Poly(ester amide)-polyether block copolymers: preparation and some physicochemical properties

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A series of elastoplastic copolymers formed of poly(ester amides) and poly(tetramethylenether glycol) segments were synthesized. Some physicochemical properties such as density, melting point, crystallinity and fusion enthalpy were determined. The influence of the structure on the properties is discussed in view of the sequence distribution statistics for finite chain length. The role of molecular weight is specified.

INTRODUCTION

The use of thermoplastic elastomers or elastoplastics, has grown considerably in recent years, with a large amount of research resulting. The peculiar properties of this polymer class arise from the elastic behaviour up to the melt temperature. Above the melt temperature, their flow is typical of non-Newtonian fluids.

These polymers contain no chemical crosslinks. Thus, they can be processed as conventional thermoplastics, lowering production costs.

Generally, elastoplastics are block copolymers with two kinds of blocks. One, the 'soft segment', is amorphous, with a low glass transition temperature, and imparts the elastic behaviour; the other, the 'hard segment', is a chain segment capable of generating intermolecular physical crosslinks to form a thermally reversible network.

These fundamental requisites may be obtained in different ways. The most usual is to enchain a glassy segment (e.g. polystyrene) with an elastomeric segment (e.g. polybutadiene). The glassy segments give rise to a glassy phase embedded in an incompatible, elastomeric phase.

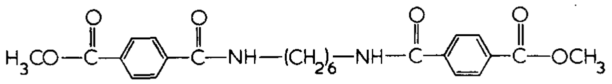
Another method is to enchain crystalline and amorphous segments randomly, via polycondensation. In this case, the crystalline phase is embedded in an incompatible, elastomeric phase. The purpose of this paper is to describe the synthesis and some physicochemical properties of elastoplastic materials obtained by this method, based on regularly alternating, linear poly(esteramide) and poly(tetramethylenether glycol)[1].

EXPERIMENTAL

Polymer synthesis

The copolymers were synthesized by melt polycondensation of:

(i) a biester with preformed amide linkages:



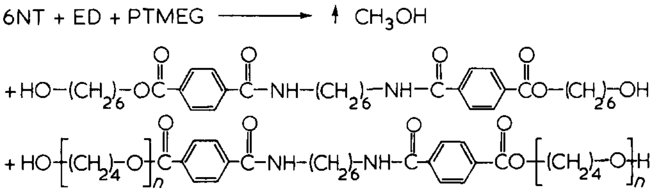
(6NT)

(ii) 1,6 hexanediol (ED); and

(iii) poly(tetramethylenether glycol) (PTMEG) with a molecular weight of 1000.

The synthesis takes place in two steps:

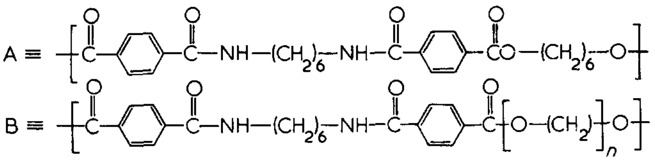
(a) catalysed transesterification of 6NT, ED and PTMEG according to the scheme:



(b) random polycondensation of the diglycol compounds formed in the first step, with removal of hexanediol by distillation *in vacuo* at high temperature. The copolymers have the general formula:

$$(A_{\bar{k}_A} B_{\bar{k}_B})_{\bar{n}}$$

where



$\bar{n}$ indicates the degree of polymerization, $\bar{k}_A$ and $\bar{k}_B$ indicate the average sequence lengths of consecutive A and B units respectively. Both steps (a) and (b) were carried out in a 0.5 l three-necked glass vessel provided with agitating device and nitrogen inflow. The transesterification step was carried out at 240°C and was considered ended when the conversion reached 90% of the theoretical methanol output. The subsequent copolycondensation step was carried out by continuously reducing the residual pressure to a value of 1 torr. At the same time, the temperature was increased to 270°C.

In order to obtain copolymers with different A:B ratios, as shown in *Table 1*, the initial 6NT–PTMEG molar ratios

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Table 1 Experimental data and calculated results

X_A	X_{A_w}	$\rho \times 10^{-3}$ kg m^{-3}	ΔH_m kcal kg^{-1}	T_{m_1} (°C)	T_{m_2} (°C)	Crystallinity content (w_3)		T_f (°C)
						From ρ	From ΔH_m	
0.0	0.0	1.0800	5.7	–	111	0	12.7	–
0.1	0.038	1.0850	2.9 + 4.0	177	113	1.3	6.1 + 8.4	170
0.2	0.083	1.0925	2.4 + 5.3	182	119	4.0	5.3 + 11.4	175
0.4	0.193	1.1105	1.3 + 7.8	205	116	11.4	3 + 17.4	203
0.6	0.350	1.1375	11.8	225	–	21.5	26.0	220
0.8	0.589	1.1820	13.5	249	–	37.7	29.8	231
0.9	0.763	1.2112	14.0	255	–	45.5	34.3	237
1.0	1.000	1.2365	14.1	261	–	41.2	35.0	243

were changed accordingly; X_A and X_{A_w} mean the molar and weight A units fraction.

Density measurements

Density (ρ) was measured by standard density gradient column technique at 25°C using xylene–nitrobenzene or xylene–carbon tetrachloride mixtures. These liquids were chosen because appreciable swelling of the copolymer samples did not occur during measurements.

The values obtained are reported in *Table 1*; no density change between 'as copolymerized' and annealed samples was observed.

Thermal analysis

Differential thermal analysis (d.t.a.) was used to determine the thermodynamic quantities. A 990 Model Du Pont instrument in the d.s.c. version was employed at a heating or cooling rate of 10°C min^{-1}.

The endotherm area peak gives the fusion enthalpy ΔH_m and the endothermal minimum is assumed to be the melting point T_m. The crystallization exotherm gives the incipient crystallization temperature T_f assumed to be the temperature at which the instrument base line begins to change direction. The determined quantities are reported in *Table 1* for different copolymer compositions. For $X_A \leqslant 0.40$ (high PTMEG content), the copolymers show two distinct melting points ($T_{m1} > T_{m2}$) and two exothermal crystallization peaks.

Crystallinity determinations

(i) Density measurements. The copolymer is formed by A and B sequences. Let w_1 be the B sequences' weight fraction, w_2 and w_3 the weight fractions of the amorphous and crystalline phases of the A sequencies, respectively.

The B sequences' density, ρ_1, 1.08×10^3 kg m^{-3}, was obtained by extrapolating the values of copolymer densities at decreasing A units content (*Figure 1*). A units can generate amorphous and crystalline phases with densities[2,3] ρ_2, 1.1875×10^3 kg m^{-3}, and ρ_3, 1.316×10^3 kg m^{-3}, respectively. Once the copolymer density ρ and w_1 are known, w_3 can be determined.

If we assume that the overall copolymer volume is the sum of the components volumes, we have:

$$\frac{1}{\rho} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} + \frac{w_3}{\rho_3} \qquad (1)$$

with:

$$w_1 + w_2 + w_3 = 1 \qquad (2)$$

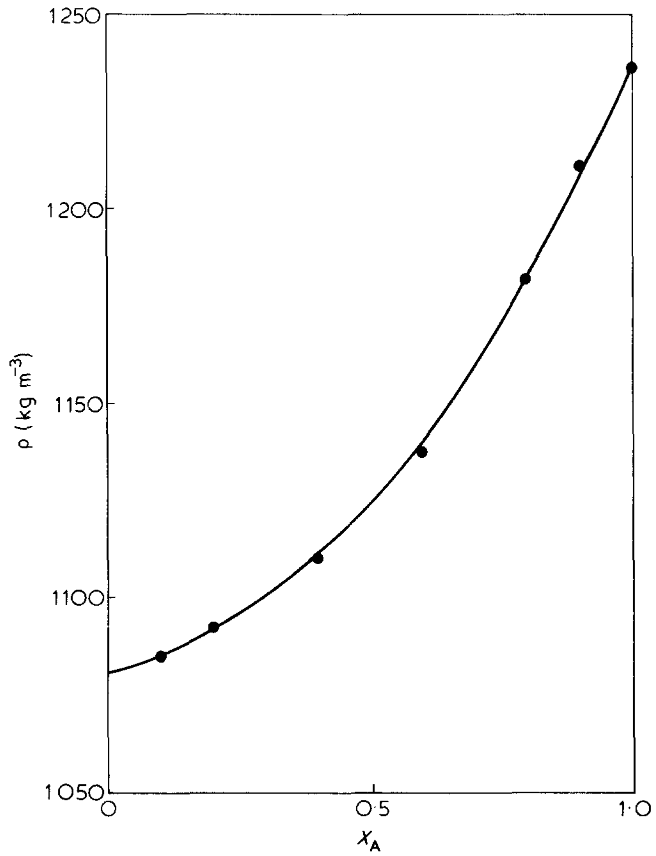


Figure 1 Density *versus* A unit weight content

Combining equations (1) and (2) we obtain:

$$w_3 = \frac{\rho_3}{\rho_3 - \rho_2}\left(\frac{\rho - \rho_2}{\rho} + \frac{\rho_2 - \rho_1}{\rho_1} w_1\right) \qquad (3)$$

which allows determination of w_3 when ρ is obtained experimentally and w_1 deduced from the chemical composition. For $w_1 = 0$, equation (3) becomes the two components formula. *Table 1* reports the calculated w_3 values for different X_A.

(ii) Fusion enthalpy. In order to determine crystallinity from the fusion enthalpy, the crystallinity must belong to the A sequences and the enthalpy of fusion for the crystalline polymer must be known.

It is reasonable to ascribe all the crystallinity to the A sequences, because an eventual crystallinity due to the PTMEG as a constituent of B units should give a melting endotherm (~40°C) far below that observed experimentally (*Table 1*).

The enthalpy of fusion, ΔH_f, of the A sequences has been measured[2] to be 45 kcal kg^{-1}. The crystallinity contents so calculated are reported in *Table 1*.

For copolymers exhibiting two fusion enthalpies, the first number in *Table 1* refers to the fusion enthalpy at the lower temperature.

DISCUSSION

Crystallinity and composition

In *Figure 2*, the crystallinity content is reported as a function of X_A. There are two main differences between d.s.c. and density data: the origin and the shape of the curves.

For $X_A = 0$, the crystallinity deduced from the density passes through the origin as assumed in the model, whereas the crystallinity content obtained via d.s.c. does not. This fact indicates that the B sequences are also capable of giving rise to a crystalline phase.

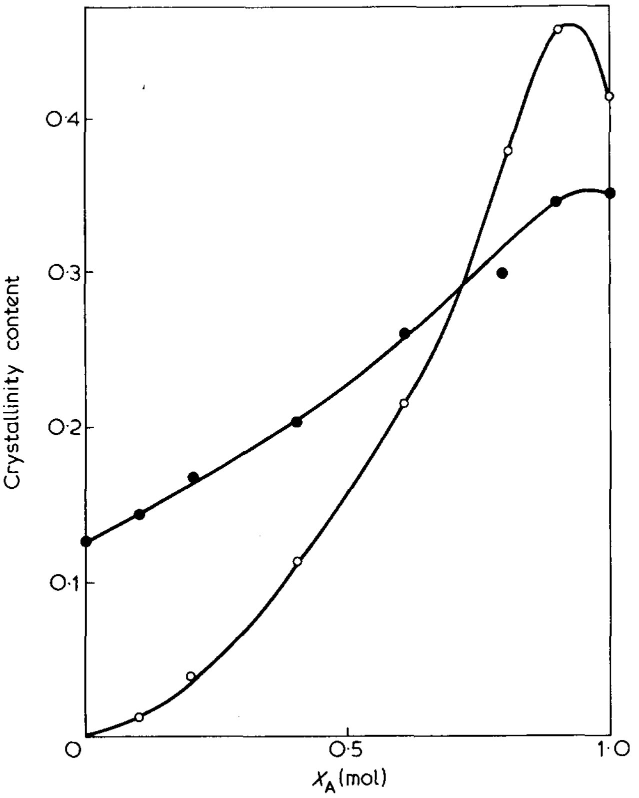


Figure 2 Crystallinity content *versus* A unit molar content. O, from density measurements; ●, from d.s.c.

The second difference is the shape of the curves. This could be due to a variation of the density ρ_1 which gives an average value due to the change of the crystalline–amorphous ratio of the B sequences. Supposing that the crystalline:amorphous ratio changes with the overall composition, i.e. $\rho_1 = \rho_1\,(X_A)$, the different shape of the curves derived from the copolymer density and from d.s.c. can be explained. That ρ_1 is composition dependent is confirmed by X-ray examination[4].

The most interesting feature of the crystallinity observed via d.s.c. lies in the fact that the crystallinity content exceeds the weight content of the A units. We believe that the explanation of this peculiar behaviour can be found by observing how the copolymer is built up (see Scheme I). The B unit can be divided in an A unit and PTMEG, so that the B unit which follows an A unit becomes an extension of the preceding A sequence; and, where there are two or more B units consecutively enchained, isolated A units are present (Scheme II).

By this means, the average length of the A sequences increases by one. The isolated A units derive only from B units, and, during the crystallization, they can join in the neighbouring A sequences or crystallize one to another in the form of clusters. The last process is relevant for high B unit content copolymers.

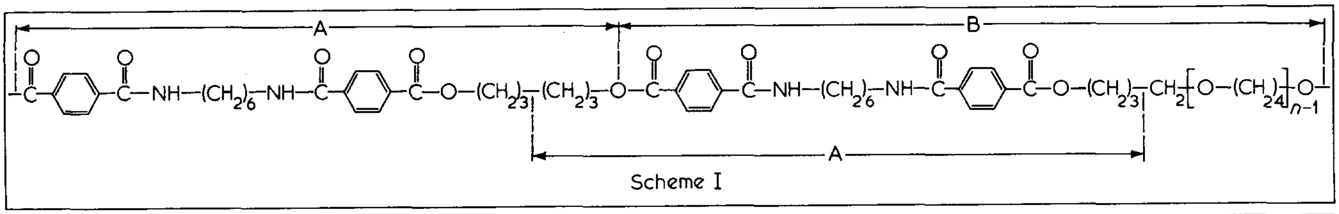
To calculate the overall A units weight content, we use a statistical theory of the block length distribution in copolymers of finite length[5].

In *Figure 3* the overall A units weight content H_T *versus* the initial A units molar fraction is shown. H_T represents the sum between the weight of the A sequences according to Scheme I and the weight (H_1) of the isolated A units according to Scheme (II) for a copolymer with $\bar{M}_n = 20\,000$. For infinite chain length, H_T and H_1 change slightly. The overall A units weight content cannot be less than 35%, well above that found experimentally.

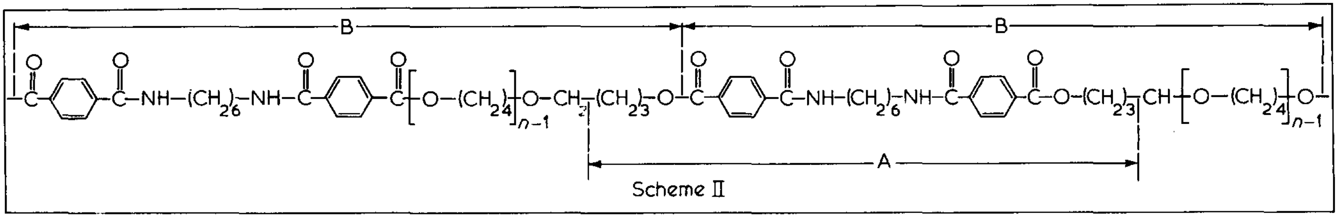
According to what was said above, it should be more realistic to assume that the copolymer is built up with overall A units and PTMEG, especially in the limiting case of $w_1 = 1$ where we have an alternating copolymer.

Melting point and composition

In *Figure 4*, we plot the observed melting points. The copolymers with $X_A \leqslant 0.4$ show two melting points. Those at higher temperatures are composition dependent, while



Scheme I



Scheme II

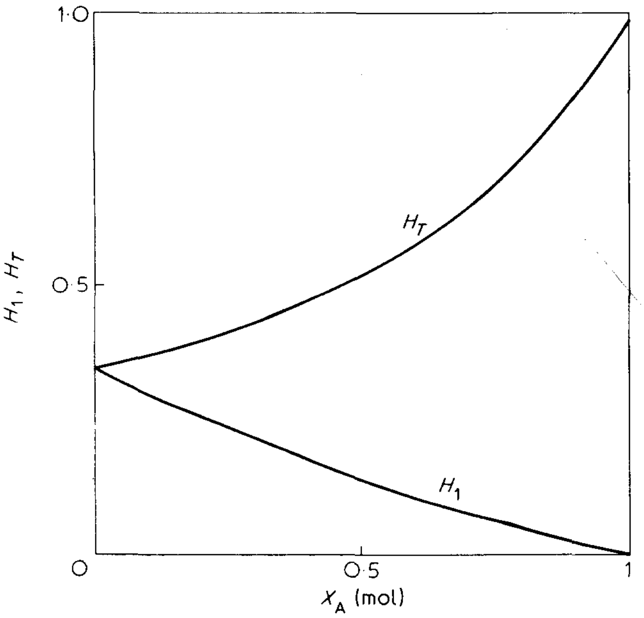


Figure 3 Overall A units weight fraction H_T and isolated A units content H_1 *versus* A units mol content

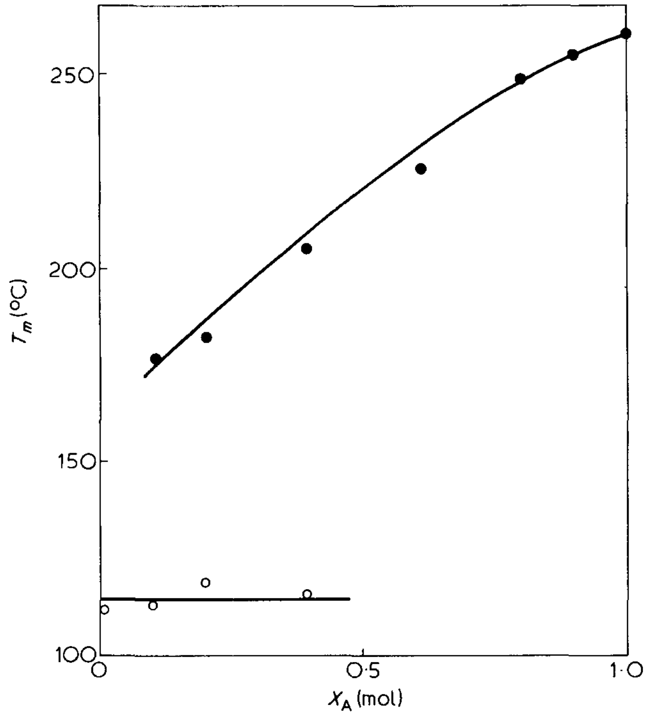


Figure 4 Melting point *versus* A units molar content

those at lower temperatures are not. We can explain this if we remember that crystallinity originates both from A sequences and isolated A units. It is reasonable to ascribe the higher melting point to the A sequences. In the absence of A sequences, the homopolymer, built up by B units, shows only one melting point situated at lower temperatures (see *Figure 4*).

Nevertheless, some isolated A units crystallize together with A sequences, as shown from the melting enthalpy of the endotherms corresponding to higher melting point. The isolated A units probably form crystalline monolayers whose melting temperature is composition independent. When $1/T_{m_1} - 1/T_m^0$ is plotted *versus* ln X_A (*Figure 5*) there is a deviation from the expected straight line by some points, corresponding to low A units content.

Such behaviour can be justified by the observation that the polycondensation material is a mixture of different species. This is particularly relevant in the case of low molecular weights, and with a prevalence of one monomer. In fact, it is possible to obtain the following species[5]:

(i) IT

(ii) $IA_{\bar{k}_A}T$

(iii) $IB_{\bar{k}_B}T$

(iv) $I(A_{\bar{k}_A}B_{\bar{k}_B})_{\bar{n}}T$

where I and T are the initial and the last chain units, $A_{\bar{k}_A}$ and $B_{\bar{k}_B}$ the average lengths of the A and B sequences, and $\bar{n}$ the average degree of polymerization.

For $\bar{M}_n = 20\,000$ and $X_A = 0.1$ (0.2) we have the following weight compositions:

IT = 0.07 (0.06)

$IA_{\bar{k}_A}T = 0.01$ (0.01)

$IB_{\bar{k}_B}T = 0.35$ (0.13)

$T(A_{\bar{k}_A}B_{\bar{k}_B})_{\bar{n}}T = 0.58$ (0.74)

The frequencies of species (iii) and (iv) are similar. The isolated A units situated in the true copolymer macromolecules more likely join in the neighbouring A sequences. The isolated A units, originated by the type (iii) homopolymer, crystallize one another.

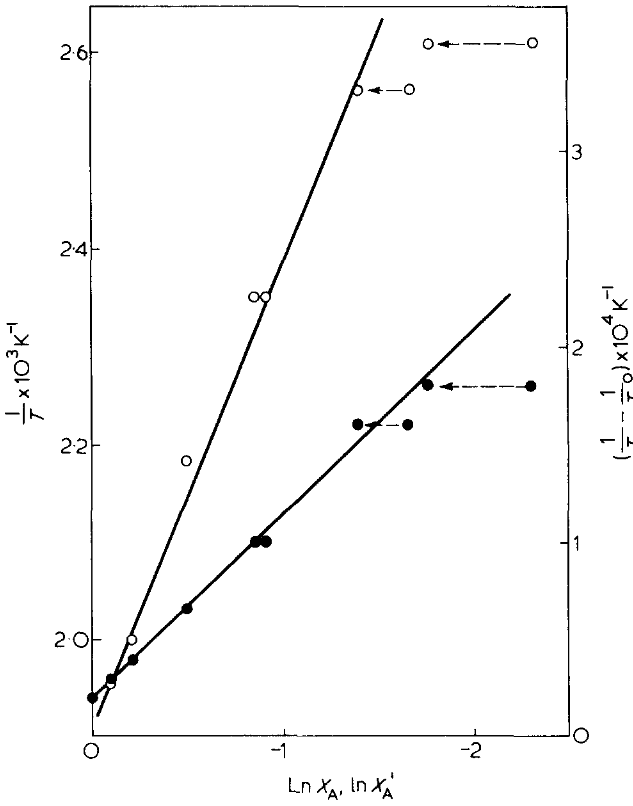


Figure 5 $1/T_m - 1/T_m^0$ (○) or $1/T_f$ (●) *versus* ln X_A. The arrows indicate the shift when X_A is changed to X_A'

As the larger part of the A units builds up species (iv), the true molar composition, X'_A of species (iv) differs from X_{A}. It can be calculated by dividing X_{A} by the frequency of species (iv). By using X'_{A} instead of X_{A}, the situation becomes regular as expected.

To avoid a possible influence of the thermal history, we plot in *Figure 5* $1/T_f$ *versus* ln X_{A}. According to Shih and Cluff[6] this representation must also be a straight line; this also occurs by use of X'_{A} instead of X_{A}.

The slope of the straight line, obtained in the former type of plot, is related to the value of ΔH_f. The value so obtained is 8 500 cal mol.$^{-1}$. This value is significantly lower than that obtained via melting point depression[2] (ΔH_f= 22 200 cal mol^{-1}); however, such a discrepancy is in accordance with the general observations in similar copolymers[7].

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