

Transitions in linear thermotropic polyesteramides*

A. H. Khan†, J. E. McIntyre and A. H. Milburn

Department of Textile Industries, University of Leeds, Leeds LS2 9JT, UK

(Received 31 January 1983)

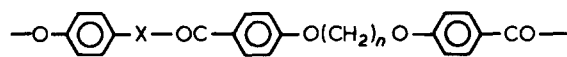
A series of linear thermotropic polymers containing rigid aromatic esteramide units alternating with flexible alkylene spacers is synthesized. Their thermal transition temperatures are compared with those for polymers containing linear aromatic diester units and the differences are correlated with those for simple liquid-crystalline esteramides and diesters. The behaviour of copolymers containing both esteramide and diester units and of blends of polymeric and non-polymeric esteramides is examined.

Keywords Polyesteramide; thermotropic; nematic; smectic; spacer; liquid-crystalline

INTRODUCTION

Many thermotropic polymers containing rigid-rod segments in the main chain have now been synthesized. The majority of them are polyesters wherein the rigid element consists of 1,4-arylene groups connected by ester groups, although other internuclear groups such as azomethine ($-\text{CH}:\text{N}-$) or thiocarbonyl ($-\text{CO}:\text{S}-$) have been used instead of or as well as ester. Incorporation of the amide group, which increases interchain bonding, tends to increase crystalline phase stability and elevate melting point, thus preventing the observation of a liquid-crystalline phase, unless the symmetry of the system is reduced. Such reductions have been brought about by the copolymerization of aminobenzoyl residues into poly(ethylene terephthalate)¹ and by the use of unsymmetrical repeating units² and have been shown to lead to formation of thermotropic polyesteramides, at least in the latter case.

A comparison of the mesogenic activity of the amide group with that of the ester group can be carried out by comparing the transitions in a series of polymers differing only in the substitution of an amide group for an ester group in the repeating unit. Accordingly a series of thermotropic polyesteramides containing flexible alkylene spacers of various lengths has been synthesized for comparison with the corresponding series of polydiesters, which has already been described³. These two series have the general repeating unit (I), where $\text{X}=\text{NH}$ and $\text{X}=\text{O}$ respectively:



(I)

EXPERIMENTAL

Intermediates

p-Acetamidophenyl acetate, m.p. 149°–150°C, was prepared by reaction of *p*-aminophenol in aqueous solution

* This paper is based on a lecture delivered at IUPAC MACRO 82, Amherst, MA, on 14 July 1982

† Present address: Indian Institute of Technology, New Delhi, India

with acetic anhydride and purified by recrystallization from ethanol. Bis(*p*-carboxyphenoxy)alkanes were prepared by two methods:

(a) For $n = 2-6$ and 8. *p*-Hydroxybenzoic acid (0.2 mole) was dissolved in water (200 ml) containing sodium hydroxide (0.4 mole). Dibromoalkane (0.1 mole) was added and the stirred solution was heated under reflux for approximately 20 h. Further sodium hydroxide (0.1 mole) was added and refluxing continued for 4 h. Acidification of the hot solution gave the dicarboxylic acid, which was filtered off, washed with hot water and recrystallized from aqueous dimethyl acetamide. Yields fell from 73% to 20% as the value of n increased from 2 to 8.

(b) For $n = 7, 9, 10$ and 12. Methyl-*p*-hydroxybenzoate (0.1 mole) was added to a solution of sodium (0.1 mole) in dry methanol (100 ml). The dibromoalkane (0.05 mole) was added and the stirred solution was heated under reflux for 8 h. Potassium hydroxide solution (300 ml, 10% w/v in water) was added and heating was continued for 2 h with removal of methanol by distillation. The solution was acidified and the precipitated acid was filtered off, washed, dried, and recrystallized from ethanol/dimethyl acetamide. Yields were from 60% to 80%.

The acids had the following melting points: $n = 2$, 350°C; $n = 3$, 329°–333°C; $n = 4$, 340°–342°C; $n = 5$, 292°–296°C; $n = 6$, 306°–309°C; $n = 7$, 268°–270°C; $n = 8$, 288°–290°C; $n = 9$, 260°–262°C; $n = 10$, 280°C; $n = 12$, 262°–265°C.

Polymer preparation

Polyesteramides were prepared by mixing equimolar quantities of *p*-acetamidophenyl acetate and the bis(*p*-carboxyphenoxy)alkane in a glass polymerization tube and heating with a stream of nitrogen flowing through the reactants at 282°C. When visible evolution of acetic acid had ceased (approximately 1 h), heating was continued under reduced pressure, ultimately about 0.1 mmHg, for 1 to 2 h. The polymer was then removed and ground to a powder.

Polydiesters were prepared analogously using hy-

Table 1 Transition temperatures for polyestaramides (I; X = NH) (bracketed values represent hot-stage observations)

n	η_{inh}	Transition temperatures (°C) (d.s.c.)				Other
		T_m (softening)	T_{SN} (flowing)	T_{NI} (isotropy)		
2	insol.	380 (380)	425 (425)	— (400+)	334	
3	insol.	335, 345 (340)	366 (362)	408 (400+)	—	
4	insol.	308, 312 (320)	382 (385)	440 (400+)	—	
5	0.95	307 (300)	327 (330)	402 (400+)	436	
6	0.45	276 (260)	344 (345)	396 (400+)	330	
7	0.70	245 (255)	320, 325 (310)	387 (380)	278, 419	
8	0.57	243 (230)	325 (330)	370 (365)	272	
9	0.52	197 (220)	310, 313 (310)	345 (350)	—	
10	0.70	255 (260)	323 (325)	347 (365)	433	
12	0.68	— (210)	277 (265)	306 (322)	—	

droquinone diacetate instead of *p*-acetamidophenyl acetate. Copolymers were prepared using mixtures of the appropriate reactants in the desired proportions.

Polymer characterization

Logarithmic viscosity numbers, η_{inh} , were measured on 0.5% w/v solutions in 60/40 v/v phenol/1,1,2,2-tetrachloroethane at 25°C. Thermal transitions and textures were observed optically on the hot stage of a Reichert Thermovar polarizing microscope (Table 1). Thermal analyses were conducted using a DuPont 990/910 Differential Scanning Calorimeter at a heating rate of 20°C min⁻¹ (Table 1).

Polymer/non-polymer blends

Blends were made by mixing the solid components in the desired proportions in ignition tubes, heating in a Wood's metal bath to a temperature such that both components become isotropic liquids, stirring briefly, then cooling to room temperature. The solid mass was ground before further examination.

RESULTS AND DISCUSSION

A series of linear thermotropic polyestaramides (I; X = NH) was synthesized from *p*-acetamidophenyl acetate and the appropriate bis(*p*-carboxyphenoxy)alkanes by a melt-phase ester exchange reaction. In general, shear opalescence characteristic of formation of a nematic phase developed from an early stage. In some cases the product solidified as the molecular weight rose, so that the final stages of polymerization were conducted in the solid phase. The polymers synthesized contained alternating rigid-rod units and flexible spacers and the spacer length was varied from $n=2$ to $n=12$. The ester and amide groups are believed to be arranged randomly in a head-to-head or head-to-tail manner in adjacent repeating units, thus introducing an element of disorder that prevents the elevation of crystalline melting point otherwise expected due to the presence of the amide group in the repeating unit.

This series is iso-conformational with the polydiester series (I; X = O) already described by Strzelecki and van Luyen³, and comparison of the two series permits an evaluation of the relative effects on mesophase stability of the ester and amide groups. Figure 1 shows the transition temperatures observed for the polyestaramides as a function of n , the number of methylene groups in the spacer, and Figure 2 shows the temperatures for the polydiester series. We synthesized a few members of this

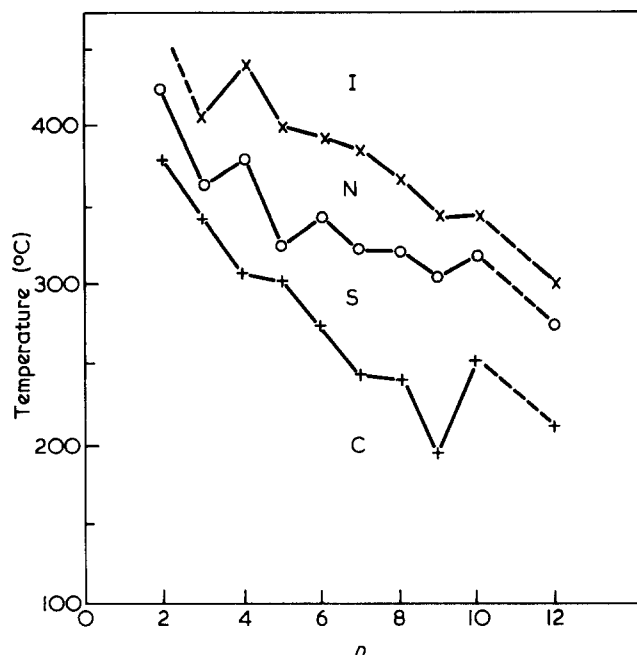


Figure 1 Transition temperatures for polyestaramides (I; X = NH, $n=2-12$)

series, and in some cases obtained different values from those previously recorded; these values are indicated by broken lines in Figure 2.

In considering the nature of these transitions, it should be noted that the points plotted are the peaks of first-order thermal transitions observed by d.s.c., and that the polyestaramide transitions were assigned on the basis of observations with a hot-stage polarizing microscope. There are reasonable grounds for confidence that the nematic phase is correctly assigned, in view of the observation of low viscosity and the onset and loss of shear opalescence, but the so-called smectic phase represents a viscous fluid whose birefringent texture is not very different from that in the crystalline solid. Smectic textures similar to those of simple liquid-crystalline compounds have been observed in fluid polymers, particularly by workers at Orsay⁴, but this appears to be the exception rather than the rule. A further complication is the common occurrence of first-order thermal transitions that cannot be correlated with visual changes. Several of the polyestaramides gave such transitions in addition to those plotted.

Comparison of the transitions in the polyestaramides and in the corresponding polydiesters shows that:

- (i) the nematic phase stability is raised by the amide

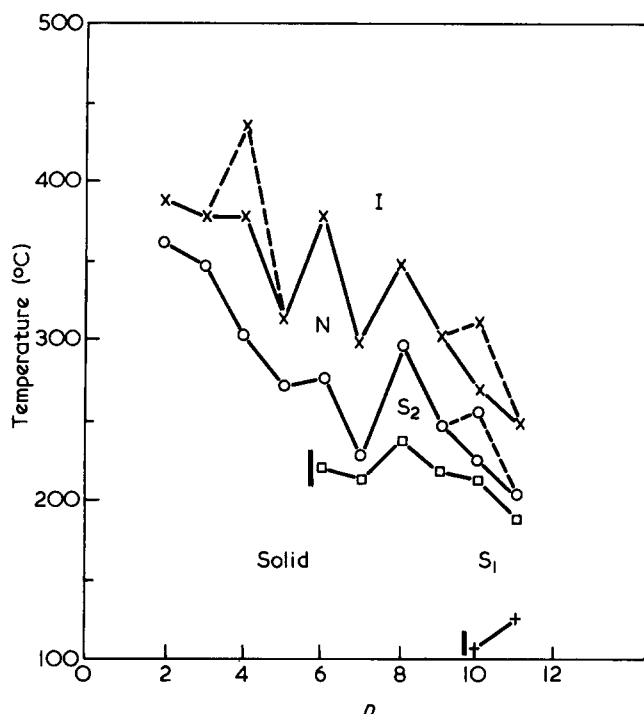


Figure 2 Transition temperatures of polydiesters (I; X=0, n=2-11)

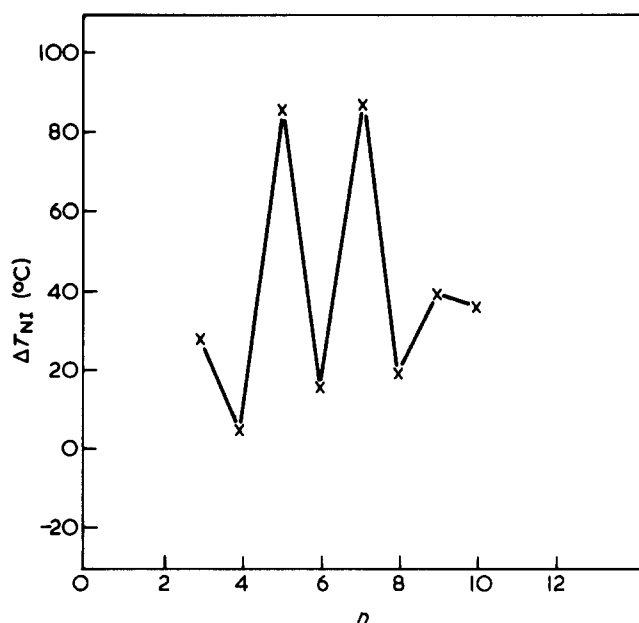


Figure 3 Differences in nematic phase stability between polyesteramides (I; X=NH) and polydiesters (I; X=0)

group (Figure 3)—there are signs of an alternation of stability differences from odd to even values of n arising from the presence of an alternation of stability within the polydiester series;

(ii) the temperature of onset of the nematic phase is raised by the amide group (Figure 4);

(iii) a 'smectic' phase is formed at low values of n from the polyesteramides but not from the polydiesters; and

(iv) the temperature of loss of crystallinity (or 'solid' character) is usually higher for the polyesteramides but its variation with n is complex.

These results may be compared with those for the simple compounds (II) containing the same pair of rigid-

rod segments, for which Figure 5, constructed from published data^{5,6}, shows the effect of introducing the amide group. Conclusions analogous to those above can be drawn, although the alternation of T_{NI} is not present.

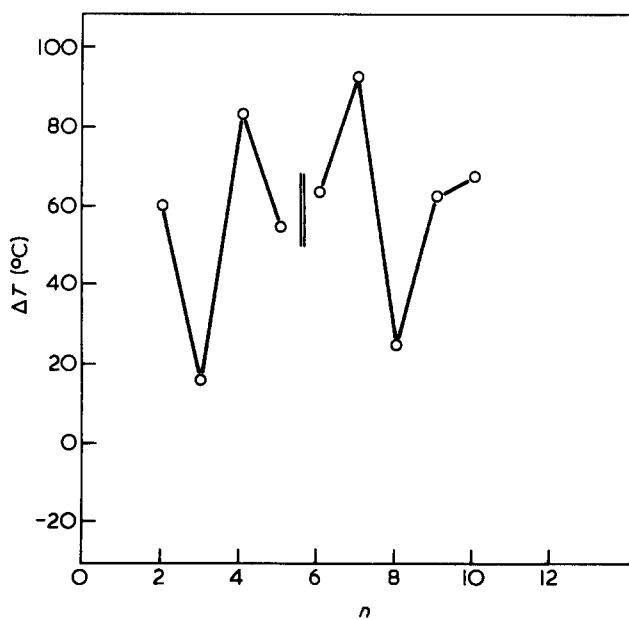


Figure 4 Differences in temperature of onset of nematic phase between polyesteramides (I; X=NH) and polydiesters (I; X=0)

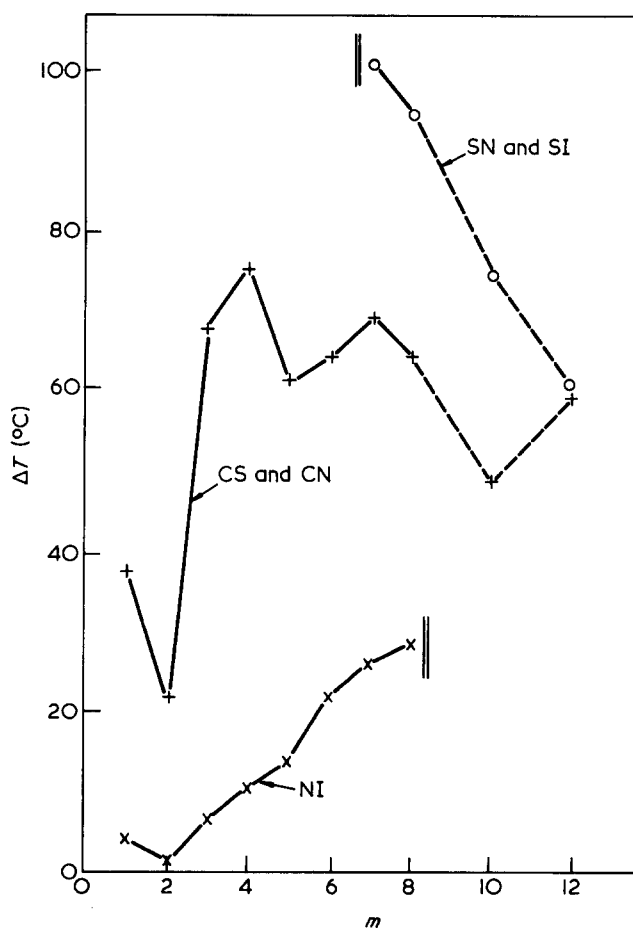


Figure 5 Differences in thermal transition temperatures between esteramides (II; Y=NH) and diesters (II; Y=0)

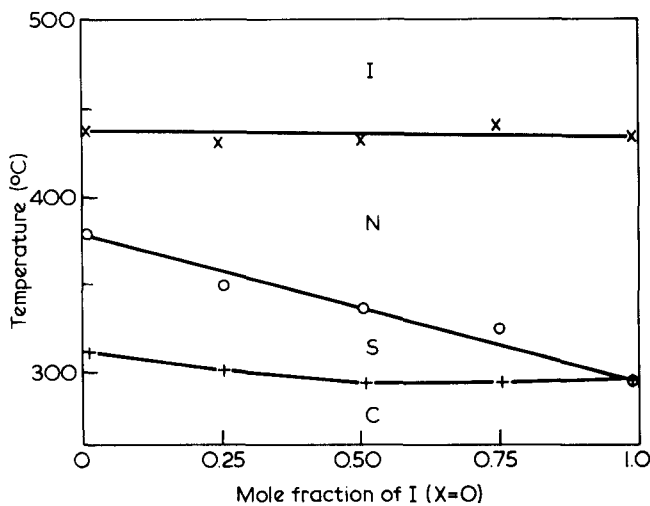
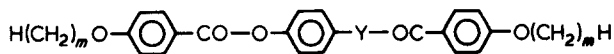


Figure 6 Transition temperatures for copolymers of repeating units (I; X=NH) (EA) and (I; X=O) (EE) where $n=4$



(II)

A series of copolymers of the esteramide (Ia) and diester (Ib) repeating units was produced for the units with $n=4$. The transition temperatures (Figure 6) showed, as expected, no minimum in T_{NI} with composition, but also showed little or no sign of minima in T_{m} and T_{SN} with composition. The suggestion that these two repeating units are capable of isomorphous replacement was confirmed by wide-angle X-ray diffraction photographs (Figure 7) on the powdered polymers.

Examination of the transition behaviour of blends of simple liquid-crystalline compounds can assist in identifying and correlating the transitions of the pure compounds and can sometimes permit observation of enantiotropic transitions that in pure compounds are unobservable or monotropic. Blends of polymeric with non-polymeric liquid-crystalline compounds can also in principle give such information. Blends of one polyesteramide (I; X=NH, $n=9$) with a range of proportions of three different simple liquid-crystalline esteramides were examined. The polymer chosen exhibited crystalline, supposed smectic, nematic and isotropic phases; the simple compounds were chosen to exhibit a nematic phase (II; Y=NH, $m=1$), nematic and smectic phases (II; Y=NH, $m=8$), and a smectic phase (II; Y=NH, $m=10$) in addition to crystalline and isotropic phases. Figures 8–10 show transition temperatures as a function of composition for the three sets of blends.

For the simple nematic additive, T_{NI} was proportional to the weight fraction of polymer; the 'smectic' phase observable in the polymer was extinguished when the weight fraction of polymer fell to 0.4; and T_{m} showed no minimum at any blend composition. The range of stability of the nematic phase was much greater in the blends than in the individual components. For the additive exhibiting both smectic and nematic phases, the transition temperatures all showed shallow minima with composition, although the minimum for T_{NI} was poorly defined. For the simple smectic additive, the nematic phase observable in the polymer was extinguished when the weight fraction of

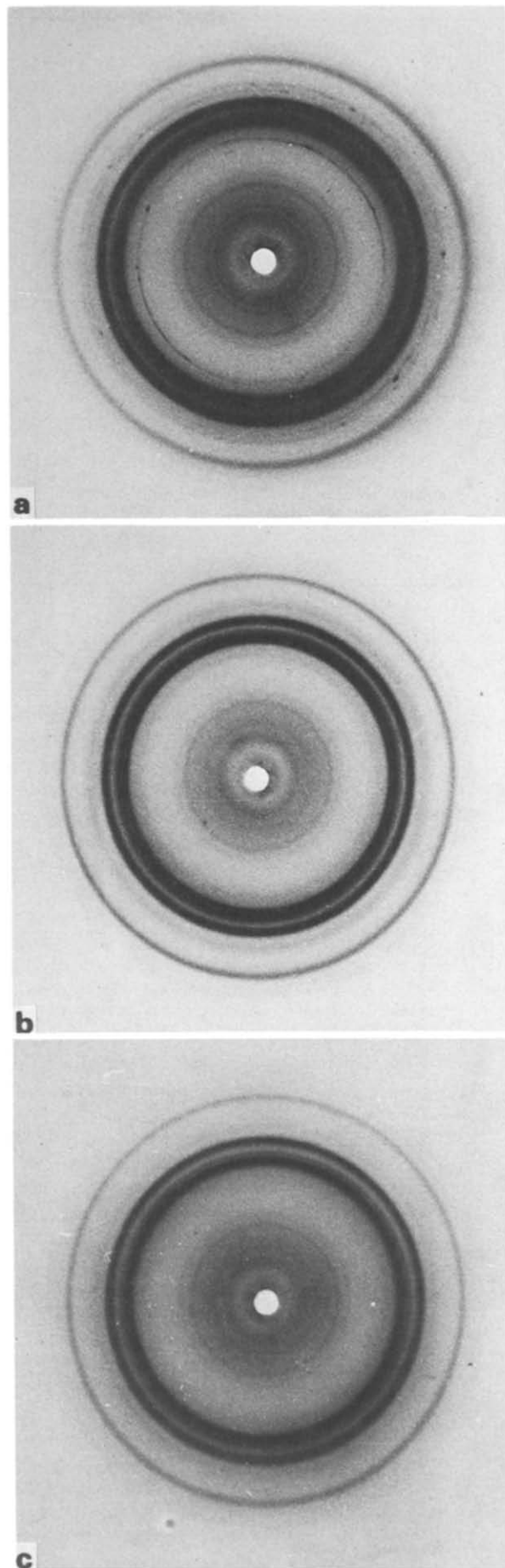


Figure 7 X-ray diffraction powder photographs for polymers (a) (I; X=NH, $n=4$), (b) (I; X=O, $n=4$) and (c) their 50/50 copolymer

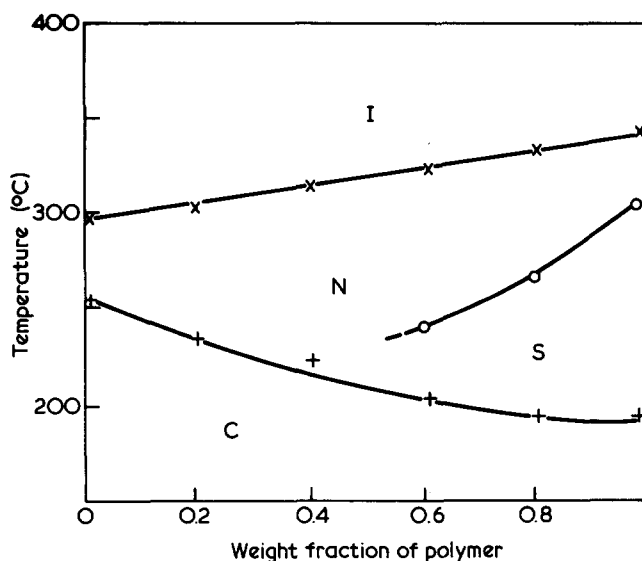


Figure 8 Transition temperatures for blends of polyesteramide (I; X=NH, $n=9$) and esteramide (II; Y=NH, $m=1$)

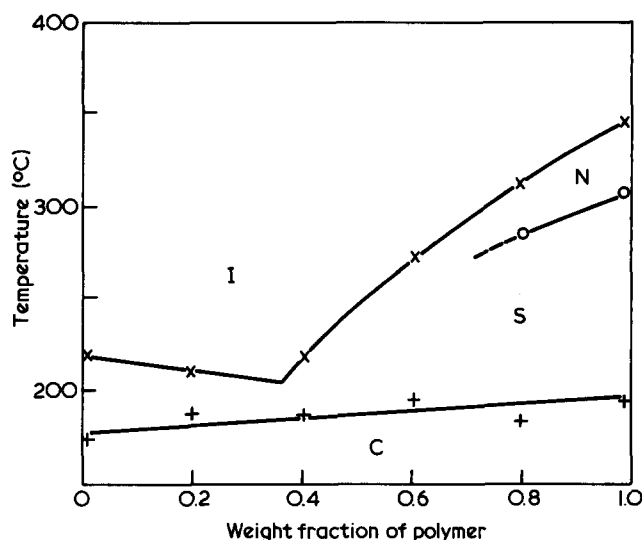


Figure 10 Transition temperatures for blends of polyesteramide (I; X=NH, $n=9$) and esteramide (II; Y=NH, $m=10$)

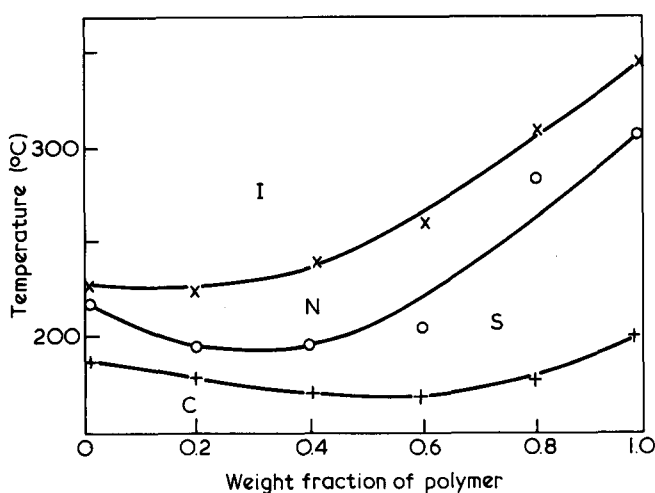


Figure 9 Transition temperatures for blends of polyesteramide (I; X=NH, $n=9$) and esteramide (II; Y=NH, $m=8$)

polymer fell to 0.6; the transition to the isotropic phase showed a pronounced minimum; and T_m showed no minimum at any blend composition.

The possibility of phase separation of the components must be borne in mind in interpreting these results. However, there was no indication of anything other than miscibility across the range either in the d.s.c. data or in the optical observation of the transitions. The continuity of observation of a relatively viscous liquid-crystalline phase across the range of compositions in blends with the simple esteramides that exhibited a smectic phase suggests that this phase in the polymer can be considered to be smectic, despite its lack of textural identity.

CONCLUSIONS

Within sets of thermotropic polyesteramides and polydiesters differing only in the presence of an amide group in the former in place of one of the ester groups in each repeating unit in the latter, the amide group has the effect of enhancing nematic phase stability, raising the temperature of onset of the nematic phase, substantially increasing the stability and ease of occurrence of the smectic phase, and usually of increasing the temperature of loss of crystallinity.

Isomorphous replacement is observed in copolymers containing both esteramide and diester repeating units and leads to values for crystalline, smectic and nematic thermal stability that are proportional to the composition.

Mixtures of polyesteramides and analogous simple liquid-crystalline esteramides provide transition data that support attribution of smectic character to the viscous liquid-crystalline phase in the polymers.

ACKNOWLEDGEMENTS

The authors thank the SERC and the University of Leeds for research fellowships (for AHM and AHK respectively). They also thank Dr D. J. Johnson for the X-ray diffraction photographs.

REFERENCES

- 1 Jackson, W. J. and Kuhfuss, H. F. *J. Appl. Polym. Sci.* 1980, **25**, 1685
- 2 McIntyre, J. E. and Milburn, A. H. *Br. Polym. J.* 1981, **13**, 5
- 3 Strzelecki, L. and van Luyen, D. *Eur. Polym. J.* 1980, **16**, 299
- 4 Bosio, L., Friedrich, C., Laupretre, F., Noel, C. and Virlet, J. *Proc. IUPAC MACRO 82*, Amherst, MA, p. 804
- 5 Kalyvas, V. and McIntyre, J. E. *Mol. Cryst. Liq. Cryst.* 1982, **80**, 105
- 6 Schroeder, J. P. *Mol. Cryst. Liq. Cryst.* 1980, **61**, 229