Synthesis and physical behaviour of poly(amidoether) block copolymers

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Random multiblock polyamide–polyether copolymers containing 13–30 wt% of polyether have been synthesized by a two-step procedure from adipoyl chloride, 1,6-diaminohexane and two α,ω-dihydroxy-poly(ethylene oxides) having $\bar{M}_n = 600$ and $1550\,\mathrm{g\,mol^{-1}}$. The compositions and architectures of the copolymers were determined by elemental analysis and by ^{1}H nuclear magnetic resonance spectroscopy. Thermal analysis showed the presence of a main crystalline component that thermal parameters indicated as polyamidic. Transport properties were analysed using water vapour as permeant; they indicated a permeability much higher than in polyamide-6,6 and suggested the presence in the amorphous component of a domain structure in which polyether volume elements are segregated from a polyamide matrix. Thermomechanical and dynamic mechanical analyses suggested that flexible polyether sequences increase the overall flexibility of the copolymer chains.

(Keywords: poly(amidoethers); block copolymers; poly(ethylene oxide); polyamide; transport properties)

INTRODUCTION

Some typical features of aliphatic polyamides, such as dyeability and hydrophilic and antistatic properties, have been modified by introducing polyether sequences along the polyamide chain[1–7]. Moreover poly(amidoether) block copolymers have recently been suggested as technopolymers of the class of thermoplastic elastomers[8] and as functional materials for medical uses[9,10]. In this paper we report on the synthesis and physical properties of a series of polyamide-6,6/poly(oxyethylene) multiblock copolymers differing in composition and/or size of the polyether blocks. Their physical behaviour was analysed using different techniques, in order to obtain a full picture of the relationships between chemical structure and physical behaviour. In particular, two aspects have been investigated. The first is concerned with the effect of the poly(oxyethylene) blocks on chain flexibility, on the crystallization phenomena and on the microstructure of the amorphous component; the second with the influence of the hydrophilic sequences on permeability to water vapour and the effects of water content on the properties.

The properties of aliphatic polyamides are greatly affected by the presence of water and the insertion of polyether hydrophilic blocks increases the permeability to water vapour, thus probably giving rise to a closer dependence of the properties on water content. Therefore, the analysis of the sorption and diffusion parameters that describe the water transport phenomenon is an important tool in obtaining information on the structure–properties relationships. Moreover, considering that in a semicrystalline polymer the permeant molecules diffuse in the amorphous component only, the transport parameters can be correlated mainly with the microstructure and the thermodynamic state of the amorphous component.

Preliminary results on the synthesis and chemical characterization of the poly(amidoethers) investigated have already been published[11].

EXPERIMENTAL

Materials

Poly(ethylene oxides) (PEO), $\bar{M}_n = 600$ and 1550 (Merck Reagents), were dried by distillation of the water–benzene azeotrope from their benzene solutions and by evaporating the residual solvent. The recovered products were stored in a dry atmosphere. Adipoyl chloride was prepared by refluxing adipic acid with a two-fold excess of thionyl chloride and the crude product was purified by distillation and stored under nitrogen. Hexamethylenediamine (HMD) (Fluka Reagent) was used without further purification.

Techniques

I.r. analysis was performed on thin films obtained by evaporating chloroform/formic acid solutions of the copolymers and the spectra were recorded on a Perkin–Elmer 276 IR spectrophotometer.

^{1}H n.m.r. analysis was carried out on a Bruker 270 MHz spectrometer. $\mathrm{CDCl_3}$ was used as solvent and TMS as internal reference.

The thermal behaviour was analysed using a Perkin–Elmer DSC 2 differential scanning calorimeter. The temperature scale was calibrated against pure reference

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samples. The scanning rate was 10°C min^{-1} and the temperature range was -30°C to $+300$°C. The melting enthalpies were measured using a pure indium sample for the calibration. For each sample two curves were detected: the first on the powder as obtained by the synthesis and the second on the same sample after fast cooling from the melt.

The linear dilatometric behaviour of the samples was investigated in a wide temperature range by a Perkin–Elmer TMS-1 apparatus. The instrument gives the relative change in length $\Delta L/L_0$ as a function of the temperature or as a function of the time at constant temperature.

Dynamic mechanical investigation was carried out using the Viscoelastometer Rheovibron of Toyo Instruments. The temperature range was -100°C to $+140$°C, and the working frequency was 110 Hz.

The transport parameters were obtained using a microgravimetric method. The microbalance used is calibrated quartz spring and the sample weight was detected as a function of time. Such a procedure gives the equilibrium concentration of the permeant in the sample and the diffusion coefficient according to the method described in a previous paper[12].

Typical preparation of a poly(amidoether) block copolymer

PEO of $\bar{M}_n = 1550$, 0.931 g (0.60 mmol), was added to a solution of adipoyl chloride, 4.58 g (25.0 mmol), in 10 cm^3 of dry, alcohol-free chloroform. The reaction mixture was stirred at 60°C for 2 h, cooled to room temperature, diluted with 50 cm^3 of chloroform and rapidly added under vigorous stirring to an ice-cooled solution of 2.83 g (24.4 mmol) of HMD and 1.95 g (48.8 mmol) of sodium hydroxide in 625 cm^3 of water. After 10 min the precipitate was collected, washed repeatedly with distilled water and dried at 50°C in a vacuum oven for 24 h (3.54 g, 56% yield based on acid chloride).

SYNTHESIS AND CHARACTERIZATION

The preparation of the block copolymers was accomplished by means of a two-step method comprising a step copolymerization between suitable reactants, one of which is an oligomer. Two different α,ω-dihydroxy-poly(oxyethylenes), HO(PEO)OH, having number-average molecular weights of 600 and 1550 g mol^{-1}, respectively, were used to build up the polyether blocks. First their hydroxy end groups were converted into acid chloride groups by reaction with a large excess of adipoyl dichloride at 60°C either in bulk or in chloroform solution (*Scheme 1*):

$$x\,\text{HO}\!\left\{\text{PEO}\right\}\!\text{OH} + 2x\,\text{ClOC}-(\text{CH}_2)_4-\text{COCl}$$

$$x\,\text{ClOC}-(\text{CH}_2)_4-\text{COO}\!\left\{\text{PEO}\right\}\!\text{OCO}-(\text{CH}_2)_4-\text{COCl} + 2x\,\text{HCl}$$

(I)

Scheme 1

Chain extension is not expected in this step owing to the large excess of acid chloride. The reaction mixture, containing the acid chloride end-capped polyether (**I**) and the unreacted adipoyl dichloride, was subsequently used in a low-temperature polycondensation step with the stoichiometric amount of 1,6-diaminohexane (HMD) (*Scheme 2*):

$$x\,(\text{I}) + y\,\text{ClCO}-(\text{CH}_2)_4-\text{COCl} + (y+x)\,\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2 \rightarrow 2(y+x)\,\text{HCl}$$

$$+ \left\{\text{OC}-(\text{CH}_2)_4-\text{COO}\!\left\{\text{PEO}\right\}\!\text{OCO}-(\text{CH}_2)_4-\right.$$

$$\left.\text{CO}\left[\text{NH}-(\text{CH}_2)_6-\text{NHCO}-(\text{CH}_2)_4-\text{CO}\right]_n\text{NH}-(\text{CH}_2)_6-\text{NH}\right\}_m$$

Scheme 2

This step was carried out by adding a chloroform solution of the reaction mixture to a chloroform solution of HMD or, alternatively, to a vigorously stirred aqueous solution of HMD[13,14].

Triethylamine and sodium hydroxide were used, respectively, as hydrogen chloride acceptors. The interfacial technique proved more satisfactory because it yields block copolymers of higher molecular weights directly as a white and flocculent precipitate, while oligomers and ionic products are dissolved in chloroform and water respectively.

Contamination of the recovered copolymers by unreacted PEO could be excluded on the basis of benzene extractions of the crude products, which yielded less than 1 wt% of a soluble fraction mainly consisting of PEO and PEO-rich oligomers. Attempts to show the presence of pure polyamide-6,6 (PA66) in the investigated copolymers by appropriate fractional precipitation techniques were unsuccessful possibly because of the fact that the solubility characteristics of PA66 and of poly(amidoethers) are very similar. The preparation of representative copolymers is summarized in *Table 1*.

The two series of poly(amidoethers) are indicated as CEA 600 and CEA 1550 according to the molecular weight of the PEO used. Slightly higher inherent viscosities were obtained with the copolymers of the CEA 1550 series. A rough estimation of the molecular weight range was obtained by determining the intrinsic viscosities of the CEA-2, CEA-3 and CEA-4 copolymers at 25°C using as solvent a 2.30 M potassium chloride solution in 90% formic acid and by using the relation: $[\eta] = 22.4 \times 10^{-4} M_v^{0.50}$ reported in the literature[15] for PA66. The molecular weights found were in the range of $(2\text{–}5) \times 10^4$ g mol^{-1}.

The copolymer architecture, expected on the basis of *Scheme 2*, is of a random multiblock type $(\text{AB})_n$ provided that adipoyl dichloride and the oligomers (**I**) have similar reactivities towards HMD and that the chain extension with HMD proceeds readily[16]. These requirements appear to have been met in our experiment. In fact, both the high-viscosity values obtained and the incorporation of significant amounts of PEO blocks in the copolymer chains are an indication of that. The polyether blocks are obviously almost monodisperse while the polyamide blocks are polydisperse. The two heterotype blocks are linked by ester groups.

The i.r. spectra of the poly(amidoethers) show characteristic absorptions[17] of hydrogen-bonded amide groups at 1645, 1540 and 695 cm^{-1} and of the $-\text{CH}_2-\text{O}-\text{CH}_2-$ groups at 1100 cm^{-1}. An additional band at 1730 cm^{-1}, attributable to the C=O stretching of ester groups, was also present in the spectrum of all the prepared poly(amidoethers). The relative intensity of the latter absorption, which is proportional to the mole fraction of ester linkages, increases as the weight percentage of PEO in both the CEA 600 and the CEA

Table 1 Preparation of polyamide–polyether block copolymers by low-temperature stirred interfacial polycondensation

Copolymer code	$\bar{M}_n$ (PEO)	X (mmol PEO)	$Y+2X$ (mmol acid chloride)	$Y+X$ (mmol HMD)	Yield (%)	η_{inh}^{a} (dl g^{-1})	PEO (wt%) Calc.[b]	PEO (wt%) Found[c]	Elemental analysis C	Elemental analysis H	Elemental analysis N
CEA 1	600	0.70	25.0	24.3	62	1.32	7	13	61.89	9.66	10.73
CEA 2	600	1.50	25.0	23.5	58	1.31	14	19	61.34	9.64	10.05
CEA 3	600	2.40	25.0	22.0	57	1.24	22	30	60.34	9.60	8.68
CEA 4	1550	0.30	25.0	24.7	58	1.73	8	13	61.98	9.77	10.67
CEA 5	1550	0.60	25.0	24.4	56	1.53	14	19	61.27	9.68	9.83
CEA 6	1550	1.00	25.0	24.0	55	1.56	21	29	60.44	9.59	8.57

[a] Inherent viscosity in *m*-cresol at 25°C ($c=05$ g dl^{-1})
[b] PEO (wt%) as calculated from the stoichiometric ratios X and Y
[c] PEO (wt%) as found by ^{1}H n.m.r. analysis

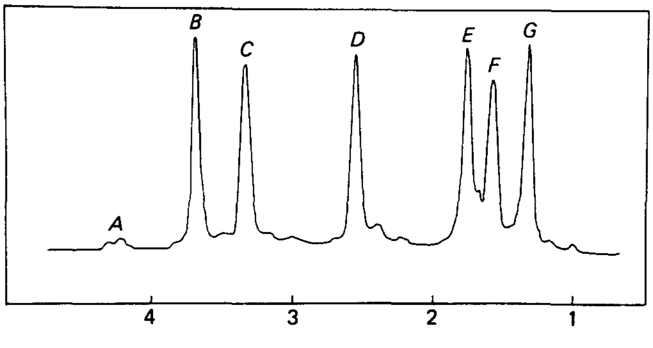

Figure 1 ^{1}H n.m.r. spectrum of CEA 5 copolymer in $CDCl_3$. Resonance assignment: (*A*) near end $-CH_2-O-$; (*B*) $-CH_2-O-$; (*C*) $-\underline{CH}_2-NH-$; (*D*) $-CH_2CO-$; (*E*) $-\underline{CH}_2-CH_2-NH-$; (*F*) $-\underline{CH}_2-CH_2-CO-$; (*G*) $-\underline{CH}_2-CH_2-CH_2-NH-$

1550 series increases. These results and the ^{1}H n.m.r. spectra are consistent with the proposed $(AB)_n$ architecture. By way of example, the 270 MHz ^{1}H n.m.r. spectrum of the CEA-5 copolymer is reported in *Figure 1* together with the resonance assignments. All the methylene hydrogen resonances appear as well separated singlets. The weight fraction of PEO was calculated from the integral intensities (*A*) and (*B*) of $-CH_2-O-$ and (*D*) of $-CH_2-CO-$ resonances as follows:

$$\text{PEO (wt\%)} = \frac{44(A+B)}{44(A+B)+226D}$$

where 44 and 226 are the molecular weights of the polyether and polyamide chain repeat units, respectively. The chemical composition values as obtained by n.m.r. spectroscopy are in good agreement with the elemental analyses (see *Table 1*).

The thermal data obtained by differential scanning calorimetry are reported in *Table 2*. All the copolymers show a main first-order transition having a maximum at 254°C–258°C, i.e. at a temperature slightly lower than the melting temperature of PA66 (263°C). The CEA 600 copolymers also show a shoulder at 247°C–249°C. The two maxima observed in their melting endotherm could be attributed to the presence of crystals of different size or perfection. No first-order transition could be observed in the melting range of the PEOs used in the first run while in the second run the thermograms of the 1550 copolymer series and of the CEA-3 sample showed a very small endotherm in the range 0°C–30°C, attributable to a PEO crystalline phase. The values of the apparent melting enthalpies of the main transition, referred to the polyamide blocks, are quite similar to that of PA66 with the exception of the CEA 3 sample. This effect is enhanced in the second melting run and is probably related to the presence in CEA 3 of short polyamide sequences deriving from the high content of short PEO sequences that increase the molecular disorder. The thermal data clearly indicate therefore that the main crystalline component consists of polyamide blocks and that their crystallization is not heavily affected by the presence of the PEO blocks, provided that the average size of the PA66 segments is sufficiently large.

Table 2 Thermal data of the prepared poly(amidoethers) and of polyamide-6,6

Sample	First run T_{m1} (°C)	First run ΔH_1 (cal g^{-1})	Second run T_{m2} (°C)	Second run ΔH_2 (cal g^{-1})
CEA 1	247; 258	14.2	246; 257	11.8
CEA 2	249; 258	14.2	250; 257	11.1
CEA 3	249; 257	11.6	253; 257	8.8
CEA 4	258	14.6	256	15.7
CEA 5	258	14.0	255	13.6
CEA 6	256	14.3	254	12.9
PA66	263	14.8	260	12.5

PHYSICAL PROPERTIES

Transport phenomena analysis

The transport parameters were obtained using the microgravimetric method that gives the diffusion coefficient D and the equilibrium concentration C_{eq} of the permeant in the bulk polymer. D and C_{eq} can be obtained as a function of the vapour activity defined as P/P_0, where P is the acutal vapour pressure and P_0 is the pressure of the saturated vapour at the temperature at which the sorption is carried out (25°C). A more detailed description of the method and a detailed definition of the transport parameters are reported in previous papers[12,17]. In *Figures 2* and *3*, C_{eq} is reported as a function of the vapour activity for the samples of *Table 1*. C_{eq} values observed at $P/P_0=0.4$ are reported in *Figure 4* as a function of the poly(oxyethylene) content for the CEA 600 and CEA 1550 samples. In *Figures 5* and *6*, the diffusion data are shown as a function of the equilibrium concentration; extrapolating to $C_{eq}=0$, the D_0 values can be obtained. D_0 is the diffusion coefficient, which is not affected by the permeant concentration and is directly related to the structural organization in the permeated sample[17].

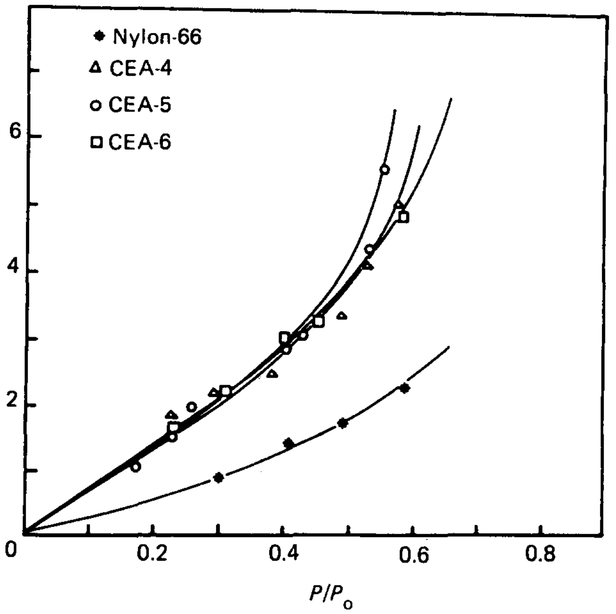

Figure 2 Equilibrium concentration of the permeant (reported as g/100 g of polymer) as a function of vapour activity for CEA 1550 copolymers and PA66

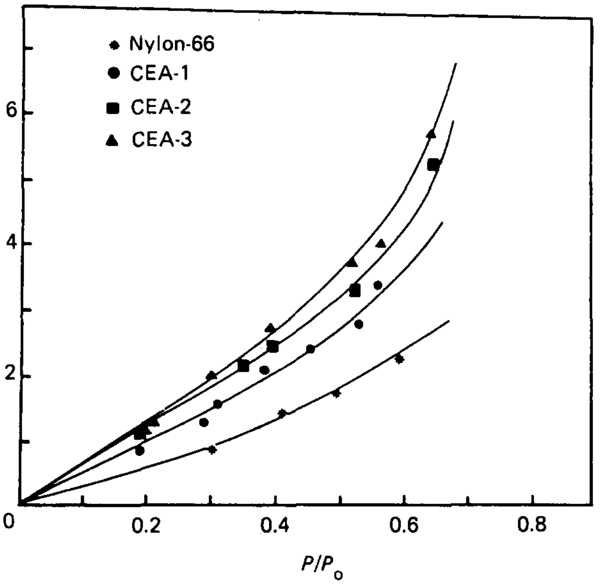

Figure 3 Equilibrium concentration of the permeant (reported as g/100 g of polymer) as a function of vapour activity for CEA 600 copolymers and PA66

In *Figure 7*, D_0 is reported as a function of the poly(oxyethylene) content for the CEA 600 and CEA 1550 copolymers.

Thermomechanical and dynamic mechanical analyses

The thermomechanical and dynamic mechanical analyses were carried out with the purpose of obtaining data on the glass transition, T_g, which is directly related to the overall chain flexibility and to the microstructural organization of the amorphous component. In the case of block copolymers, T_g can give an indication of the possible presence of phase segregation. In the samples examined the existence of a biphasic amorphous component may indeed be a consequence of the block-like nature of the copolymer and of the different chemical nature, in terms of composition and polarity, of the polyamide and polyether sequences. However, the thermomechanical and dynamic mechanical data were affected by the marked tendency of the samples analysed to sorb and desorb water under the experimental conditions of the analyses. In *Figure 8* the effect of water vapour on the thermomechanical analyses is clearly seen for the CEA-6 copolymers. The relative change in length as a function of time is reported at constant temperature (25°C), changing the tension on the sample as well as the humidity in the cell. By using nitrogen alternatively dry or saturated with water vapour, a marked variation of the sample length was observed as a

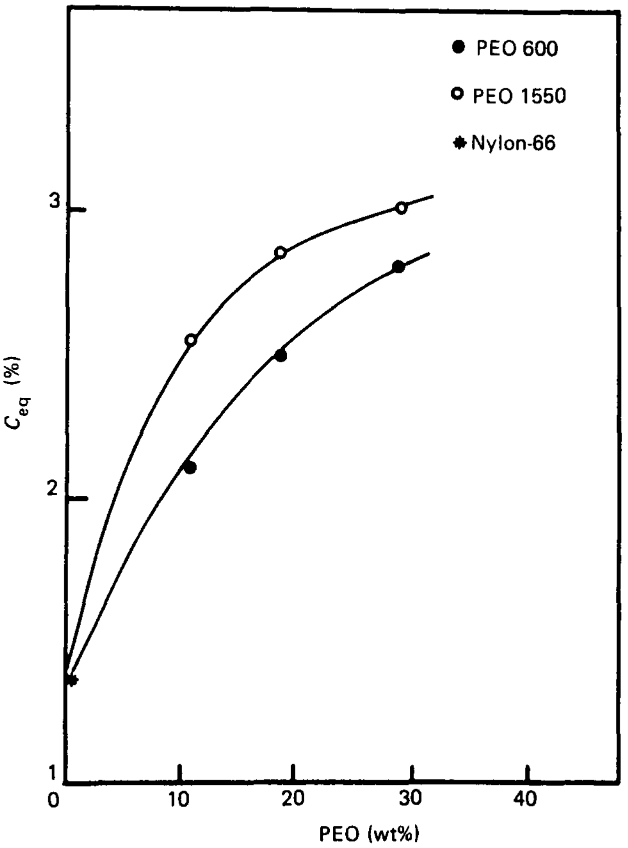

Figure 4 Influence of the PEO content on the equilibrium concentration of the permeant (wt%) detected at $P/P_0 = 0.4$

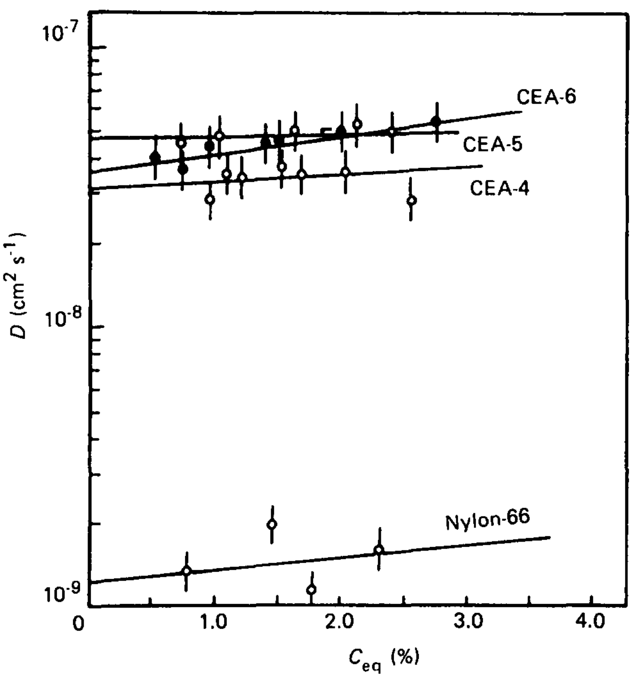

Figure 5 Influence of the permeant equilibrium concentration on the diffusion coefficient of CEA 600 copolymers and of PA66

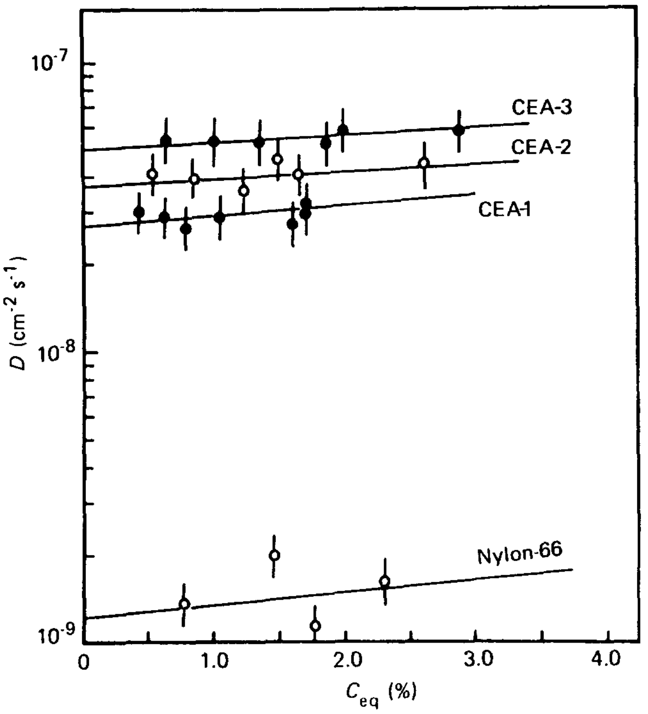

Figure 6 Influence of the permeant equilibrium concentration on the diffusion coefficient of CEA 1550 copolymers and of PA66

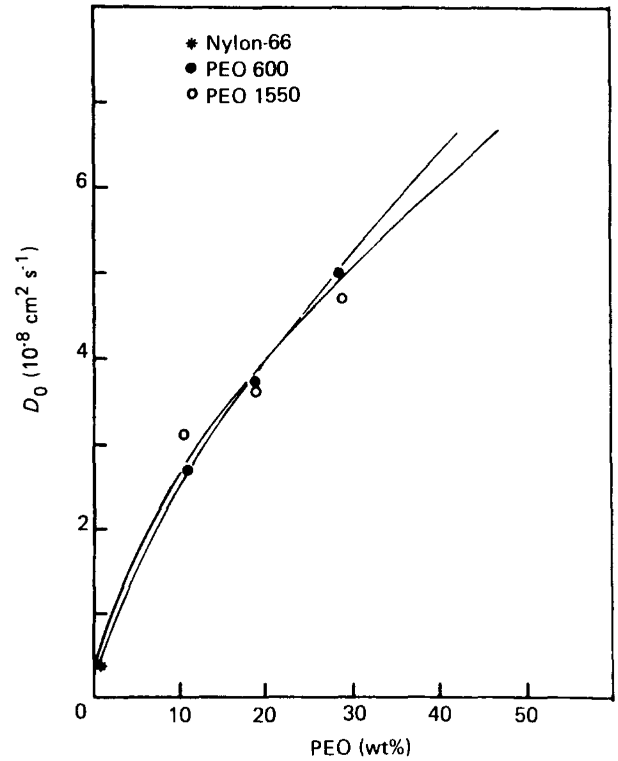

Figure 7 Dependence of D_0 (value of D at $C_{eq}=0$) as obtained from *Figures 5* and *6* on the PEO content

consequence of sorption and desorption phenomena, and a marked creep behaviour under the applied tension was also superimposed.

These perturbing phenomena made it impossible to obtain reliable values of the glass transition from the thermomechanical data. As a matter of fact, only by using a very high flow of the thermostating dry nitrogen can the influence of water be made to disappear, but of course then the temperature control drops to a level no longer acceptable.

In *Figure 9* we report for comparison purposes the dynamic mechanical data obtained on the CEA 1550 samples and on a PA66 sample. The modulus E^* decreases with temperature and, at each temperature, with PEO content. In the case of PA66, a variation in the slope at about 80°C is observed and this temperature can be identified as the glass transition or rather as the incipient glass transition, in good agreement with the literature data[19]. The block copolymers show a shift of this temperature to lower values, the shift being more significant in the samples of higher PEO content. Moreover, the poly(amidoether) samples show a relative minimum at about 40°C, while in the temperature range 50°C–80°C the modulus E^* increases as the temperature increases and then at $T=80°C$ starts to decrease as the temperature increases. This peculiar behaviour is again related to the presence of water in the samples, which starts to be desorbed at about 40°C, giving rise to the relative minimum followed by the relative maximum due to the end of the desorption phenomenon. Unfortunately, these phenomena make the data on the loss factor, tan δ, unreliable; together with E^*, this is generally given by the dynamic mechanical analysis. Therefore tan δ is not reported in the figure. However, in spite of the disturbing effects, the dynamic data give a basis for some qualitative evaluation at the structural level.

DISCUSSION

The values of the diffusion coefficient D_0 of the

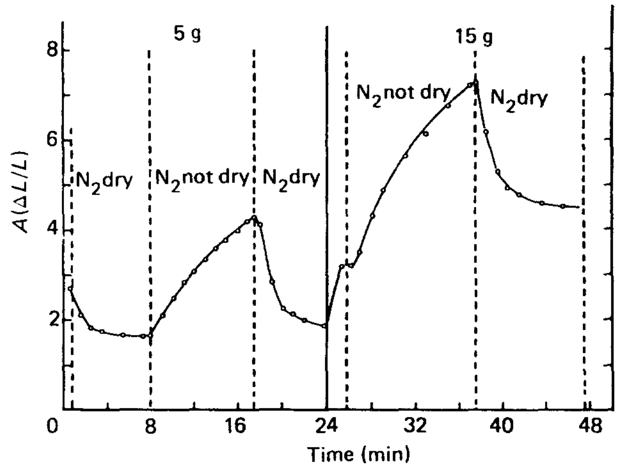

Figure 8 Relative variation of sample length at 25°C as function of time for CEA 6 copolymers under different humidity conditions; 5 g and 15 g indicate the weight applied on the sample section; A is a constant (1.85×10^3) that depends on the instrument calibration

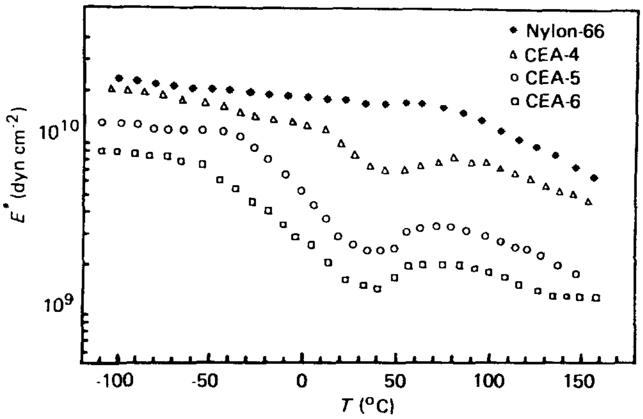

Figure 9 Dependence of the complex modulus, as obtained from the dynamic mechanical analysis, on the temperature for PA66 and CEA 1550 copolymers

copolymers are much higher than the corresponding value of PA66 (see *Figure 7*). This effect, which is independent of the molecular weight of the polyether blocks, shows the dramatic influence of poly(oxyethylene) sequences on the water sorption rate. Moreover, it is evident that the increase is higher when the PEO content passes from 0% to 10%, while a further increase of PEO content up to 30% produces a relatively weaker effect on D_0. For many aspects, similar results were obtained in the study of the equilibrium concentration of the permeant (see *Figure 4*). As a matter of fact, the main effect is the increase of C_{eq} as the PEO content increases, and this is again more marked in the case of samples containing 10% of PEO. The sharp change of the transport parameters in the range of low PEO concentrations is confirmed by results obtained on other poly(amidoethers) prepared by a different route and containing 3–4% of PEO, from which emerge D_0 and C_{eq} values close to those found[20] for PA66. Unlike D_0, the C_{eq} parameter depends on the PEO molecular weight since, at a given PEO content, the observed C_{eq} is higher for copolymers having longer polyether sequences. This effect, although not very relevant, may be of some interest in terms of microstructural organization. More generally, the whole of the observed transport phenomena may yield some qualtitative information on the microstructure of the amorphous component. We suggest that in the range of 0–10% of PEO content, and very likely for contents higher than 3–4%, some microstructural transition could take place in the amorphous component. In particular, assuming the possibility of phase segregation, a critical PEO concentration value at which segregation takes place or segregated polyether phase becomes continuous might be present in the lower PEO content range. The appearance of segregated, probably continuous, polyether domains could determine the formation of a preferential, even though random, path for the water permeant molecules and consequently the presence of a sharp increase of the transport parameters. The influence of block size on C_{eq} is more difficult to explain. However, we can assume that the water concentration is not homogeneously distributed in the sample, and this means that in the more hydrophilic domains the water concentration is higher. The larger swelling of the hydrophilic domains results in a mechanical pressure on the surrounding, less permeable phase; therefore C_{eq} depends not only on the thermodynamic parameters but also on mechanical constraints. Different domain sizes give rise to different volume/surface ratios, and therefore to different values of the hydrostatic forces on the interphase surface thus affecting the equilibrium swelling. Therefore, the overall indication that can be inferred at the qualitative level is that domain segregation takes place and that longer polyether sequences seem to give rise to a larger size of the segregated domains. The hypothesis of domain segregation seems to be supported by the appearance of a weak PEO melting endotherm in the case of some copolymers. It is important to point out that more certain conclusions require further, more thorough and direct structural investigations. The results of the dynamic mechanical analysis add some other elements to the overall picture of the structure–properties relationships. In fact, the presence of PEO sequences decreases the modulus values as well as the temperature at which the sharper modulus temperature dependence appears with respect to PA66 (see *Figure 9*). This temperature can be identified as the lower value of the glass transition temperature range. The copolymer behaviour can be explained on the basis of the presence of flexible polyether sequences. However, it is important to point out that the observed shift of the glass transition temperature, which is about 130°C comparing PA66 and CEA 3, is strongly amplified by the presence of water, which increases as the PEO content increases as demonstrated by the transport data. Water plays the role of a plastifying component and this means that the observed shift is the result of both the presence of flexible polyether sequences and of water.

The loss factor tan δ could be used to investigate more thoroughly the glass transition mechanism and the organization of the amorphous component. In particular the presence of a domain structure might be identified by the trend of the loss factor[18]. Unfortunately, the phenomena of water sorption and desorption that give rise to the observed trend in the modulus spectrum as reported greatly disturb the tan δ data. Our dynamic mechanical data may therefore give only qualitative information on the higher overall flexibility of the copolymer chains, if compared with the PA66 chains. Work is in progress to obtain mechanical data in dry conditions on dry samples or in the presence of a controlled water content, with the aim to support the polyphasic structure suggested by the thermal and transport data.

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