polymer communications

6NT6 copolymers. Physicochemical study on samples precipitated from dilute solutions

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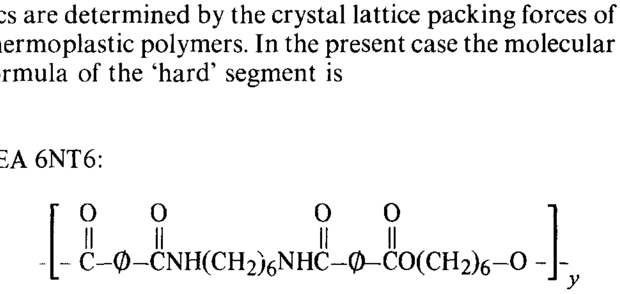
The copolymers discussed here belong to a class of polymeric materials whose physical properties are intermediate between elastomeric and thermoplastic[1–3]. Their formula is of the type $[A_xB_y]_z$, where z indicates the degree of polymerization, and x and y the segment lengths of the A and B repeating units.

The A segments constitute the 'soft' phase, responsible for the elastomeric properties of the material, while B segments constitute the 'hard' phase, whose characteristics are determined by the crystal lattice packing forces of thermoplastic polymers. In the present case the molecular formula of the 'hard' segment is

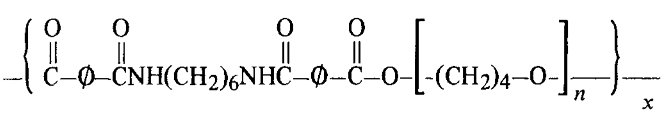
PEA 6NT6:



$$\left[-\overset{O}{\overset{\|}{C}}-\phi-\overset{O}{\overset{\|}{C}}NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}-\phi-\overset{O}{\overset{\|}{C}}O(CH_2)_6-O-\right]_y$$

while for the 'soft' segment we have the ester of an esteramide:

PTMEG–T′:



$$-\left\{\overset{O}{\overset{\|}{C}}-\phi-\overset{O}{\overset{\|}{C}}NH(CH_2)_6NH\overset{O}{\overset{\|}{C}}-\phi-\overset{O}{\overset{\|}{C}}-O-\left[-(CH_2)_4-O-\right]_n-\right\}_x$$

These copolyesteramides can be prepared by transesterification of N,N'-(p-carbomethoxybenzoyl) hexamethylene diamine (6NT) and hezane-1,6-diol (6G) and poly(tetramethylene ether glycol) (PTMEG) of $M_n \simeq 1000$, followed by a polycondensation reaction[4,5]. The copolymer obtained is a random sequence of 'hard' 6NT6 segments and 'soft' PTMEG-T′ segments.

Copolyesteramide parents are the Hytrel type polyether-ester copolymers[1–3] in which the 'hard' segment is given by the 4GT ester of 1,4-butanediol (4G) and dimethyl terephalate (DMT). Morphological investigations[6,7] on melt-crystallized copolyesteramide have shown that a phase segregation occurs between the crystalline and amorphous regions, giving rise to lamellar phases. In this paper, following research aimed at clarifying the chain-folding problem[8–12], we have studied some morphological and thermodynamic characteristics of copolyesteramide samples containing different amounts of 'soft' phase, crystallized from dilute solutions.

Experimental

The copolyesteramide samples examined in this work were supplied by the Assoreni Laboratories of San Donato Milanese. In *Table* 1 some physicochemical characteristics of the copolymers studied are reported. The samples were dissolved in dimethyl sulphoxide ($c = 0.1\%$ w/w at $T \simeq 170°C$ and crystallized at $T_c = 30°C$ in thermostatically controlled oil baths. The crystallized materials were filtered at the crystallization temperature (T_c), then dried in vacuum.

Small-angle X-ray scattering (SAXS) measurements were carried out on dried crystallized samples by means of an Elliot GX-6 rotating anode (Cu Kα radiation, $\lambda = 1.54$ Å) as X-ray generator and a Luzzatti-Baro small-angle camera. The X-ray diffraction patterns were recorded on a flat film, the film specimen distance being in the range 220–250 mm. The long spacing (L) of the lamellae was computed by means of the Bragg equation.

Apparent enthalpies of fusion (ΔH_{app}) and melting temperatures (T_m) of dried crystal mats were measured by means of a Perkin–Elmer differential scanning calorimeter DSC-1B.

Results and discussion

The chemical complexity of these random macromolecules made it particularly difficult to find the right crystallization solvent. Some of the solvents used, the protic ones, were able to degrade the polymers, as in the case of 1,3-propanediol and N,N'-dimethylformamide. The degradation was assessed by viscometric measurements of $[\eta]$, indicating a decrease in the molecular weight of the sample with increasing soft phase content. Degradation effects were avoided by using dimethyl sulphoxide as crystallization solvent. In *Figure* 1 the long spacing (L) of the crystallized materials, assessed by means of SAXS measurements, is plotted *versus SC*. The trend in L, which is constant up to a soft phase content of 40% w/w, shows a marked deviation for samples containing 50% w/w of PTMEG-T′ and more.

The L values for $SC \leqq 40\%$ are those of the PEA 6NT6 single crystals[12], while an increase in L is found for SC

Table 1 Some physicochemical characteristics of the copolymers PEA–PTMEG–T′

Sample	% Hard phase Weight	% Hard phase Moles	% Soft phase Weight	% Soft phase Moles	$\bar{M}_n \times 10^{-3}$
M 175	76.3	90.08	23.7	9.91	15–20
M 187	58.9	80.17	41.1	19.82	
M 188	45.5	70.20	54.5	29.80	
M 189	35.0	60.31	65.0	39.69	
M 190	26.3	50.17	73.7	49.82	
M 191	19.3	40.29	80.7	59.71	
M 208	13.3	30.21	86.7	69.79	
M 209	8.3	20.34	91.7	79.65	

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≧50%. For the latter samples the experimental points lie on a straight line which, extrapolated to $SC=0\%$ coincides with the observed value of ~80 Å of the homopolymer. A broadening of the diffraction peaks was observed as the soft phase content increased, indicating a lowering of the crystallinity. In *Figure* 2 the d.s.c. thermograms are shown for samples crystallized at $T_c = 30°C$. The higher temperature peak is larger for the homopolymer and for copolymers with *SC* 40%, while it becomes smaller and disappears with increasing content of soft segments in the chain. A peak broadening is also observed, in agreement with the SAXS peak width evidence.

In *Figure* 3 the melting temperature (T_m) of the crystallized samples is plotted against *SC*. The two curves refer to the T_m relative to the first (low temperature) and the second (high temperature) peaks, respectively.

A variation in slope of the T_m curve is observed for $SC > 50\%$. The same trend is shown by the apparent enthalpy curves (ΔH_{app}) of *Figure* 4. It is then apparent from the experimental evidence obtained that both the morphological and physicochemical characteristics of the PEA 6NT6-PTMEG-T′ copolymers are drastically influenced by the molar ratio of the two components, as expected. The variation, however, is not linearly dependent upon the molar ratio or the wt % soft phase in the samples.

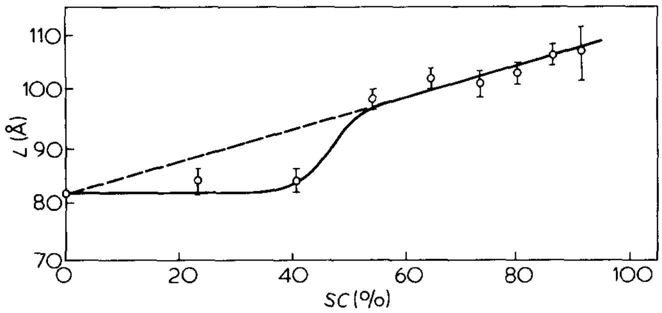

Figure 1 Dependence of long spacing (*L*) upon PTMEG–T′ content for sample crystallized at T_c = 30°C

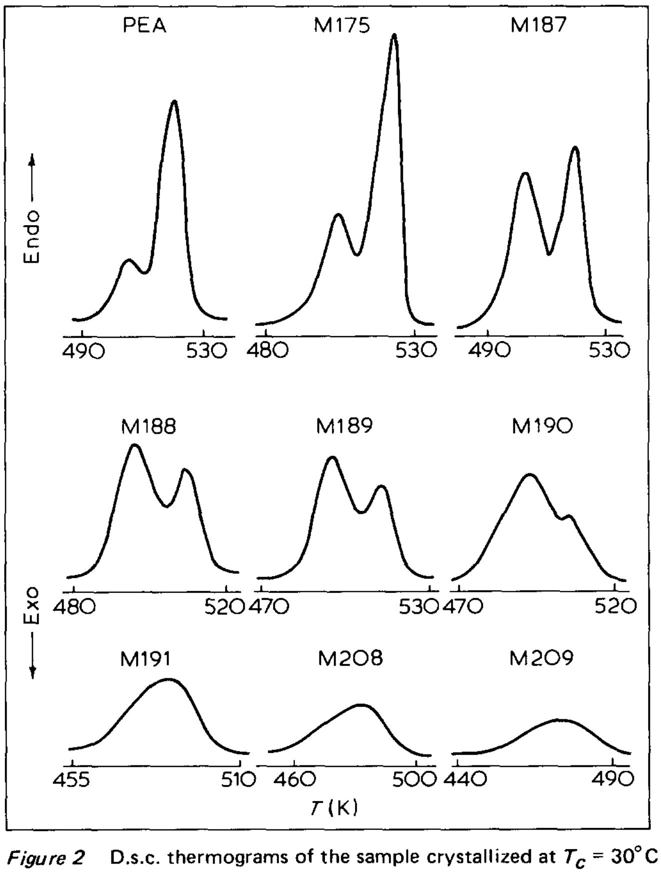

Figure 2 D.s.c. thermograms of the sample crystallized at T_c = 30°C

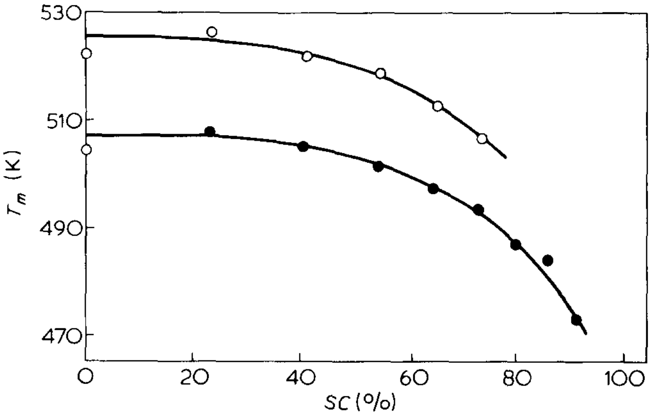

Figure 3 Dependence of T_m upon the PTMEG–T′ content for the samples crystallized at T_c = 30°C. ●, First peak; ○, second peak

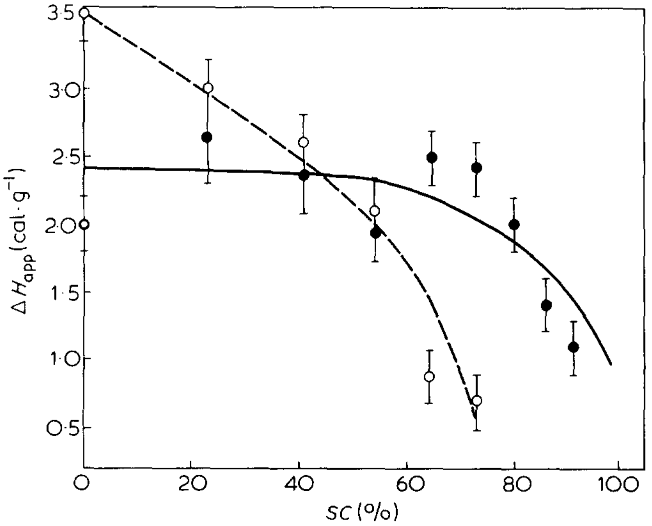

Figure 4 Dependence of ΔH_{app} upon the PTMEG–T′ content for samples crystallized at T_c = 30°C. ●, First peak; ○, second peak

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