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Poly(amidoether) Block Copolymers: Synthesis and Characterisation

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Abstract

Random multiblock polyamide-polyether block copolymers were prepared by a two step interfacial polycondensation process from terephthaloyl chloride, 1,6-diaminohexane and α,ω-dihydroxy poly(ethylene glycols) of three different molecular weights. Polymer structure was deduced from the mode of synthesis and infrared spectroscopy. Thermal analysis was used to establish phase separation and to establish that the main crystalline component was a polyamide. X-ray diffraction studies indicated increase in amorphous nature with increase in molecular weight of α,ω-dihydroxy poly(ethylene glycols) with one anomalous situation.

Introduction

Incorporation of flexible elastomeric segments in crystalline polymers like polyamides is one method of overcoming certain disadvantageous properties like crack propagation and low impact strength(1,2). This can be achieved by block copolymerisation. The materials so obtained show improved impact strength, phase separation and reduced crystallinity as compared to the homopolymer(3). These block copolymers are termed poly(amidoethers) and find use as thermoplastic elastomers and in biomedical applications(4). In this paper we report the synthesis of block copolymer compositions where the crystalline polyamide part is provided by terephthaloyl chloride and 1,6-diaminohexane and the elastomeric segment is provided by α,ω-dihydroxy poly(ethylene glycols). The block copolymers so prepared are chemically linked. Structure phase separation and crystallinity of these polymers have been studied.

Experimental

Materials : Terephthaloyl chloride (purum, Fluka Reagent) and 1,6-diaminohexane (Fluka Reagent) were used as received. Dry, alcohol-free chloroform was used for the low temperature polycondensation step. α,ω-dihydroxy poly(ethylene glycol) (PEG) of molecular weights 400, 600 and 1540 were obtained from Fluka and dried over 4A molecular sieves before use.

Analysis : IR analysis was performed on a Perkin-Elmer 681 IR spectrophotometer. Samples were analysed in the form of KBr pellet. Thermal behaviour was determined using a Du Pont 2910 Thermal Analyser. Temperature scale was calibrated against pure reference Indium. Scanning rate was 10°C/min and the temperature range investigated was -100°C to 400°C. X-ray diffractograms were recorded for finely powdered samples on a Phillips PW 1728 model with a PW 1820 diffractometer. The target was Fe and the instrument was operated at 40kV and 30mA.

Typical preparation of a poly(amidoether) block copolymer : To a solution of 2.03 g (10 mmol) terephthaloyl chloride in 25 mL dry, alcohol-free chloroform was added 1.54 g (1 mmol) PEG of $\bar{M}n$ = 1540 and the solution refluxed for two hours at 60°C. After cooling, low temperature polycondensation is carried out by adding the chloroform solution to a chilled solution of 1.05 g (9 mmol) 1,6-diaminohexane and 0.72 g (18 mmol) sodium hydroxide in 50 ml of water with rapid stirring. After 15 min the precipitated polymer was filtered, washed repeatedly with water and dried under vacuum at 80°C.

Results and Discussion

Block copolymerisation carried out to obtain poly(amidoethers) is accomplished by a two-step method(5,6). Three different α,ω-dihydroxy poly(ethylene glycols) [HO(PEG)OH] of molecular weights 400, 600 and 1540 were used to provide the "soft" elastomeric polyether block, by reacting PEG with an excess of terephthaloyl chloride in chloroform solution to prevent chain extension (y > > x) (step 1) :

$$\text{x OH-(-PEG-)-OH} + \text{y ClOC-}C_6H_4\text{-COCl}$$

$$\Big\downarrow \ -2x\ \text{HCl}$$

$$\text{x ClOC-}C_6H_4\text{-COO-(-PEG-)-OCO-}C_6H_4\text{-COCl} + (y-2x)\ \text{ClOC-}C_6H_4\text{-COCl}$$

[I]

(Step 1)

Low temperature polycondensation of the acid chloride end-capped PEG (I) and unreacted terephthaloyl chloride with an aqueous solution containing stoichiometric amount of 1,6-diaminohexane was carried out (step 2):

$$\text{x I} + (y-2x)\ \text{ClOC-}C_6H_4\text{-COCl} + (y-x)\ H_2N\text{-}(CH_2)_6\text{-}NH_2$$

$$\Big\downarrow \ -2x\ \text{HCl}$$

$$\text{-[-CO-R-COO-PEG-OCO-R-CO-(-NH-}(CH_2)_6\text{-NHCO-R-CO-)}_n\text{-NH-}(CH_2)_6\text{-NH-]}_m\text{-}$$

$R=C_6H_4$

(Step 2)

The block copolymers are obtained directly as white flocculant precipitates of high molecular weights: oligomers and ionic products are dissolved in chloroform and water respectively. The homopolymer poly(hexamethylene terephthalamide) could not be isolated as the solubility characteristics of the homopolymer and block copolymer are similar. The three block copolymers are designated as PAE 400, PAE 600 and PAE 1540 based on the molecular weight of the polyether segment.

The copolymer structure deduced from the mode of synthesis (step 2) is of the random multiblock type, $(AB)_n$ assuming that terephthaloyl chloride and oligomer (I) show similar reactivity towards 1,6-diaminohexane and that chain extension with 1,6-diaminohexane proceeds easily. The polyether blocks are monodisperse while the polyamide blocks, due to experimental conditions, are polydisperse. The two blocks are linked together by ester groups. Besides this, IR also give an indication of block copolymer formation. Formation of the oligomer [I] is followed by IR spectroscopy and is indicated by the disappearance of the hydroxyl absorption band at 3400 cm^{-1} and the presence of bands at 1720 and 1760 cm^{-1} due to carbonyl absorption of acid chloride. The IR spectra of block copolymers show characteristic absorptions of hydrogen-bonded amide groups at 3310, 1640, 1530 and 1300 cm^{-1}. The band at 1720 cm^{-1} could be attributed to the ester linkage formed between the two heterotype blocks. A broad band centered around 1110 cm^{-1} can be attributed to the ethereal C-O-C antisymmetric stretch(7).

Thermal analysis data is reported in Table 1. DSC measurements show two endotherms in all the copolymers. The first, observed at sub-ambient temperatures can be attributed to the polyether phase(8). The second endotherm is observed above 300 °C and can be attributed to the polyamide phase. The observed Tm lies close to that of the homopolymer(9).

Table 1 : Thermal analysis data of copolymers

Code	T_g(°C)	T_m(°C)	H_m (J/g)
PAE 1	-36.39	323.55	157.00
PAE 2	-56.39	312.50	143.20
PAE 3	-61.21	307.35	89.08

Glass transition values lying close to that of polyether homopolymer indicate that the segmental mobility of polyether in the block and homopolymer is similar. This is also indicative of the presence of a segregated polyether phase. As expected, the glass transition value is seen to decrease with increasing molecular weight of the polyether block. Melting temperatures lying close to that of polyamide homopolymer indicate that the polyamide component in the block copolymer exists in a segregated phase. Additionally, depression of melting point is seen with increasing molecular weight of the polyether block. The observed depression in melting points is related to the crystallite dimensions which is determined by the length of polyamide segments. The T_g of the polyether segment and T_m of the polyamide segment are not significantly influenced by the existence of polyether segments in the block copolymer, indicating the presence of a distinct phase separation between the polyether and polyamide segments(10). From the data in Table 1 it is seen that the apparent heat of fusion decreases as the polyether molecular weight increases. This indicates increasing amorphous content in the block copolymer with increasing polyether molecular weight.

The WAXD pattern of the PAE 3 block copolymer is shown in Fig 1. For all the block copolymers, characteristic scattering angles are obtained at 21.87, 31.58, 34.87, 40.24 and 58.11. Since the polyamide component is phase segregated,

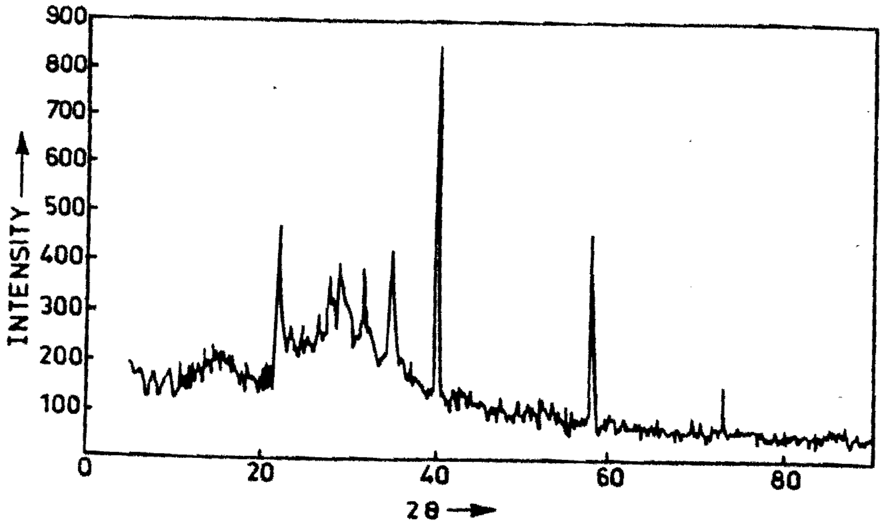

Fig 1 : Intensity of X-ray diffraction (in arbitrary units) vs. angle 2θ (in degrees) for block copolymer PAE 3

the polyamide block length in the copolymer should give the crystalline packing observed in the polyamide homopolymer. This evidence is supported by diffraction angles that do not change with the composition. From the DSC data it can be observed that the molecular weight of the polyether affects some of the properties which arise due to the polyamide phase. Increasing molecular weight and hence greater polyether content affects the packing of the polyamide segment and hence the ability to crystallize. % crystallinity data reported in Table 2 is however, ambiguous and does not show the expected trend, namely, decreased crystallinity with increasing polyether molecular weight.

Table 2 : Percentage crystallinity of block copolymers

Code	Molecular weight of PEG	% crystallinity
PAE 1	400	29.87
PAE 2	600	24.79
PAE 3	1540	27.69

Crystallinity decrease is related to the reduced size of the polyamide block, resulting in difficulty in packing polyamide sequences diluted by polyether blocks. This factor in conjunction with DSC data was expected to cause minimum crystallinity in PAE 3. However, this is not observed.

In conclusion, it was found that block copolymers could be easily prepared by a two step interfacial polycondensation method. The copolymers so prepared showed characteristic IR absorptions indicating block copolymerisation. Support for a phase segregated structure came from thermal analysis which indicated both the segregation of the polyamide and polyether phases as well as the effect of increasing polyether molecular weight in the block copolymers. Further evidence was sought from XRD. However, due to the anomalous behaviour of PAE 3, confirmation for a biphasic structure for the polyamide-polyether block copolymers should await electron microscopic studies which are currently in progress.

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