed new absorptions around 1680 and 2220 cm^{-1} associated with the carboxylic carbonyl and cyano group, respectively. The ^1H n.m.r. spectra of these compounds (*Figure 3*) showed a broad peak at about $\delta = 10.50$ ppm assigned to the carboxylic and phenolic protons, which were exchangeable with D_2O.

Upon heating into a capillary tube, compounds **1** and **2** displayed melting at 258–261°C and 218–221°C, respectively, accompanied by decomposition. Their d.t.a. traces (*Figure 4*) exhibited melting endotherms with onset temperatures of 260 and 221°C, respectively, ascribable to melting. A second d.t.a. scan of the cooled samples did not display an endotherm at these temperature regions owing to the decomposition that occurred during melting. Since the *FT*i.r. spectra of the melted compounds showed a significant reduction in the intensity of the absorption band near 1680 cm^{-1} assigned to the carboxylic carbonyl, it is believed that evolution of carbon dioxide and hence decarboxylation took place during thermal decomposition.

Figures 1 and *2* present typical *FT*i.r. spectra of homopolyesters PE_{100} and PEV_{100}. Upon comparing these spectra with those of the corresponding starting materials **1** and **2**, certain differences can result. More particularly, the carbonyl absorption band shifted to a considerably higher wavelength (from 1672 to 1734 cm^{-1} and from 1686 to 1734 cm^{-1} in the case of polyester PE_{100} and PEV_{100} respectively), because the ester carbonyl absorbs at higher frequency than the corresponding carboxylic one. In addition, polyesters showed new absorptions near 1200 and 1160 cm^{-1} assigned to the C–O–C stretching vibration. Note that the broad absorption band at about 3500–3000 cm^{-1} of polyesters was attributed to their terminal carboxylic and phenolic groups. Copolyesters also displayed these characteristic absorption bands, but the intensity of the absorption near 2220 cm^{-1} was decreased with decreasing concentration of cyano segments.

The X-ray diffraction studies revealed that polyesters were completely amorphous. *Figure 5* presents typical X-ray diffractograms for powder specimens of homopolyesters PE_{100} and PEV_{100}. The amorphous nature of polyesters conformed with their enhanced solubility in common organic solvents (see below) and this could be attributed to certain structural features. *Figure 6* shows the optimized geometry for three repeating units of the macromolecule of homopolyester PE_{100} as calculated by means of the CSC ChemDraw 3D PlusΣ Molecular Modeling System. First, it is seen that its phenyl rings are not coplanar and each of them is almost vertical to the next one. However, this feature is also encountered in the macromolecule of the reference homopolyester PE_0. Furthermore, in the case of PE_{100} the chain packing is much more disrupted by the pendent cyano groups.

The solubility behaviour of homopolyesters PE_{100} and PE_0 is given in *Table 2*. It is seen that the cyano-substituted polyester PE_{100} showed higher solubility in certain organic solvents such as DMF, NMP, DMSO, CH_3CN and 1,4-dioxane than did the reference polyester PE_0. The solubility of homopolyester PEV_{100} was almost

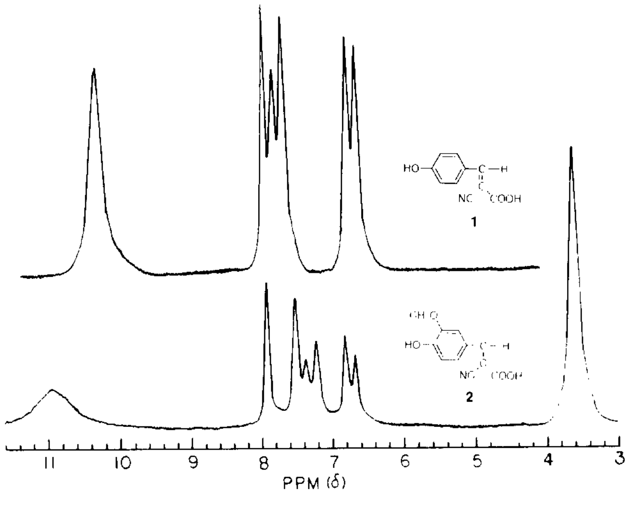


Figure 3 ^1H n.m.r. spectra of compounds **1** and **2** in DMSO-d_6 solution

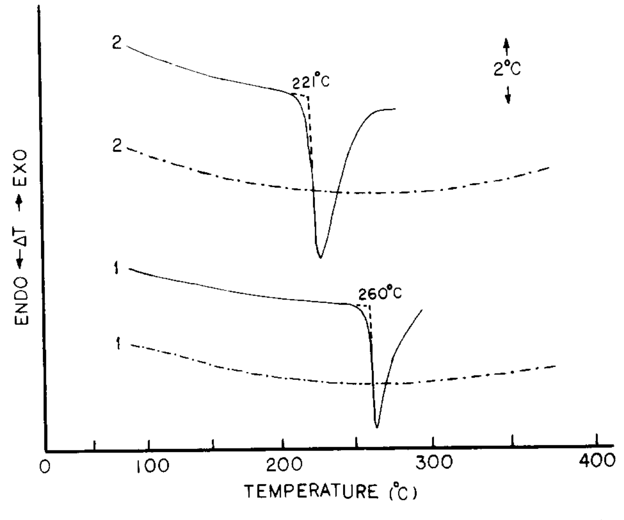


Figure 4 D.t.a. traces of compounds **1** and **2** (——) and rerun of these compounds after cooling (–·–·–). Conditions: N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

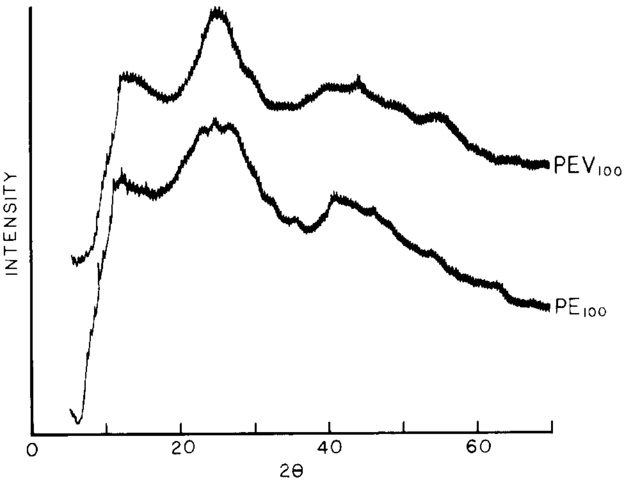


Figure 5 X-ray diffractograms of polyesters PE_{100} and PEV_{100}

Table 2 Solubilities[a] of polyesters

	Solvents								
Sample	DMF[b]	NMP[c]	DMSO[d]	CH_3CN	1,4-Dioxane	CH[e]	$CHCl_3$	Acetone	H_2SO_4 98%
PE_{100}	++	++	++	+	+	+	+−	+−	++
PE_0	+	+	+	+−	+−	+	+−	+−	++

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +−, partially soluble
[b] DMF = *N,N*-dimethylformamide
[c] NMP = *N*-methylpyrrolidone
[d] DMSO = dimethylsulfoxide
[e] CH = cyclohexanone

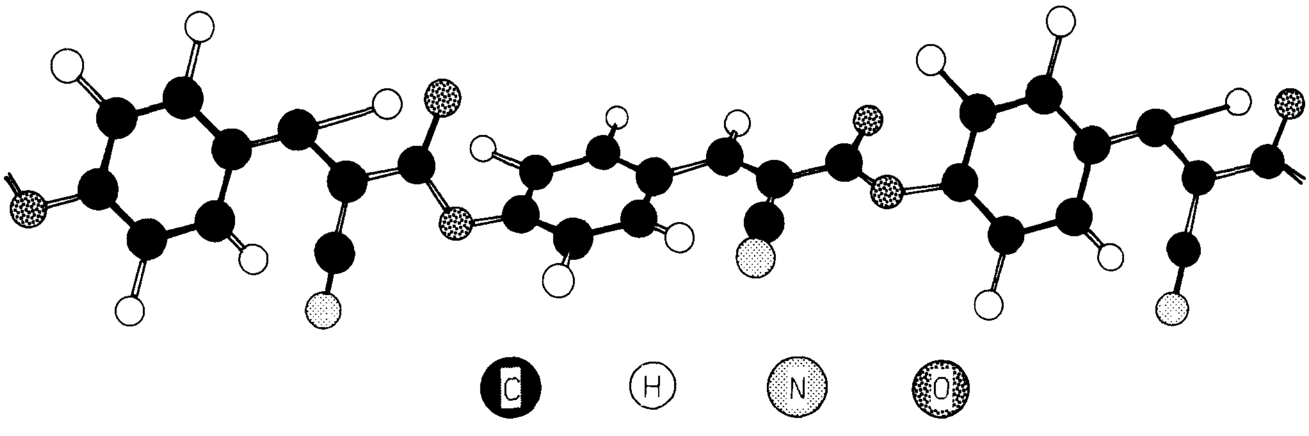


Figure 6 Optimized geometry for three repeating units of the macromolecule of polyester PE_{100} (ChemDraw 3D PlusΣ Molecular Modeling System, Version 3.1.1, 1993, Cambridge Scientific Computing Inc.)

the same as that of PE_{100}. The improved solubility of modified polyesters was attributed to the pendent cyano groups, which did not allow a dense packing of their chains.

The equilibrium water absorption for the pair of homopolyesters PE_{100} and PE_0 was determined (*Figure 7*). A saturation in the water absorption was observed for both polyesters after a time exposed of about 100 h. For this time the number of moles of absorbed water per ester equivalent weight was 0.23 and 0.08, respectively, which correspond to water uptake of 2.37 and 1.22%. The higher disorder in the chain of PE_{100}, which increased the accessibility of water, should be responsible for its improved hydrophilicity.

The thermal behaviour of all polyesters was investigated by d.t.a. and dynamic t.g.a. All polyesters displayed comparable thermal behaviour. *Figure 8* presents typical d.t.a. and t.g.a. traces in N_2 of copolyester PE_{75}. It was stable up to approximately 200°C and lost roughly about 40% of its weight in one step. The anaerobic char yield (Y_c) at 800°C of this copolyester was 37%. Note that the anaerobic Y_c at 800°C of polyesters PE_0–PE_{100} was increased with increasing concentration of cyano groups and ranged from 22 to 42%. The d.t.a. trace of PE_{75} showed a broad endotherm at 171°C (onset temperature 110°C) ascribable to its softening. The softening of copolyester at this temperature region was confirmed upon gradual heating into a capillary tube. The exotherms above 300°C were attributed to crosslinking reactions and partial thermal degradation.

The polyesters were thermally crosslinked through their olefinic bonds as well as the cyano groups to afford heat-resistant resins. The reference polyester PE_0 was also cured under the same conditions for comparison. The initial decomposition temperature (*IDT*) and the Y_c at 800°C in N_2 of the resins obtained by heat curing at 300°C were increased with increased curing time up to about 48 h and they remained almost unchanged beyond this time. Therefore, the time of 48 h was selected for curing at 300°C.

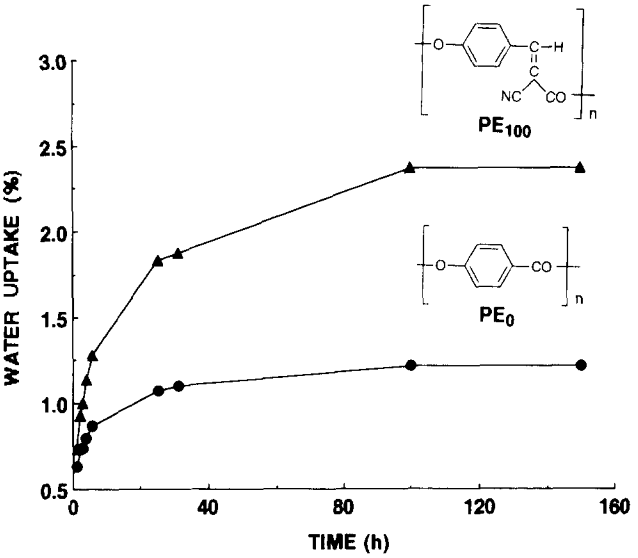


Figure 7 Water absorption (%) *versus* time for polyesters PE_0 and PE_{100}

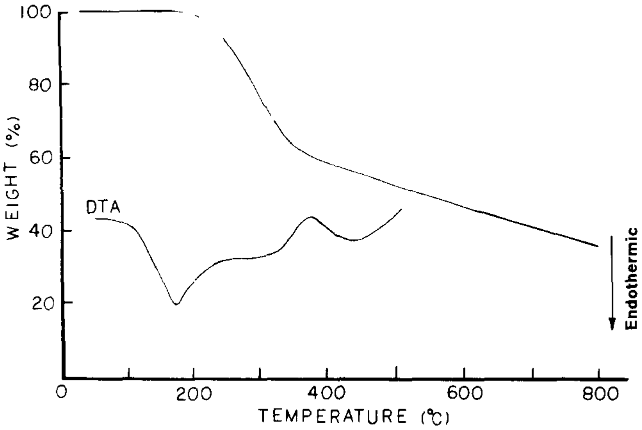


Figure 8 T.g.a. and d.t.a. traces of polyester PE_{75}. Conditions: N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

The crosslinked polymers obtained from polyesters PE_0–PE_{100} by curing in static air at 300°C for 48 h are referred to by the designations PE'_0–PE'_{100} respectively. They were obtained as infusible dark brown solids and were insoluble in solvents for the untreated samples. Their *FT*i.r. spectra were much broader than those of the corresponding uncured samples and displayed a considerable reduction of the absorption band around 2220 cm^{-1} assigned to cyano groups.

The thermal stability of cured polyesters was evaluated by t.g.a. and isothermal gravimetric analysis (i.g.a.). *Figure 9* presents typical t.g.a. thermograms of cured polyesters PE'_{75} and PE'_{100} in N_2 and air. The *IDT*,

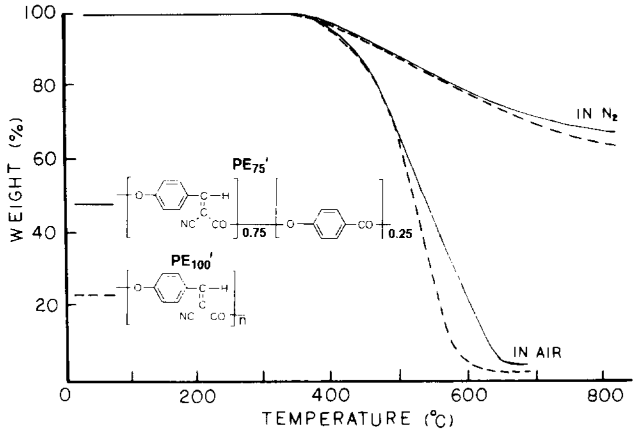


Figure 9 T.g.a. thermograms of cured polyesters PE'_{75} and PE'_{100} in N_2 and air. Conditions: gas flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

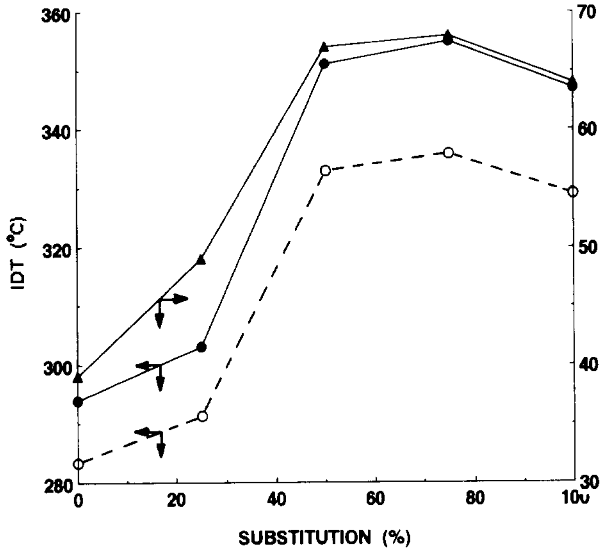


Figure 10 *IDT* and Y_c in N_2 (——) and air (– – –) of cured polyesters PE'_0–PE'_{100} *versus* the percentage substitution of compound **1** in them

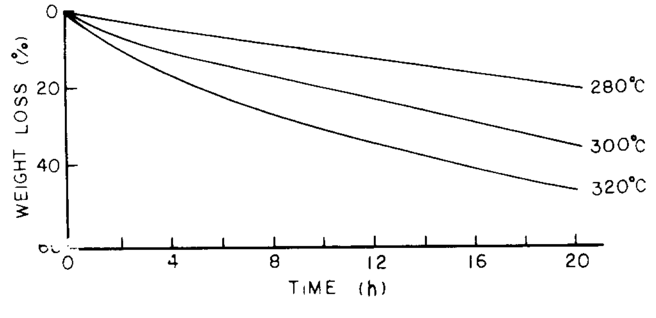


Figure 11 I.g.a. traces in static air of cured polyester PE'_{50} at 280, 300 and 320°C

Table 3 Thermal stabilities of cured polyesters

	N_2				Air		
Sample	IDT^a (°C)	PDT^b (°C)	$PDT_{max}{}^c$ (°C)	$Y_c{}^d$ (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)
PE'_0	294	441	527	39	283	385	498
PE'_{25}	303	433	508	49	291	397	512
PE'_{50}	351	482	445	67	333	441	498
PE'_{75}	355	483	460	68	336	430	493
PE'_{100}	347	475	456	64	329	429	517
PEV'_{100}	346	498	545	50	336	467	518

[a] Initial decomposition temperature
[b] Polymer decomposition temperature
[c] Maximum polymer decomposition temperature
[d] Char yield at 800°C

the polymer decomposition temperature (*PDT*), the maximum polymer decomposition temperature (PDT_{max}) in both N_2 and air as well as the anaerobic Y_c at 800°C of all cured polyesters are summarized in *Table 3*. The *IDT* and *PDT* were determined for a temperature at which 0.5 and 10% weight loss was observed respectively. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

The cured cyano-substituted polyesters were stable up to 291–355°C in N_2 or air and afforded anaerobic Y_c at 800°C of 49–68%. The cured reference polyester PE'_0 was remarkably less thermally stable, being stable up to 283–294°C and affording anaerobic Y_c at 800°C of 39%. Obviously, the crosslinking attained through the olefinic bonds and cyano segments was responsible for the higher thermal stability of the former. The cured polyesters PE'_{100} and PEV'_{100} displayed comparable *IDT* values, but the latter afforded lower anaerobic Y_c at 800°C (50% *versus* 64%).

Upon comparing the t.g.a. data of cured polyesters PE'_0–PEV'_{100}, some interesting results can arise. Specifically, the *IDT* in both N_2 and air as well as the anaerobic Y_c at 800°C were increased with increasing percentage substitution of compound **1** in them up to 75% and were reduced beyond this value (*Figure 10*). Taking these t.g.a. data as a criterion of thermal stability, it is seen that the thermal stability of PE'_{75} was slightly higher than those of PE'_{50} and PE'_{100}. Therefore, cured polyesters PE'_{50}, PE'_{75} and PE'_{100} were the best among the polyesters synthesized with respect to thermal stability.

Figure 11 presents the i.g.a. traces of a typical cured polyester PE'_{50} at 280, 300 and 320°C in static air. After 20 h isothermal ageing, it displayed weight losses of 20.0, 34.6 and 45.8% respectively. Under these conditions, the cured reference polyester PE'_0 showed weight losses of 36.5, 40.6 and 51.7% respectively. These i.g.a. results confirmed the significantly higher thermal stability of the cured cyano-substituted polyester.

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