Segmented block copolymers based on polyamide-4,6 and poly(propylene oxide)

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(*Received 26 May 1989; accepted 17 July 1989*)

Segmented copolymers were obtained through copolymerization of polyamide-4,6 and poly(propylene oxide) (PPOx). An amine-terminated PPOx ('soft') segment of molar mass 430 was reacted with nylon-4,6 salt in an autoclave (30 min, 210°C, 7 bar). In this reaction a prepolymer was prepared, which was postcondensed afterwards. In ethanol, a considerable amount of material could be extracted from the solid copolymers of low polyamide content. Extractability was found to be strongly reduced with increasing polyamide content, i.e. increasing length of the polyamide ('hard', crystallizable) segments. Torsional tests showed an extended rubber plateau of fairly constant modulus. Whereas PPOx has a T_g of -60°C, the T_g values of the copolymers were higher as a result of (i) the restricted length of the PPOx segments and (ii) dissolution of uncrystallized polyamide segments in the PPOx phase. The high melting point of polyamide-4,6 was approached by the copolymer of high polyamide content, but the softer copolymers had lower melting points because of insufficient length of the polyamide segments.

(Keywords: segmented block copolymer; poly(ether amide); polyether; polyamide-4,6; nylon-4,6)

INTRODUCTION

Semicrystalline homopolymers of moderate crystallinity are characterized by a region of rubbery behaviour between the glass transition temperature and the melting point. Above T_g, the crystallites serve as crosslinks between flexible chains, just like the chemical crosslinks in a conventional rubber. The difference is, however, that the crystallites are thermally labile and that the thermoplast can be melt-processed.

This paper focuses on thermoplastic elastomers (TPE). Their development started with pioneering work on polyurethanes at I.G. Farben (Germany) in the late 1930s[1]. More insight into structure–property relationships of TPE was gained in the 1950s as a part of the development of polyester fibres[2]. The idea behind TPE is to extend the temperature range between T_g and T_m, in order to obtain materials that are truly rubbery from room temperature (or below) up to a fairly high temperature (say 250°C) and can be melt-processed at a somewhat higher temperature. Since thermoplasts usually satisfy the relation $T_g/T_m \simeq 0.6$ (temperature in kelvins), the above end is not likely to be attained for any homopolymer. One must therefore construct a block copolymer, the chains of which consist of two types of blocks, flexible (low-T_g) ones and stiff, fast-crystallizing ones. These blocks are commonly referred to as 'soft' and 'hard' blocks, respectively. In the solid state such a copolymer shows a phase-separated morphology: hard, crystalline domains are more or less dispersed in an elastomeric matrix.

Hard blocks excluded from the crystalline domains might either be molecularly mixed with the soft blocks, or form a separate amorphous phase. The former case results in displacement of T_g to higher values, whereas a three-phase system shows multiple glass transitions. In copolymers obtained through condensation polymerization, block lengths have to be small, and so-called multiblock or 'segmented' TPE are obtained. Nonetheless, the solid copolymer has a microphase-separated structure, be it on a very fine scale. Examples of segmented TPE copolymers are: polyurethane[3–5], poly(siloxane urea)[6], copolyester and poly(ether ester)[7–11] and poly(ether amide)[12–16].

The aim of this investigation is to develop new types of TPE with a larger service temperature range, and thereby to enlarge the applicability of these materials. As indicated above, this comes down to extending the rubber region between T_g and T_m. This is achieved by selecting a high-melting, fast-crystallizing hard block.

In view of our experience with polyamide-4,6 ($T_m \simeq$ 290°C), which has been extensively studied in our laboratory[17], we have chosen this polyamide to be the hard component in a number of different TPE. For this application, high crystallinity (>40%) and high crystallization rate are distinct advantages of nylon-4,6 over other polyamides.

In a previous research study, the TPE of nylon-4,6 and poly(tetramethylene oxide) (PTMO) soft segments was investigated[18]. In these copolymers the presence of two amorphous phases was evident from the occurrence of two glass transitions. One of these was found at an unfavourably high temperature of 50–80°C, and attributed to a mixed phase containing polyamide as the major component. Moreover, many of the copolymer preparations proved to be molecularly inhomogeneous. A substantial mass fraction of the material was found to be extractable in ethanol, the extract containing copolymer of very low polyamide content. This was ascribed to melt phasing during the polymerization reaction (which was carried out in an autoclave).

As an alternative, we have prepared poly(ether amides) with poly(propylene oxide) (PPOx) instead of PTMO as

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the soft segment. Commercially obtainable PPOx oligomers are said to have a narrower chain-length distribution than PTMO oligomers[10]. TPE based on nylon-4,6 (N46) and PPOx will be the subject of this paper.

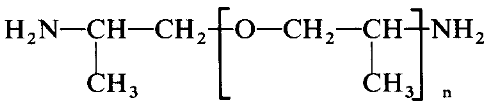
EXPERIMENTAL

Materials and copolymer synthesis

The synthesis of N46-PPOx copolymers is carried out in two steps: first a prepolymer is prepared, which is postcondensed afterwards in order to increase the molar mass.

The prepolymer syntheses were carried out in a 1.4 litre autoclave (Juvo 142) equipped with anchor stirrer and heating device.

We used commercial PPOx diamines (Jeffamine D-400 and Jeffamine D-2000 from Texaco Chemical Co) as starting substances. These are oligoethers capped with an amino group at both ends of the chain:



$$H_2N{-}\underset{CH_3}{CH}{-}CH_2{-}\left[O{-}CH_2{-}\underset{CH_3}{CH}\right]_n{-}NH_2$$

The molar masses amounted to 430 and 2090, respectively, as determined by amino end-group analysis.

Along with the PPOx diamine, a stoichiometric amount of adipic acid (Merck, Pure Food Grade) was added in order to have the right functionality for copolymerization with the nylon-4,6 blocks.

Nylon-4,6 was added in the form of the salt, which was prepared from adipic acid and 1,4-diaminobutane (Merck, Synthetic Grade, distilled) as described previously[17].

The total mass of the reaction mixture amounted to ~100 g. In order to reduce the tendency to phasing, *m*-cresol was added to the reaction mixture in amounts of 1 ml per gram of reactants.

The reaction was carried out at 210°C for 30 min, in which time a maximum pressure of about 7 bar was attained. At the end of the reaction period the pressure was released and the temperature was raised to 260°C in order to have water and *m*-cresol evaporate from the mixture (1 h).

Postcondensation took place in a rotating glass vessel situated in an oven. The finely divided prepolymer (milled autoclave product) was kept in a stream of dry nitrogen at 260°C for 24 h.

Characterization

Viscometry. The inherent viscosity of 1 g dl^{-1} solutions of copolymer in *m*-cresol was measured in an Ubbelohde viscometer at 25°C.

End-group analysis. The concentration of amine end-groups was determined by potentiometric titration of a 100–150 mg sample in 35 ml 85% phenol, the reagent being 0.1 M trifluoromethanesulphonic acid in t-butanol. Carboxylic acid end-groups in a 100–150 mg sample were measured potentiometrically in a mixture of 3 g *o*-cresol and 35 ml benzyl alcohol, with 0.1 M KOH in t-butanol.

Compression moulding. Test specimens were melt-pressed in a simple mould kept between the heating plates of a hydraulic press (Lauffer). The copolymer grains were compressed and kept at a temperature 20–30°C above the melting point for ~5 min, after which water cooling of the heating plates was started.

Ethanol extraction. A Soxhlet apparatus was used to extract the ethanol-soluble material from compression-moulded bars. Extraction was continued for 16–18 h.

Differential scanning calorimetry. D.s.c. measurements were carried out with a DuPont 990 Thermal Analyzer. The scales of temperature as well as heat flux were calibrated by using an indium standard. The sample compartment was purged with nitrogen. Sample weights varied between 5 and 10 mg and open sample containers were employed.

The usual procedure for postcondensed copolymer grains was as follows:

(i) first heating run at 20°C min^{-1} up to 20°C above T_m;
(ii) equilibration for 5 min at the latter temperature;
(iii) cooling run at 10°C min^{-1} down to 150°C below T_m;
(iv) second heating run at 20°C min^{-1}.

Baselines for melting endotherms and crystallization exotherms were found by linear extrapolation of a straight portion of the d.s.c. trace on the high-temperature side of the peak. Although this procedure does not take into account any difference in specific heat between solid and melt, it could be carried out with little ambiguity in most cases.

Torsional modulus. A computer-controlled Myrenne torsion pendulum was employed. Samples of approximate dimensions 50 × 9 × 2 mm were machined from compression-moulded bars and dried in vacuum at 110°C for 16 h prior to testing. The computer calculated storage and loss moduli from damped oscillations at a frequency of 1 Hz, while the sample was continuously heated from −150°C to the onset of melting (flow) at a rate of ~1°C min^{-1}.

Wide-angle X-ray diffraction. WAXD photographs were obtained in a Kiessig flat-plate camera. Ni-filtered Cu Kα radiation was obtained from a Philips generator operated at 35 kV and 25 mA.

Compression-moulded samples of 2 mm thickness were dried in vacuum at 110°C prior to mounting. Exposure in the evacuated camera took 6–8 h, at a sample-to-film distance of 38.5 mm.

The optical transmission of the photographs was recorded with a Nonius densitometer.

Small-angle X-ray scattering. SAXS measurements were carried out by means of a Kratky camera (model 1970) equipped with a step-scanning device. Cu Kα radiation ($\lambda = 0.1542$ nm) was produced by a Philips generator operated at 45 kV and 45 mA. Monochromatization was achieved by using a Ni filter in combination with pulse-height discrimination of the detector signal.

Sample thickness amounted to ~1.5 mm, and the length of the sample in the X-ray beam was sufficient for the infinite-slit assumption to be valid. The angular scan ranged from $s = 0.009$ to 0.45 nm^{-1} ($s = 2 \sin \theta/\lambda$). Scattering curves were corrected for parasitic scattering. They were put on an absolute scale by means of a Lupolen calibration sample and by correcting for sample thickness and absorption.

Long-period values were calculated from desmeared and Lorentz-corrected scattering data by application of Bragg's formula. Implicit in this procedure is the assumption that scattering is produced by lamellar stacks.

All calculations were done by means of the well known computer program by Vonk[19].

REMARKS ON BLOCK LENGTH AND POLYAMIDE CONTENT

In polycondensation, the reactivity of a monomer is usually not dependent on its size, and the products obtained from monomer mixtures have the properties expected for random copolymers, such as intermediate values of the elastic modulus. Block formation is purely statistical in a homogeneous reaction mixture. Phase separation of the reactants, on the other hand, will lead to pronounced blockiness or even separate homopolymers being formed.

In the paper by Frensdorff[20] it is demonstrated that random copolymerization leads to a very broad distribution of block lengths. This must be borne in mind when one considers properties that depend on the number of hard domains (crystallites) and/or their size, e.g. melting temperature. In pure nylon-4,6 a crystallite thickness of 7 nm, which corresponds to approximately five repeat units, yields a melting temperature of 290°C.

The polyamide content w_{PA} (mass fraction) of a copolymer is defined such that each amide bond is included. This is accomplished by putting:

$$w_{PA} + w_{PEth} = 1$$

in which w_{PEth} refers to the polyether part of the PPOx diamine segments; the -NH- groups are excluded. These amine groups are thus included in the value of w_{PA}. The copolymer that was obtained from PPOx diamine and adipic acid, being a true polyamide, is rightly characterized by a positive value of w_{PA}. For pure nylon-4,6, $w_{PA} = 1$.

RESULTS AND DISCUSSION

Characterization of as-prepared copolymers

The prepolymers obtained from the autoclave syntheses were varying in colour from beige to pale yellow. After postcondensation, the material's appearance had become much darker, varying from orange brown to dark brown.

When PPOx of molar mass 2090 was employed in the copolymerization, the solids produced were inhomogeneous. We have ascribed this to a macroscopic phase separation in the reaction mixture, resulting in a crude morphology of the solid. These materials will not be discussed further in this paper.

Solution viscosity measurements and end-group analysis served to characterize the overall result of the copolymer syntheses. The results for copolymers based on PPOx of molar mass 430 are contained in *Table 1*. Potentiometric titration of end-groups showed that excess acid was present in the samples investigated. This resulted in low values of the number-average molar mass. Another indication of low molar mass was found in the values of the inherent viscosity. Obviously, there has been an imbalance regarding the stoichiometry of the reactants. This is attributed to uncertainties in functionality and molar mass of the PPOx diamine starting material. Moreover, evaporation of diaminobutane may have played a role. This has been found to take place in the polycondensation of nylon-4,6[17]. In order to compensate for this, we have employed slightly basic nylon salt in our syntheses (a 1% aqueous solution of the salt has a pH of 7.8), but apparently this has not been an adequate measure.

Ethanol extraction

Pure PPOx is soluble in water and in ethanol. The poly(ether amide) prepared from PPOx diamine and adipic acid (sample PA26) proved to be completely soluble too. It is therefore expected that, in the case of N46-PPOx copolymers, those chains which are not anchored in the polyamide crystallites will be extractable in ethanol. The hard-block content or the length of the hard blocks in these chains may be insufficient for taking part in crystallization.

Compression-moulded samples were subjected to Soxhlet extraction with ethanol for 16 h. The results are contained in *Table 1* and shown in *Figure 1*. The mass fraction of extractable material is plotted vs. the average polyamide content, w_{PA}. The extract was not analysed

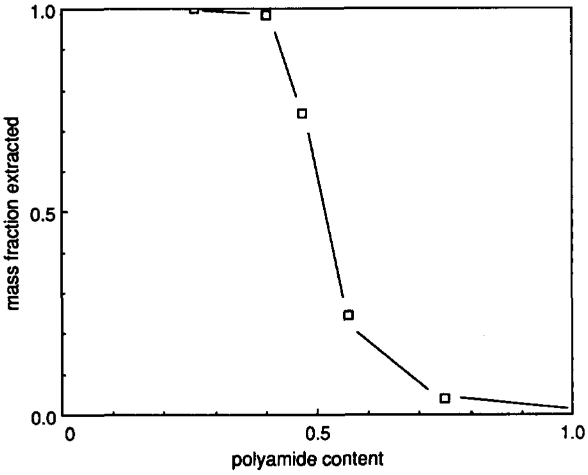


Figure 1 Soxhlet extraction of N46-PPOx copolymers with ethanol. The mass fraction of material extracted is plotted vs. the polyamide content w_{PA}

Table 1 Characterization of as-prepared N46-PPOx copolymers

Sample	w_{PA}	[-COOH] (mEq g^{-1})	[-NH$_2$] (mEq g^{-1})	$\bar{M}_n$ (10^3 g mol^{-1})	η_{inh}[a] (dl g^{-1})	Ethanol-extractable
PA26	0.26	–	–	–	0.35	1.0
PA40	0.40	0.147	0.034	11.1	0.47	0.99
PA47	0.47	–	–	–	0.54	0.74
PA56	0.56	–	–	–	0.73	0.24
PA75	0.75	0.102	0.011	17.7	0.76	0.04

[a] 1 g dl^{-1} solution in *m*-cresol at 25°C

further, but in similar experiments on N46-PTMO copolymers, the extract proved to be of high polyether content[18].

At a polyamide content of 0.4, the N46-PPOx copolymer is almost fully extractable. This implies that most of the polyamide is extracted as well. Obviously the elastomer network is not fully developed. Either the chains are too short, or too few hard blocks are long enough to form crystals that are stable in a swollen network.

Torsional modulus

Figure 2 shows the storage moduli of the dry N46-PPOx copolymers; the loss moduli are presented in *Figure 3*. Some data are collected in *Table 2*. In *Figure 4* the glass transition temperature (taken to be the maximum in G'' here) is plotted vs. the polyamide content. It appears that the glass transition lies around −15°C for low polyamide contents. This T_g value is ~40°C higher than the T_g of PPOx homopolymer[14]; it is close, however, to the T_g of the liquid copolymer that was obtained from PPOx diamine and adipic acid (sample PA26). The T_g of the latter was determined on a sample of filter paper impregnated with the highly viscous liquid copolymer. This result shows that the introduction of amide bonds at short intervals along the chain strongly reduces the mobility of a PPOx chain.

With increasing polyamide content, T_g is displaced to higher temperatures, until at 75% polyamide two separate transitions can be distinguished. The temperature shift results from the mixing of non-crystallizable polyamide blocks with the polyether blocks, so as to form a single amorphous phase. The peak splitting at higher polyamide content indicates partial segregation, but pure phases (consisting of one type of block only) are not formed.

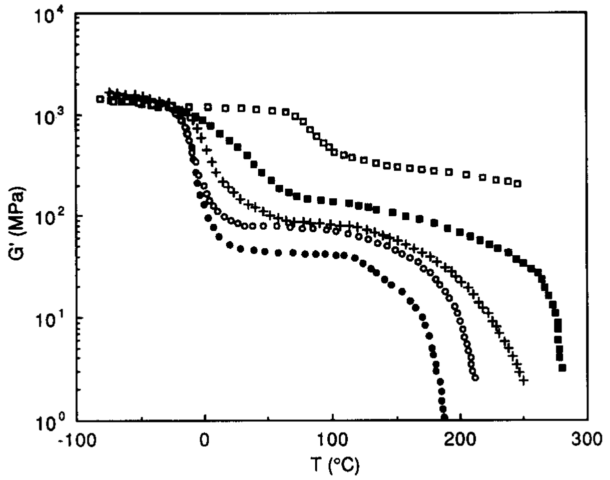


Figure 2 Torsional storage moduli of N46-PPOx copolymers of varying polyamide content w_{PA}, as a function of temperature: (●) $w_{PA}=0.40$; (○) $w_{PA}=0.47$; (+) $w_{PA}=0.56$; (■) $w_{PA}=0.75$; (□) $w_{PA}=1.0$

Table 2 Torsional modulus data for N46-PPOx copolymers

Sample	T_g (°C)	G' at 20°C (MPa)	G' at 100°C (MPa)	T_{flow} (°C)
PA26	−20	–	–	−20
PA40	−12	50	40	170
PA47	−12	85	70	200
PA56	−3	170	80	220
PA75	2, 38	550	140	270
Nylon-4,6	82	1100	400[a]	>270

[a] G' at 100°C is close to 300 MPa when extrapolated from the plateau range

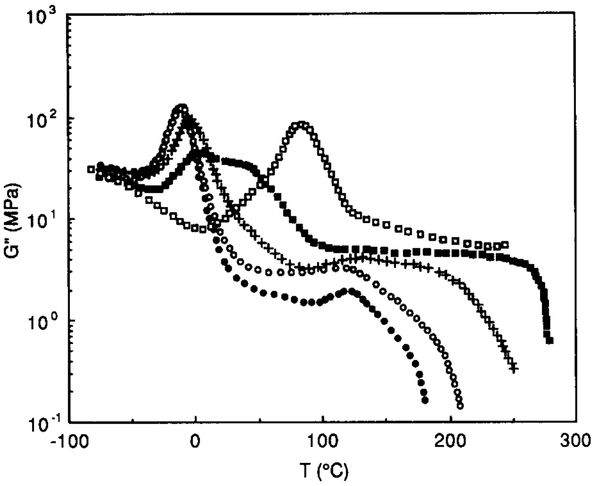


Figure 3 Torsional loss moduli of N46-PPOx copolymers of varying polyamide content w_{PA}, as a function of temperature: (●) $w_{PA}=0.40$; (○) $w_{PA}=0.47$; (+) $w_{PA}=0.56$; (■) $w_{PA}=0.75$; (□) $w_{PA}=1.0$

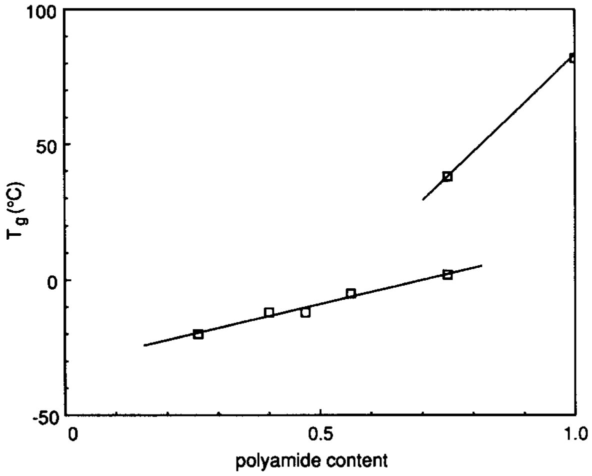


Figure 4 Glass transition temperatures of N46-PPOx copolymers as a function of polyamide content w_{PA}. T_g is defined as max(G'')

As shown in *Figure 2*, the copolymers containing 47% or more polyamide maintain a fairly constant value of the rubber modulus up to 150°C, and the onset of flow occurs above 200°C. These temperatures are still far from the melting point of nylon-4,6 (≃290°C), however. Copolymer sample PA75 begins to approach this value, but this material is no longer rubber-like.

Differential scanning calorimetry

D.s.c. results for as-prepared copolymers are presented in *Figure 5* and in *Table 3*. After heating to 20°C above T_m and subsequent cooling at a rate of 10°C min^{-1}, the melting points found in the second heating run are 10–15°C lower than those recorded during the first heating run of the as-prepared copolymer.

Sample PA56 exhibits an unexpectedly high melting point compared to sample PA47. Presumably, the post-condensation procedure has been an effective annealing treatment for sample PA56, with crystallization being a driving force for a block-length increase.

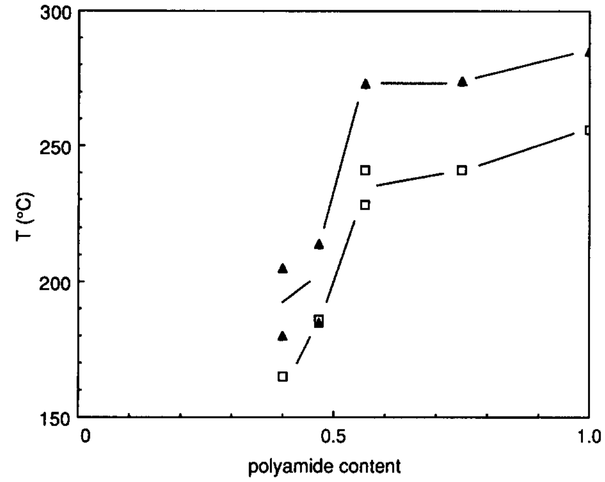


Figure 5 D.s.c. results for N46-PPOx copolymers of varying polyamide content w_{PA}: (☐) crystallization temperature; (▲) melting temperature found in the second heating run

Table 3 Thermal data for N46-PPOx copolymers, obtained by d.s.c.

Sample	T_c (°C)	$\Delta H_m{}^a$ (J g^{-1})	$\Delta H_{m,PA}$ (J g^{-1} PA)	$T_m{}^a$ (°C)
PA40	165	1.9	4.8	180, 205
PA47	186	3.2	6.8	185, 214
PA56	241, 228	14	25	273
PA75	241	43	58	274
Nylon-4,6	256	84	84	285

[a] Values obtained in the second heating run

Table 3 lists the overall heats of fusion, ΔH_m, as well as the values of $\Delta H_{m,PA}$, which were calculated on the basis of the nylon-4,6 mass fraction of the copolymers. For the copolymers of low polyamide content, the values of both melting point and heat of fusion are low in comparison with nylon-4,6. In these softer copolymers crystallization is hampered, since the average number of repeat units in the hard blocks is much lower than five, the value for high-melting nylon-4,6 crystallites. In sample PA75 the average hard-block length is approximately five, too.

In *Figure 6* the torsional storage modulus at 100°C is plotted as a function of the overall heat of fusion, which is of course a measure of the concentration of hard domains in the copolymer[11].

Wide-angle X-ray diffraction

The crystal structure of nylon-4,6 was elucidated by Doeksen[21], who has indexed many reflections. Using WAXD photography and densitometry we have concluded that the diffraction patterns of the copolymers are very similar to those of pure nylon-4,6. The interplanar distances of the stronger reflections are presented in *Table 4*.

A change in the relative intensity of the 1 0 0 and 0 1 0 reflections (*Figure 7*) suggests that the lateral aspect ratio (i.e. roughly perpendicular to the chain axis) of the crystallites in the copolymers differs from that in nylon-4,6. Our interpretation is that the growth of the planes containing the hydrogen bonds (*ac* planes) is much less hampered by the reduced length of the hard blocks than growth of the *bc* planes. (Note that the densitometer curves are transmission curves, for which no conversion to optical density has been carried out.)

Small-angle X-ray scattering

The technique of small-angle X-ray scattering primarily provides us with two types of information, the first concerning phase dispersion (geometry) and the second characterizing phase composition (density). The degree of dispersion can be estimated from the scattering curve through the calculation of various length parameters with different meanings, such as the inhomogeneity length l_p, the correlation length l_c and the long period L. The results for our N46-PPOx samples are collected in *Table 4*. The trend is similar for each of these parameters. Samples PA40 and PA47 appear to have a finer substructure than samples PA56 and PA75. This is in agreement with the d.s.c. experiments, which suggest a much larger hard-domain (crystallite) size for the latter two copolymers. The long-period values for samples PA56 and PA75 are in the usual range for semicrystalline materials. One must

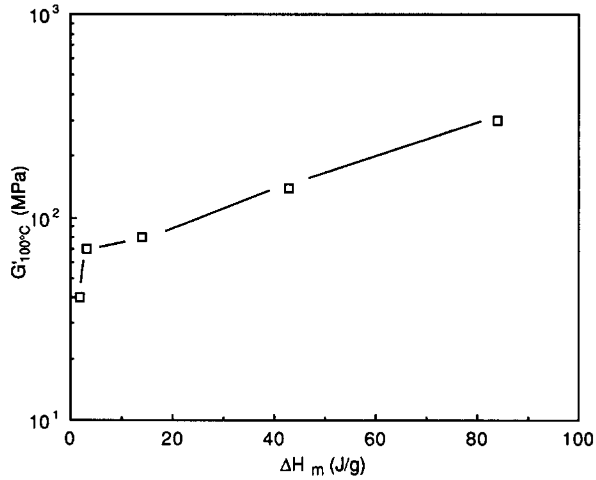


Figure 6 Torsional storage moduli at 100°C of N46-PPOx copolymers of varying polyamide content as a function of the heat of fusion ΔH_m measured in the second d.s.c. heating run

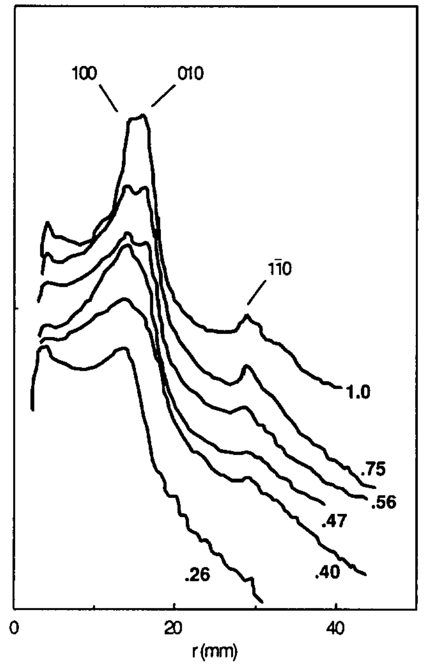


Figure 7 Wide-angle X-ray diffraction patterns of N46-PPOx copolymers of varying polyamide content. (The curves represent densitometer transmission data; they are arbitrarily displaced along the ordinate for comparison; r is the radial distance on the film at a sample-to-film distance of 38.5 mm)

Table 4 X-ray data for N46-PPOx copolymers

Sample	d_{hkl}[a] (nm)	d_{010} (nm)	d_{100} (nm)	L (nm)	l_c (nm)	l_p (nm)	$\overline{\Delta\rho^2}$[b]
PA26	–	–	0.44 ± 0.01[c]	–	–	–	–
PA40	0.238 ± 0.004	0.380 ± 0.008	0.44	6.4	2.4	1.6	0.185
PA47	0.236	0.385	0.44	6.7	2.6	1.7	0.162
PA56	0.238	0.377	0.44	16.7	4.4	2.2	0.193
PA75	0.237	0.375	0.44	11.9	4.4	2.7	0.158
Nylon-4,6	0.237	0.387	0.41	–	–	–	–
Nylon-4,6[d]	–	0.382	0.43	–	–	–	–

[a] Overlapping reflections 2 0 0, 1 2 0 and 1 1 0

[b] Mean-square electron density difference, in 10^{-2} (mol electron cm^{-3})^2

[c] Amorphous halo

[d] Data by Doeksen[21]

realize that the thickness of the crystalline domain will be smaller than L, and the l_p values (which equal four times the volume-to-surface ratio for randomly dispersed particles) suggest that the domains are much smaller indeed.

Absolute values for the scattering power, $\overline{\Delta\rho^2}$, of the samples are also presented in *Table 4*. Interpretation of these values will not be pursued here, since the calculation of the degree of phase separation requires precise knowledge of the densities of the pure phases as well as their volume fractions. Sufficiently accurate density values for the polyether and amorphous nylon-4,6 are lacking, however.

Analysis of the 'tail' of the SAXS curves did not suggest the existence of a transition layer exceeding 1 nm in thickness between hard and soft phases.

CONCLUSIONS

This work has shown the feasibility of preparing thermoplastic elastomers (TPE) based on polyamide-4,6 and a polyether soft segment, in this case poly(propylene oxide) (PPOx). Because of its intrinsically high melting temperature and its strong tendency to crystallization, polyamide-4,6 is well suited to be the hard component in multiblock copolymers, even those with very short segments.

The incorporation of PPOx of molar mass 2090 led to inhomogeneous products. The underlying cause is thought to be phase separation of the reaction mixture ('melt phasing'), which eventually gives rise to a crude microstructure in the solid state.

The solids obtained with PPOx of molar mass 430 look more promising, but the number-average molar mass is still low (<20000).

If one assumes random copolymerization, the average number of repeat units in the polyamide hard blocks of the softer materials is so small (<2) that only a very broad distribution of block lengths will allow crystallization to occur at all. This is in agreement with our finding that the heat of fusion of the N46-PPOx copolymers, with respect to the polyamide content, is low. A low heat of fusion implies the presence of a considerable amount of uncrystallized polyamide blocks. Owing to their restricted length, these polyamide segments do not segregate from the polyether phase but rather mix with the latter. This was inferred from the appearance of one, rather broad, glass transition in torsional modulus experiments.

The glass transition is found at temperatures considerably higher than the T_g of pure PPOx ($\simeq -60$°C). The poly(ether amide) of lowest possible polyamide content, synthesized from oligomer PPOx diamine and adipic acid, already has its T_g at -20°C. This shows that the high T_g values are to be attributed to the restricted length of the PPOx chains between amide bonds. This has a stiffening effect on the chain and moreover it introduces a certain degree of compatibility with polyamide-4,6 blocks.

For this TPE, the lower bound of the rubber region is raised when the polyamide content is increased. Resorting to a somewhat higher molar mass, e.g. 1000, of the PPOx diamine oligomer may improve on this, promoting crystallization and reducing compatibility in the amorphous phase. This will lower the glass transition temperature and raise the melting point, and thus extend the service temperature range of this poly(ether amide).

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