Eur. Polym. J. Vol. 20, No. 6, pp. 539–547, 1984
Printed in Great Britain. All rights reserved

0014-3057/84 \$3.00 + 0.00
Copyright © 1984 Pergamon Press Ltd

COPOLYESTERAMIDES—III

ANIONIC COPOLYMERS OF ε-CAPROLACTAM WITH ε-CAPROLACTONE

CRYSTALLINE CHARACTER AND MECHANICAL PROPERTIES

I. GOODMAN*†‡ and R. N. VACHON*
*Department of Polymer and Fibre Science, University of Manchester Institute of Science and Technology, Manchester M60 1QD and
†School of Polymer Science, University of Bradford, Bradford BD7 1DP, U.K.

(*Received* 17 *October* 1983)

Abstract—The crystalline character of anionic copolymers of ε-caprolactam with ε-caprolactone and of some alternatingly-sequenced analogues has been studied and investigations made of the mechanical and dynamic mechanical properties of the anionic copolymers. The anionic copolymers are crystalline over the whole range of compositions. Depending on the proportions of $NH(CH_2)_5CO$ and $O(CH_2)_5CO$ units and the thermal history of the copolymers, the crystalline phases present are either wholly of polyamide type or composed of co-existing and mutually incompatible polyamide and polyester entities. However, the constituents appear to be miscible in the amorphous phase. The mechanical properties of the copolymers (like their crystalline melting temperatures) change discontinuously with composition, showing minima in the values of initial modulus, yield stress and breaking stress at *ca* 25–40% amide-group content where dual crystallinity exists. In addition to their variation with composition, the properties are also affected by changes in the procedure of anionic copolymerisation.

INTRODUCTION

The previous paper of this series [1] described the anionic ring-opening copolymerisation of ε-caprolactam with ε-caprolactone yielding copolyesteramides. From the scheme of reaction envisaged initially, the products were expected to possess the general structure (I) which is that of a diblock polymer composed of nylon 6 polyamide and poly(ε-caprolactone) polyester segments, with end-groups X(H or RCO) and

$$Y(\overline{N(CH_2)_5C}O,\ ONa\ \text{or}\ OH)$$

resulting from the chemistry of polymerisation or from reactions caused by the termination or work-up procedures.

$$X[O(CH_2)_5CO]_x\text{——}[NH(CH_2)_5CO]_yY$$

(I)

The characteristics of the copolymers were consistent with structures composed essentially of 6-iminohexanoyl ($NH(CH_2)_5CO$) and 6-oxyhexanoyl ($O(CH_2)_5CO$) units in proportions approximating to those in the comonomer feeds, but there were indications that these units might be more randomly sequenced than is implied by (**I**); experimental evidence confirming that view will be presented in a later paper.

The present contribution deals with the crystalline character and mechanical properties of the copolymers, considered in relation to two hypotheses: (a) that the apparent formal structural resemblance between the iminohexanoyl and the oxyhexanoyl units might lead to their co-crystallisation by isomorphism across the whole range of compositions; (b) that with change in the $NH(CH_2)_5CO/O(CH_2)_5CO$ unit ratio and irrespective of the possibility of isomorphic co-crystallisation, the properties of the copolymers would change continuously between those of the hydrogen-bonded nylon 6 and the non-hydrogen-bonded poly(ε-caprolactone) homopolymer extremes.

As in the earlier papers [1, 6], iminoalkanoyl groups ($NH(CH_2)_{n-1}CO$) and oxyalkanoyl groups ($O(CH_2)_{n-1}CO$) will be abbreviated as nA and nE respectively.

EXPERIMENTAL

Materials

The anionic copolyesteramides were those designated as series **II** in the earlier paper [1], Table 6 and Fig. 3 of which give the relevant compositional and thermal transition data. All the copolymers were prepared by copolymerisation at temperatures above the product T_ms. Their compositions are denoted here by ciphers such as 70/30 which represent the ε-caprolactam/ε-caprolactone (i.e. 6A/6E) molar ratio in the starting reactants; in most cases the 6A unit contents of the copolymers were a few % less than in the comonomer feeds, probably because of equilibration of the chains with free lactam at the reaction temperatures used. Copolymers 60/40(4) and 40/60(3) were prepared at the same comonomer ratios as 60/40 and 40/60, respectively, but by a modified procedure involving the stepped (portionwise)

---

‡Address correspondence to: Professor I. Goodman, School of Polymer Science, University of Bradford, Bradford, West Yorkshire BD7 1DP, U.K.

Table 1. Crystallisation temperatures (T_{cryst}) by DSC

Material	Peak temperature of crystallisation (T_{cryst}) on heating from the quenched state* (°C)	Temperature of crystallisation on cooling from the melt† (°C)	
		Start	Finish
Nylon 6	—	182	160
90/10	57.5	161	138
80/20	52.5	125	97
70/30	39	112	74
60/40	29–36	79	34
60/40(4)	25	98.5	indefinite
50/50	8	76	indefinite
40/60	−3	28	indefinite
40/60(3)	4.5	94	67
25/75	−21	9.5	−15.5
10/90	−41.2	—	—
Poly(ε-caprolactone)	—	37	26

*Quenched in liquid N_2 and reheated from −73° at 16° min^{-1}.
†Cooled at 16° min^{-1}.

introduction of lactone to the reacting system. *alt*$[AB]_n$ and *alt*$[A_2B]_n$ denote two related copolyesteramides prepared by polycondensation and composed of recurring 6A6E and $(6A)_26E$ sequences, respectively. The homopolymer reference samples were those described previously.

Fabrication

As already shown [1], the T_m and T_g values change over a wide range with copolymer composition so that no single set of thermoplastic fabrication conditions could be used to prepare specimens for mechanical and dynamic mechanical properties measurements. The conditions of fabrication were therefore selected individually on the basis of the T_ms and of the crystallisation behaviour (a) from the quenched state; and (b) from the melt, as observed by differential scanning calorimetry (DSC).

For the former, specimens were first melted in sample pans of a Perkin–Elmer DSC-1, removed from the calorimeter and quenched in liquid N_2, and then re-heated from −73° in the instrument at 16° min^{-1}. Table 1 shows the peak temperatures of crystallisation so obtained; the values lie from 14 to 40° above the T_gs, the difference (T_{cryst}–T_g) being greatest in the copolymers with 40–60% 6A units. Crystallisation from the melt was studied at various cooling rates. At a rate of 16° min^{-1} crystallisation commenced for most of the materials at 30–40° below T_m and continued over a range of *ca* 25–45° from the onset temperature, the range being greatest towards the middle of the composition range. At lower rates of cooling (down to 4° min^{-1}) crystallisation commenced at some 10–15° higher temperature and was completed, where this could be measured, over a narrower temperature range than at 16° min^{-1}. The finish of primary crystallisation could not be located with certainty by DSC for copolymers with 40–70% 6A units but it was evident that, for most of the copolymers, crystallisation from the melt was substantially complete before reaching room temperature. It was also noted that 60/40(4) and 40/60(3) began to crystallise from the melt at higher temperatures than did 60/40 and 40/60, respectively.

Based on the above, films were prepared by compression-moulding of the copolymers (previously dried *in vacuo*) from temperatures of (T_m + 20°) for nylon 6, 90/10, 60/40(4) and 40/60(3); 150° for 70/30; 130° for 60/40; 120° for 50/50; and 100° for 40/60, 25/75 and 10/90, with slow cooling to about (T_m-30°) in each case followed by final quicker cooling to 15° by passage of water through the plates of the press.

The following copolymers were also melt-spun to fibres by candling cut-up polymer sheet and extruding as monofil through a 15/1000 in. die at the temperatures shown below; 25/75 and 10/90 did not yield coherent fibres in this way.

Copolymer	*Extrusion temperature (°C)*
40/60	65
50/50	95
60/40	115
70/30	145

In a number of cases, moulding or extrusion liberated some vapours of caprolactam but solution viscosity measurements showed no loss in mol wt (and, in some cases, an apparent small increase) as a result of fabrication.

Properties measurements

Wide-angle X-ray diffraction (WAXD) patterns of the materials were obtained using Cu–K_α radiation and photographic recording; *d*-spacings were derived from microdensitometer traces of the diffractograms.

The mechanical properties of the moulded films were measured according to ASTM D638-67T, using dumbell-shaped test samples (with test portions 3 mm wide and 1 mm thick) which had been conditioned at 20° and 50% relative humidity for at least 12 hr prior to testing with an Instron tensometer. Values of Young's modulus were obtained with an initial gauge length of 2.54 cm and at a strain rate of 1 cm min^{-1}; yield, break and extensibility measurements were made using a strain rate of 10 cm min^{-1}. Measurements were also made on a number of samples that had been annealed for 24 hr at temperatures increasing with 6A content from 48° for 10/90 to 89° for 70/30. Tensile properties of the monofils were measured similarly, using both as-spun filaments and filaments drawn to a draw ratio of 5:1 and then heat-set. Strain recoveries of the drawn fibres were determined according to ASTM D1774–64.

Densities were determined by displacement in liquid paraffin at 25° (ASTM D972–66), and equilibrium moisture absorptions by gravimetry following immersion in liquid water at room temperature. Dynamic mechanical properties were measured using a torsion pendulum operating at 1 Hz.

RESULTS AND DISCUSSION

Crystalline character

Although no measurements were made of the degrees of crystallinity, it was apparent from their general characteristics that the copolymers were substantially crystalline over the whole range of compositions, though with some reduction in the range from 40 to 50% 6A as shown by the density values

Table 2. Density and moisture uptake of 6A/6E copolymers and related homopolymers

Materials	Density (d_{25}°C) Unannealed sheets	Density (d_{25}°C) Annealed sheets	Moisture absorption at 23° (wt%)
Nylon 6	1.148		
90/10	1.139		
80/20	1.133*, 1.144		6.45
70/30	1.144	1.146	4.95
60/40	1.146	1.143	4.38
60/40(4)	1.136		
50/50	1.133	1.133	3.89
40/60	1.133	1.133	3.16
40/60(3)	1.127		
25/75	1.142	1.139	1.43
10/90	1.157	1.153	0.85
Poly(ε-caprolactone)	1.149 (at 20°)†		0.43†

*As isolated. †Data from [24].

(Table 2). The type of crystallinity displayed varied in some cases with sample history.

The characteristic *d*-spacings, derived from the WAXD patterns, are summarised in Fig. 1. The identification of crystal phases is complicated in 6A/6E copolymers by the known sensitivity of the nylon 6 diffraction pattern to the effects of moisture and temperature, arising from the existence of polymorphic forms of varying stability [2–4]. Therefore, in assigning the diffraction features of the copolymers, band and shoulder profiles were considered in addition to the spacings of the principal maxima. The main indicators of poly(ε-caprolactone) crystallinity were thus taken to be the medium intensity features at $d = 2.99$ and 5.52 Å (the latter being in the same region as a very weak reflection shown by highly annealed nylon 6) and the very strong 4.13 Å band which lies close to the strong 4.16 Å reflection of the γ-form of nylon 6. The principal reflections due to the stable α-form of nylon 6 are at $d = 3.73$ and 4.40 Å.

The anionic copolymers with 6A contents ≥50% showed crystallinity only of the nylon 6 type. As initially isolated, 80/20 had an unusually low density and showed a prominent diffraction at $d = 4.14$ Å; on moulding, its density increased (Table 2) and annealing developed the two characteristic major reflections of α-nylon 6 whilst concurrently eliminating the 4.14 Å feature which is therefore assigned to γ-nylon 6 crystallinity. Polyester crystallinity was not found in copolymers with 6E contents below 60%. Copolymer 40/60, as first isolated, showed the

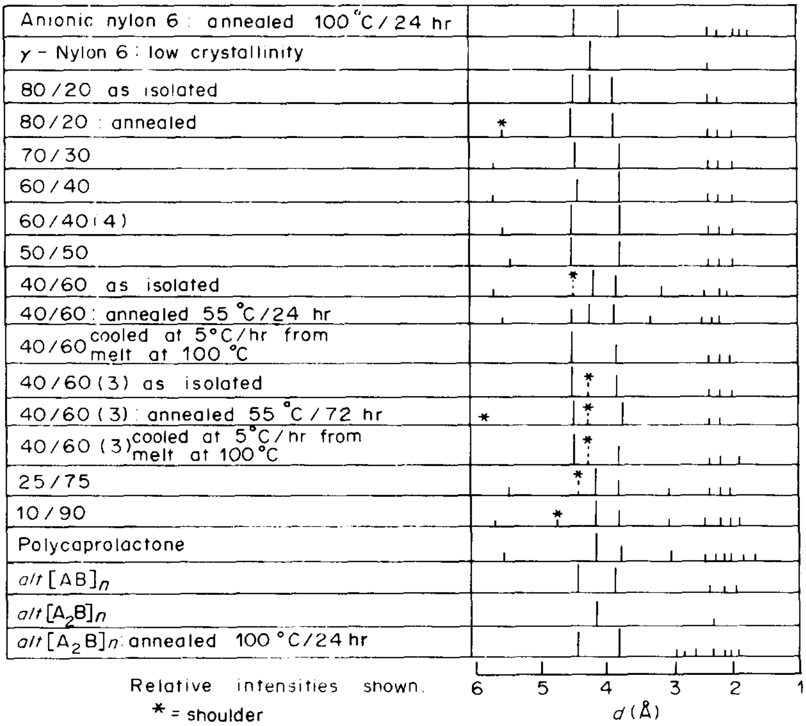


Fig. 1. Characteristic X-ray spacings of the anionic copolymers, related homopolymers and alternating copolymers.

Table 3. Values of slope p and melt viscosity

Material	p	Temperature range (°C)	Melt viscosity ($\times 10^3$ poise at temperature shown) (°C)
Nylon 6	8.1	228–235	0.35 (228°) 0.25 (235°)
60/40	8.35	125–130	1.56 (115°) 1.2 (130°)
40/60	2.93	80–110	5.3 (80°) 1.16 (110°)
25/75	2.1	90–110	3.2 (75°) 1.76 (90°)
Poly(ϵ-caprolactone)	1.48	75–140	1600 (75°) 260 (125°) 140 (140°)

4.4 Å (200) reflection of α-nylon 6 only as a shoulder, but annealing caused this feature to become well resolved, with retention of the polyester reflections, whereas slow crystallisation from the melt eliminated the polyester reflections entirely. DSC scans of 40/60 did not reveal any melting transition ascribable to physically admixed poly(ϵ-caprolactone) homopolymer; the polyester crystallinity shown by WAXD must therefore be due to organized 6E sequences forming part of the copolymer chains. Copolymers 25/75 and 10/90 showed predominant polyester crystallinity, with weak shoulders in both cases that might be attributable to minor proportions of α-nylon 6 crystallites. As regards the copolymers prepared by stepped introduction of lactone, 60/40(4) showed strong reflections entirely of α-nylon 6 type whilst 40/60(3) showed stronger α-nylon 6 crystallinity than 40/60, together with a shoulder at *ca* 4.2 Å which survived annealing and slow crystallisation from the melt and was more probably due to γ-nylon 6 than to polyester.

Figure 1 also includes the diffraction patterns of *alt*$[AB]_n$ and *alt*$[A_2B]_n$. Although formally 6A/6E copolymers, these substances can also be regarded as homopolymers having complex and specifically sequenced repeating units. *alt*$[AB]_n$ solidified from the melt in highly crystalline form, with its principal WAXD reflections (3.82, 4.41 Å) more closely spaced than in α-nylon 6 and in the 50/50 anionic copolymer. As first obtained, *alt*$[A_2B]_n$ showed only a single major WAXD band but annealing eliminated this and developed two major reflections (3.80, 4.39 Å) again closer than in α-nylon 6 or in the anionic copolymers. Neither alternating copolymer showed the diagnostic features of poly(ϵ-caprolactone) crystallinity.

Thus despite the formal structural resemblance between the 6A and 6E units, sequences of these appear to crystallise independently in the anionic copolymers of *ca* 40–10% 6A content giving separate coexisting crystalline domains of polyamide and polyester type, whilst at higher 6A contents only the amide component crystallises. At least within the upper part of the composition range where dual crystallinity can be observed, that due to polyamide is dominant and can extinguish the polyester crystallinity in samples cooled from the melt. This sensitivity of crystal type to sample history was also found in the X-ray diagrams of melt-spun yarns from copolymers with 80–40% 6A units which, both as-spun and after drawing and heat-setting, displayed oriented crystallinity only of the α-nylon 6 type (but with decreasing perfection of crystalline order at the lower 6A contents); however, when specimens of 40/60 were extended to break and the WAXD recorded near to the point of break, the patterns, although essentially of α-nylon 6 type, included streaks corresponding to the 7th layer line of oriented poly(ϵ-caprolactone) indicating that this component behaved discretely under stress.

Jasse [5] has studied 11A/11E copolyesteramides which, like the present series, are potentially susceptible to isomorphism and had found dual crystallinity over the composition range from 70 to 90% 11E. Our own investigations on the 12A/6E series [6], which do not have this structural relationship, showed a more sudden transition between the crystal types of the homopolymer extremes, with only a narrow range of composition (75–80% 6E) in which polyester crystallinity apparently coexisted with a distorted form of crystalline γ-nylon 12.

Microscopical examination of poly(ϵ-caprolactone) and of the copolymers 60/40, 25/75 and 10/90 (all crystallised from the melt) showed fine-grained texture with spherulites of diameter 2–15 μm in 60/40 and up to 30 μm in 10/90. The differences were insufficient to account for the large difference in mechanical properties across this range of compositions.

Polymer melt characteristics

Melt viscosities and first normal stress differences in steady shear were measured over a range of temperatures using a Weissenberg rheogoniometer in cone-and-plate configuration. The first normal stress differences were obtained by a total thrust measurement. Plots of $\log p_{12}/G^1$ vs $\log (p_{11}-p_{12})/G^n$, where p_{12} is the shear stress, $(p_{11}-p_{12})$ is the normal stress difference, G is the shear rate and n, 1 are constants, gave straight lines whose slopes p are given in Table 3 together with the observed (Newtonian) melt viscosities.

For polymers in general, p is independent of molecular weight and temperature but is related to the stress needed to obtain melt-orientation (i.e. to the dependence of elasticity on shear stress) which, in turn, reflects differences in extents of molecular interaction. The p values in Table 3 increase with 6A content, reflecting the increasing extents of hydrogen-bonding which, as shown by i.r. spectroscopy, persists in the melt at the temperatures used in these measurements.

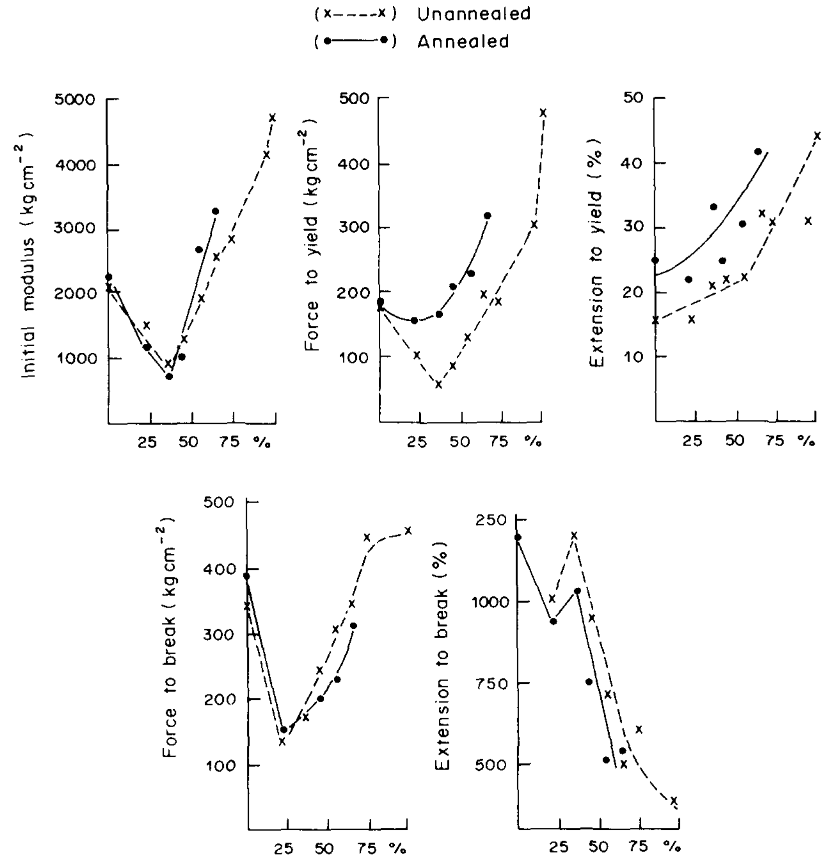


Fig. 2. Mechanical properties of anionic 6A/6E copolymers (moulded sheets) vs % 6A groups.

Moisture uptake

For polyamides composed in general of CONH and aliphatic hydrocarbon groups, the uptake of moisture at equilibrium is related to the proportion of CONH groups present, these being the sites for hydrogen-bonding of water molecules [7, 8]. The values for 6A/6E copolymers (Table 2) conform to this pattern. The moisture uptake at saturation increases nearly linearly with 6A content, indicating that this uptake is not affected appreciably by the changes in crystalline character over the composition range studied, and that the O.CO groups of the 6E units do not serve as water-receptive sites.

Mechanical properties

Fabricated sheets of the anionic copolymers had the character of typical crystalline thermoplastics materials, varying in stiffness and extensibility with 6A content. The 25/75 and 10/90 copolymers were markedly brittle. Thus, whilst moulded sheets of poly(ϵ-caprolactone) and 40/60 could be folded about a crease for at least 250 times before breaking, the 75 and 90% 6E copolymers fractured at the first folding.

The primary tensile properties of the normal series of 6A/6E copolymers, both as-moulded and after annealing, are plotted in Fig. 2 against their 6A contents as abscissae. In general, the stress vs strain curves showed distinct yield peaks and drawing regions. The values of initial modulus, yield stress and breaking stress changed discontinuously with copolymer composition, with minima for each property in the range from *ca* 25–40% 6A. Since the copolymers within this range had similar solution viscosities to the other members, both before and after moulding, the minima cannot be ascribed to molecular weight differences but they do correspond to the composition range of minimum T_m reported previously [1] and to that of dual or of changing crystallinity as described above. 11A/11E copolyesteramides also show mechanical weakness in the composition range of dual crystallinity [5] and the 12A/6E series, although not studied in detail, showed a qualitatively similar effect [6].

The extensions to yield showed a smooth progression throughout the 6A/6E series but the breaking extensions showed a maximum at 40% 6A corresponding to the modulus minimum at about the same composition. Annealing had little effect on modulus and breaking stress but appreciably increased the yield strain and stress values probably by an enhancement of crystallinity.

Table 4 compares the properties of the stepped-addition copolymers with those of their normal counterparts. Initial modulus, yield stress and breaking stress were all less for 60/40(4) than for 60/40 but the corresponding values for 40/60(3) were higher than for 40/60 indicating, in this case, a more developed stress-bearing molecular structure.

The tensile properties of 6A/6E melt-spun filaments are shown in Table 5. As mentioned above, the copolymers examined possessed only nylon 6

Table 4. Mechanical properties of normal and stepped-addition anionic copolymers (unannealed sheets)

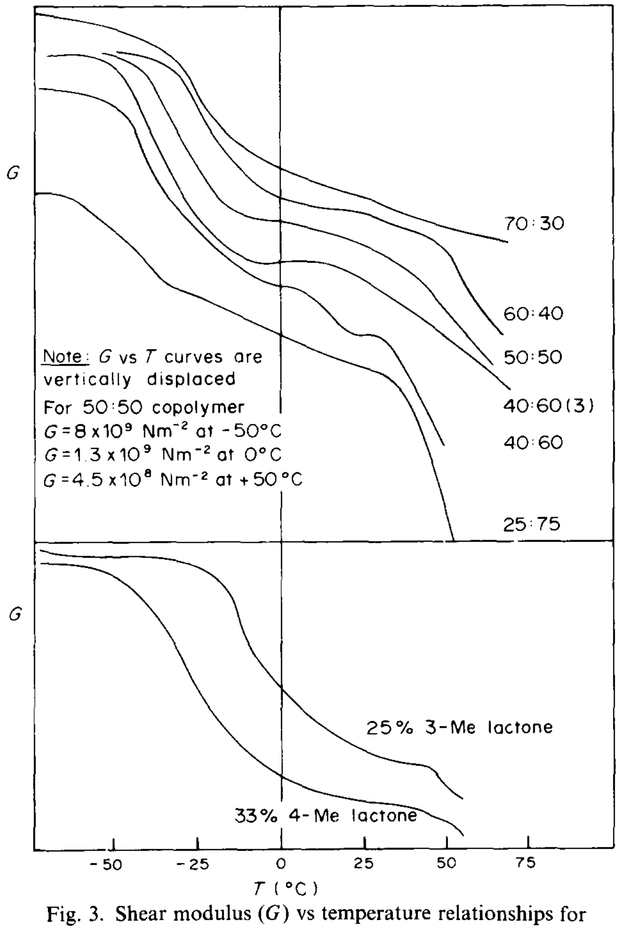
	60/40	60/40(4)	40/60	40/60(3)
Initial modulus (kg cm^{-2})	1970	1594	916	1085
Extension to yield (%)	22	27	21	19
Force to yield (kg cm^{-2})	132	101	57	67
Extension to break (%)	710	706	1200	1065
Force to break (kg cm^{-2})	306	254	169	274

Table 5. Tensile properties of 6A/6E copolymer fibres

Copolymer	80/20	70/30	60/40	50/50	40/60
(a) *Filaments as spun from the melt*					
Extension to yield (%)	8.5	9.0	6.0	10.4	11.0
Yield stress (g dtex^{-1})	0.21	0.18	0.13	0.10	0.08
Tenacity (g dtex^{-1})*	0.56	0.38	0.23	0.23	0.16
Extension to break (%)	840	833	752	1050	1085
Initial modulus (g dtex^{-1})	5.86	4.99	3.06	2.05	1.21
(b) *Filaments drawn (draw ratio* 5:1) *and heat-set at temperature shown for* 5 *min*					
Setting temperature (°C)	150	120	90	65	45
Tenacity (g dtex^{-1})*	1.09	1.26	0.54	0.90	1.08
Extension to break (%)	42	62	45	106	45
Initial modulus (g dtex^{-1})	6.3	5.4	2.7	3.6	6.3

*Calculated on initial fibre tex.

crystallinity in the oriented state and the relation of their properties to composition paralleled that for the moulded specimens. Table 5 also includes some results for drawn and heat-set specimens made by drawing the spun filaments singly on the Instron machine and setting at constant length in the conditions stated, followed by conditioning for tensometry at 21° and 67% relative humidity. Because of the drawing procedure used and the small number of replicates available the values are of limited statistical



Note: G vs T curves are vertically displaced
For 50:50 copolymer
$G = 8 \times 10^9$ Nm^{-2} at -50°C
$G = 1.3 \times 10^9$ Nm^{-2} at 0°C
$G = 4.5 \times 10^8$ Nm^{-2} at +50°C

Fig. 3. Shear modulus (G) vs temperature relationships for 6A/6E and 6A/methyl-6E anionic copolymers.

Table 6. Strain recovery of 6A/6E copolymer fibres

Extension (%)	Recovery* (%)
2	100
5	95–97
10	85–92
20	64–72

*Range of values for copolymers of 40–80% 6A content.

accuracy but, as compared with the undrawn specimens, they display the increase in tenacity and the large decrease in extensibility characteristic of crystalline melt-spun fibres. The strain recoveries of drawn fibres from copolymers with 40–80% 6A were also measured; the results (Table 6) were little affected by copolymer composition.

Considering the tensile properties as a whole, the copolymers fall into two distinct groups—those of low amide content (25/75 and 10/90) which are mechanically weak and brittle, and the higher amide-content ($\geqslant$40% 6A) materials for which, from the WAXD evidence, oriented nylon 6 units constitute the load-bearing component. The copolymers of highest amide content (90–70% 6A) have characteristics related to, though significantly modified from, those of nylon 6. In particular, the modulus and breaking stress are reduced and the elongation to break is increased; the effect is equivalent to internal plasticisation. The copolymers of 60–40% 6A content have properties tending towards those of low-density polyethylenes, though with rather higher values of strength, extensibility and modulus. The copolymers prepared by stepped addition of lactone differ appreciably in tensile characteristics from copolymers of similar 6A/6E ratios prepared in the normal way and no copolymer showed high recoverable extensibility (i.e. elastomeric character). The change in properties over the range 90–40% 6A reflects the progressive attenuation of that component which can absorb mechanical stress whilst the ester component remains amorphous, above its T_g and incapable of contributing to mechanical strength.

Dynamic mechanical properties

Shear modulus (G) vs temperature and damping (tan δ) vs temperature relationships for several of the copolymers are shown in Figs 3 and 4. To facilitate comparison, the curves are placed on unscaled ordinates but the magnitudes of the quantities did not differ greatly across the series; the G values were thus broadly within the range from 10^9 to 10^7 N m^{-2}, and the tan δ values were within the range 0.13–0.3. The lower part of each Figure gives the corresponding curves for anionic copolymers of ϵ-caprolactam with 3- and 4-methyl-ϵ-caprolactones, prepared to typify materials in which the ester component could neither crystallise nor co-crystallise.

Each shear modulus curve shows a major subambient temperature transition occurring at lower temperatures as the 6E component increases. The broad oblique slopes below the plateau regions indicate substantial component mixing as had already been inferred from the DSC data [1]. Similar compatibility between low mol wt poly(ϵ-caprolactone) soft block segments and various cyclic and acyclic carbamate ester hard blocks has been found in segmented polyurethanes which have some structural analogy with the present copolymers [9–11].

The tan δ vs composition relationships are complex. All the copolymers show a major transition below 0°, with peaks located at progressively lower temperatures as the ester (6E or methyl-6E) content increases; the peak temperatures correlate well in most cases with the T_gs determined by DSC. However, the features seen above 0° cannot be assigned with certainty. From simplistic *a priori* considerations, the temperature range studied might include glass transitions due to 6A blocks or sequences and/or melting transitions due to organised 6E sequences. The features seen at 30, 35 and 47° for 70/30, 60/40 and 50/50 respectively, lie in the inverse order to reasonable expectation for nylon 6 T_gs and find no support from DSC or WAXD evidence if interpreted as polyester segment T_ms. The 20 and 35° peaks shown by 40/60 and 25/75 likewise do not correspond with the polyester T_ms found by DSC. On the other hand, the methyl-6E copolymers show substantial peaks that can only be assigned to their 6A components. In addition, several of the copolymers show inflexions in the range of 2–8° and 40/60(3) has a definite maximum in this region; these might possibly correspond to plasticisation of the 6A component (as

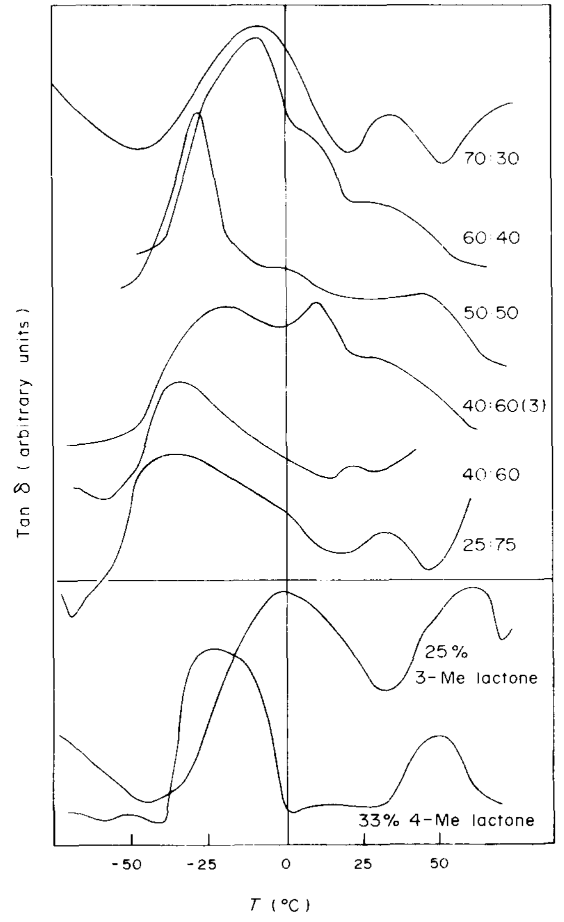


Fig. 4. Damping (tan δ, 1 Hz) vs temperature relationships for 6A/6E and 6A/methyl-6E anionic copolymers.

is known in nylon 6 homopolymer and some copolymers [12–15]) or alternatively to the special features of molecular interaction that will be discussed in the next paper of this series.

General discussion

The properties of the anionic 6A/6E copolymers reported in this and in the preceding paper differ considerably from those predicted by the considerations posed in the Introduction. Copolymers of structure (**I**), assuming no interaction between the sub-species, should display characteristic block copolymer behaviour [16], with substantially independent behaviour of the 6A and 6E sequences as regards crystalline nature and thermal transitions; evidently, this was not the case. Alternatively, if (as will be established elsewhere [17]) the materials are more random in structure, then they conform neither to the expectation of isomorphism nor to that of progressive change of properties with change of hydrogen-bonding group content. Furthermore, for polymerisation in a homogeneous phase, the scheme of chain growth originally envisaged should be unaffected, for a given 6A/6E ratio, by minor variations in polymerisation technique; yet, as has been shown, stepwise rather than "single shot" introduction of lactone yields products of perceptibly different properties and hence, by inference, of different chain structures. Of the characteristics examined, only three (T_g, moisture uptake and melt rheology) change continuously with change of 6A/6E ratio, each being a property of the amorphous state of the materials. The discontinuously changing properties are all associated with the crystalline character with which the remainder of this discussion is concerned. The most striking features, in relation to the starting hypotheses, are (a) the minima in T_m and in the major mechanical properties at *ca* 20–30% 6A content, (b) the coexistence of discrete polyamide and polyester crystalline phases over a certain range of compositions, (c) the surprising mechanical weakness near to the composition of minimum T_m.

The concept of copolymer isomorphism, defined as the statistical substitution, within a *single* crystalline phase, between monomer units differing either in chemical structure or in conformation or in configuration, has been reviewed by Allegra and Bassi [18]; other relevant publications are those of Baker and Fuller [19] and Kibler *et al.* [20]. The common characteristic of copolymer systems recognised as isomorphic is the possession of a monotonic T_m vs composition curve and of a constant or a monotonically changing pattern of crystal lattice spacings.

For the anionic 6A/6E copolymers, the existence of dual crystallinity over a particular range of compositions points to a fundamental incompatibility between the polyamide and polyester sub-species in their crystalline states. Figure 5, based on published crystal structures of α-nylon 6 [21, 22] and poly(ε-caprolactone) [23], indicates schematically the difference between the structures and the probable source of their incompatibility. For α-nylon 6 [which, from the IR and WAXD evidence, persists at least

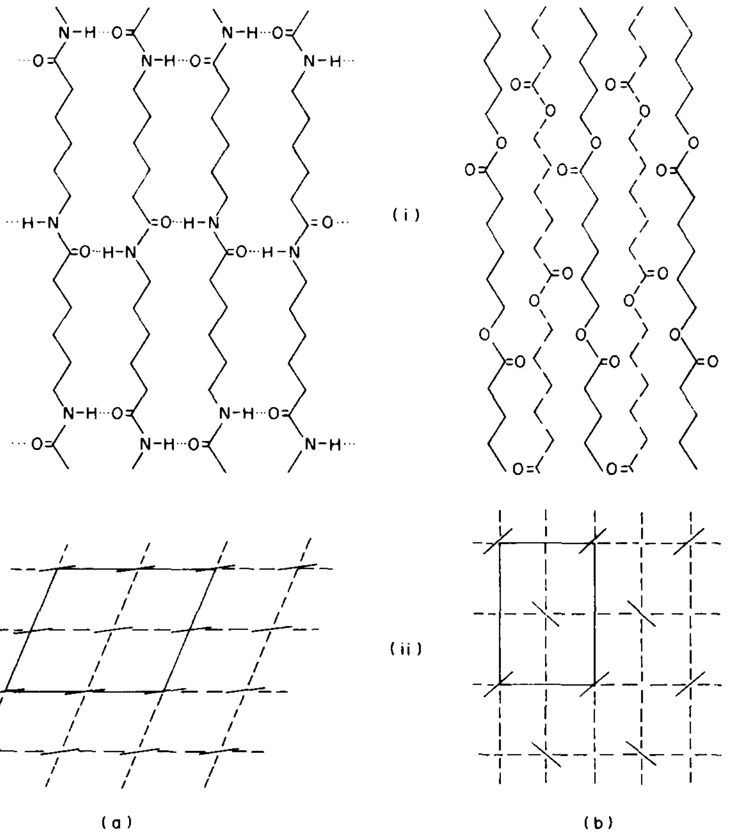


Fig. 5. Arrangement of molecular chains in crystals of: (a) α-nylon 6; (b) poly(ε-caprolactone); projected onto (i) face, (ii) base of the respective unit-cell assemblies. (Adapted from [21–23].)

down to 40% 6A and is prominent in 40/60(3)], the hydrogen-bonded CONH groups lie in parallel bands of uniform height along the molecular chains and disposed across the face of the monoclinic unit cell. The planes of the molecular axes projected onto the base of the unit cell are unidirectional and parallel. By contrast, in poly(ϵ-caprolactone) the heights of the polar groups in alternate layers of molecules are displaced by 3/14 c along the fibre axis, and the chain axis projections onto the base of the orthorhombic unit cell lie in planes of alternately opposed orientations.

Substitution of some 6A units for 6E in the poly(ϵ-caprolactone) structure (i.e. the replacement of some chain O atoms by NH) would therefore place amide groups opposite to the methylene sequences of neighbouring molecules and remote from the positions required for hydrogen-bonding. This is inconsistent with the finding from i.r. spectroscopy that the NH groups are fully hydrogen-bonded throughout the whole composition range. On the other hand, since the fibre repeat distances of α-nylon 6 and polycaprolactone are nearly the same, substitution of 6E units into the polyamide chain (i.e. replacement of NH by O) can occur without significant spatial distortion though in a way that leaves facing $C=O$ groups of adjacent chains unbonded (which is inconsequential from the standpoint of structural order) but, more importantly, that is inconsistent with the generation of polyester crystallinity.

The onset of polyester crystallinity at 40% 6A content (which, as is apparent from Fig. 1, is sensitive to the thermal history) occurs where the volume fraction of amide units is approaching insufficiency to maintain an organised nylon network throughout the bulk of the material. With further reduction in 6A content that condition is reached but, whilst the 6E component can now undergo substantial *unoriented* crystallisation in the polycaprolactone mode, the hydrogen-bonding requirement of the CONH groups interferes with the larger-scale orientation of polyester chains as a stress-bearing network leading to the mechanical weakness shown by the 25/75 and 10/90 copolymers.

Acknowledgements—We are grateful to the Science Research Council for the financial support of the work described in this and in the previous paper [1], and to Professor R. H. Peters for his interest. The rheological measurements were made and interpreted by Dr G. H. West (UMIST) and the dynamic mechanical measurements by Mr S. J. Kettle (now at ICI Central Toxicology Laboratory, Cheshire), to both of whom we express our thanks.

REFERENCES

1. I. Goodman and R. N. Vachon, *Eur. Polym. J.* **20,** 529 (1984).
2. G. A. Campbell, *J. Polym. Sci.* B, **7,** 629 (1969).
3. A. Reichle and A. Prietzschk, *Angew Chem.* **74,** 562 (1962).
4. C. Ruscher, V. Gröbe and H. Versäumer, *Faserforsch. Text Tech.* **12,** 214 (1961).
5. B. Jasse, *Bull. Soc. chim. Fr.* **1965,** 1640.
6. I. Goodman and V. Valavanidis, *Eur. Polym. J.* **20,** 241 (1984).
7. K. Dachs and E. Schwartz, *Angew. Chem.* **74,** 540 (1962).
8. R. Puffr and J. Šebenda, *J. Polym. Sci.* C, **16,** 79 (1967).
9. C. G. Seefried, J. V. Koleske and F. E. Critchfield, *J. appl. Polym. Sci.* **19,** 2493, 2503, 3185 (1975).
10. J. W. C. van Bogart, P. E. Gibson and S. L. Cooper, *J. Polym. Sci., Polym. Phys. Ed.* **21,** 65 (1983).
11. A. P. Brazier, Ph.D. thesis, University of Bradford (1981).
12. A. E. Woodward, J. M. Crissman and J. A. Sauer, *J. Polym. Sci.* **44,** 23 (1960).
13. W. B. Brown, G. A. Campbell and J. B. Nowell, *Polym. Prepr.* **10,** 647 (1969).
14. D. C. Prevorsek, R. H. Butler and H. K. Reimschuessel, *J. Polym. Sci.* A-2, **9,** 867 (1971).
15. V. Frosini and E. Butta, *J. Polym. Sci.* B, **9,** 253 (1971).
16. I. Goodman (Ed.), *Developments in Block Copolymers*—1. Applied Science, London (1982).
17. I. Goodman, *Eur. Polym. J.* **20,** 549 (1984).
18. G. Allegra and I. W. Bassi, *Fortschr. Hochpolym Forsch.* **6,** 549 (1969).
19. W. O. Baker and C. S. Fuller, *J. Am. chem. Soc.* **64,** 2399 (1942).
20. C. J. Kibler, A. Bell and J. G. Smith, *J. Polym. Sci.* A, **2,** 2115 (1964).
21. D. R. Holmes, C. W. Bunn and D. J. Smith, *J. Polym. Sci.* **17,** 159 (1955).
22. V. Malta, G. Cojazzi, A. Fichera, D. Ajò and R. Zannetti, *Eur. Polym. J.* **15,** 765 (1979).
23. Y. Chatani, Y. Okita, H. Tadokoro and Y. Yamashita, *Polym. J.* **1,** 555 (1970).
24. Union Carbide Corp., New Polycaprolactone Thermoplastic Polymers, Technical Data Publication F-42501 (undated).