

Micromechanical Properties of Polyether Block Amide Copolymers

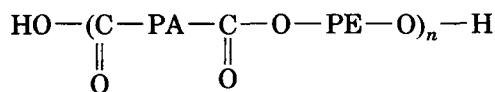
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Synopsis

A series of polyether block amide copolymers based on poly(tetramethylene oxide) of molecular weight 1000 or 2000 and polyamide 12 of molecular weight between 600 and 4000 with varying PE/PA weight ratio (from 80 to 20%) were studied by using dynamic mechanical spectroscopy and differential scanning calorimetry. Dynamic mechanical experiments showed three main relaxation peaks related to, the subglass transition of the soft segments, the glass transition of the soft segments, and the glass transition of the hard segments. A quench, carried out on a 70% PA copolymer from 110 to 15°C, leads to a decrease in the storage modulus. This result should be related to the destruction of physical ties.

INTRODUCTION

Polyether block amide copolymers (PEBA) consist of alternating soft and hard segments. The soft segments are based on poly(tetramethylene oxide) of low molecular weight (1000 or 2000). The hard segments are based on low molecular weight (600–4000) polyamide (PA).¹ The structure of PEBA is:



These copolymers show microphase separation which is due to the high polarity difference between hard and soft segments and the likely development of a three-dimensional hydrogen-bonding network between the amide units.^{2,3} Faruque and Lacabanne² have shown multiple relaxations in a peculiar PEBA sample (PA 12 2135 block PTMG 2032) by using thermally stimulated current method. The two main relaxation peaks were related to the glass transition of the soft segments (-65°C) and to the glass transition of the hard segments (19°C), respectively, showing microphase separation. Secondary relaxation peaks have been shown by these authors, a relaxation peak about -150°C also present in the PTMG homopolymer and a less defined relaxation peak at -29°C related to microbrownian motion. A subglass relaxation peak (5°C) and a well defined peak (-12°C) are exhibited by the PA 12 and PTMG homopolymers, respectively. Furthermore, Xie and Camberlin³ have investigated a series of PEBA based on PA 12 of various molecular weight between 600 and 4000 and poly(tetramethylene oxide) of molecular weight 1000 or 2000 by using three methods, dynamic mechanical

spectroscopy, differential scanning calorimetry, and transmission electron microscopy. Thermal analysis shows two main transitions, the glass transition of the soft segments at -80°C and two melting endotherms of the hard crystalline phase about 80°C and 180°C , respectively. Moreover, PEBA copolymers based on polyether of molecular weight 2000 exhibit a third transition related to the melting endotherm of the soft segment crystalline phase. PEBA copolymers based on polyether of molecular weight 1000 do not show such a transition. According to these authors, soft phase based on such a polyether of molecular weight 1000 could not crystallize because the chain length between crosslink ties is too weak. Furthermore, mechanical analysis carried out on each PEBA sample at a frequency of 11 Hz shows two internal friction peaks related to the glass transition of the soft segments (between -80°C and -20°C) and to the melting of the soft crystalline phase (between -10°C and 20°C), respectively. However, some discrepancy appears between thermal analysis data and the conclusions suggested by these authors about mechanical data. Thus, as shown by thermograms, PEBA samples based on polyether of molecular weight of 1000 do not exhibit a soft crystalline phase. As a result, the internal friction peak exhibited by such PEBA samples in the (-10°C , $+20^{\circ}\text{C}$) temperature range could not be again related to the melting of the soft crystalline phase. Thus, the α_1 internal friction peak could be due to another phenomenon. Transmission electron microscopy results are in agreement with phase separation occurring in these copolymers.

The aim of this work is to complete the investigation of such PEBA copolymers. To this end, a series of PEBA copolymers are investigated by means of a low frequency inverted torsion pendulum. Further analysis was carried out by differential scanning calorimetric experiments.

EXPERIMENTAL

PEBA Samples

PEBA samples were provided by ATOCHEM Co. (France). Hard segments are based on polyamide 12 (PA 12) of molecular weight between 600 and 4000. Soft segments are based on polytetramethylene oxide (PE) of molecular weight 1000 or 2000. Sample characterization is reported in Table I. PA 12 homopolymer (ATOCHEM Co.) was also investigated. The samples were cut to the following dimensions: $60 \times 6 \times 2 \text{ mm}^3$ for micromechanical experiments and $2 \times 2 \times 1 \text{ mm}^3$ for calorimetric experiments.

TABLE I
Composition of the Investigated PEBA Copolymers
(M_n are Molecular Weight in Number)

PEBA code	PA 12 (% wt/wt)	M_n (PA 12)	PE (% wt/wt)	M_n (PE)
A	80	4000	20	1000
B	70	2000	30	1000
C	50	2000	50	2000
D	30	850	70	2000
E	20	600	80	2000

Dynamic Mechanical Spectroscopy

Dynamic mechanical measurements were performed by using a low frequency inverted torsion pendulum.⁴ The temperature range between -160°C and 120°C was scanned at $0.5^{\circ}\text{C}/\text{min}$ at 1 and 0.1 Hz. Measurements of storage modulus G , and the dissipation factor $\tan \Phi$, at increasing and decreasing temperature were also carried out on particular samples.

Moreover, the apparent activation energy E (kcal/mol) was calculated as follows for every relaxation process.

The temperature-dependent shift of a mechanical relaxation process along the frequency axis can be used to calculate the apparent activation energy E defined by:

$$E = -R d(\ln f_0)/d(1/T)$$

f_0 is the frequency (1 or 0.1 Hz) of the maximum in the loss factor or of the inflection point in the storage modulus curve at a temperature T .

Differential Scanning Calorimetry (DSC)

DSC thermograms, over the temperature range 20 to 220°C , were recorded using a Perkin Elmer DSC 1B. The experiments were carried out at heating rate of $8^{\circ}\text{C}/\text{min}$.

RESULTS

Mechanical Spectroscopy

PA 12 Homopolymer

Mechanical measurements carried out at 1 and 0.1 Hz on the material as received show two relaxation peaks at -75°C (β peak) and about 47°C (α peak), respectively. Plots of $\log G$ and $\tan \Phi$ versus temperature are displayed in Figure 1.

Furthermore, five torsional pendulum runs are performed on this sample in the temperature range between 0 and 120°C at a frequency of 1 Hz.

First run, material as received. By increasing the temperature to 120°C , at $0.5^{\circ}\text{C}/\text{min}$, the α relaxation peak located about 47°C exhibits a magnitude of 0.11.

Second run. After the first run, a second run performed in reverse by decreasing the temperature from 120°C to 0°C at $0.5^{\circ}\text{C}/\text{min}$ shows three features: an increase in the α peak magnitude ($\tan \phi$ is about 0.14), a storage modulus decrease in the α temperature range, and a slight shift toward lower temperatures of the α spectrum (about 2°C) (Fig. 2).

Third run. Immediately after the second run, a third run is performed on this specimen by increasing the temperature from 0 to 120°C . This third run gives the same results as the second run (no changes in the location and in the magnitude of the α peak, no changes in the storage modulus curve).

Fourth run. After the third run, a fourth run performed by decreasing the temperature from 120 to 20°C gives the same results as the second and the third runs.

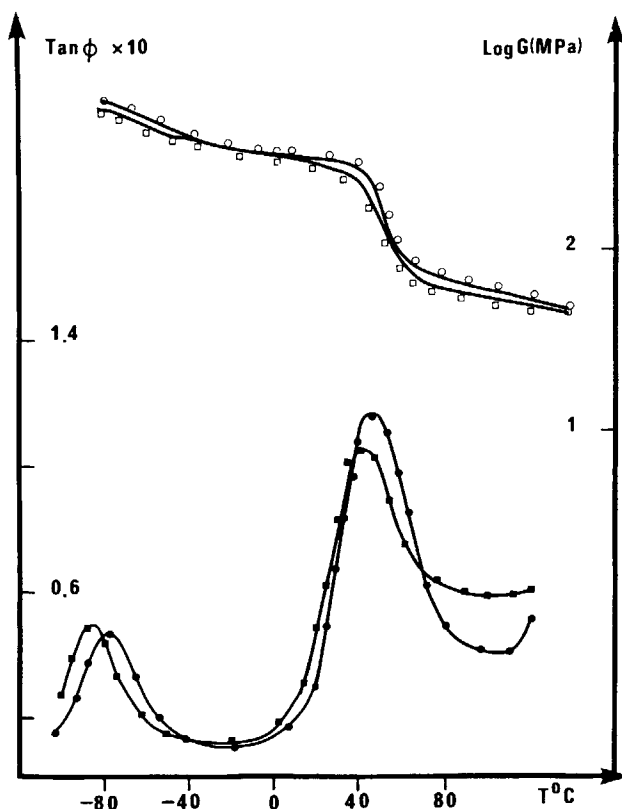


Fig. 1. Storage modulus, G , and dissipation factor, $\tan \phi$ as a function of temperature of polyamide 12 (PA). (\bullet , \circ), 1 Hz; (\blacksquare , \square), 0.1 Hz.

Fifth run. After the fourth run, the specimen is kept at room temperature for seven days. A fifth run carried out on this sample by increasing the temperature from 20 to 120°C gives the same results as the first run.

PEBA Series

Plots of $\log G$ and $\tan \phi$ versus temperature are displayed in Figure 3. For any PA 12 content and at the two frequencies, $\tan \phi$ spectra exhibit three main relaxation peaks, defined at increasing temperature as β_1 , α_2 , and α_1 peaks, respectively. Mechanical spectra of PEBA are shifted toward higher temperatures with increasing PA 12% wt/wt. Spectra are characterized by the three following features: (1) the β_1 peak shows a slight shift toward lower temperatures with increasing PE% wt/wt, while its magnitude and its area do not change with increasing PE content, (2) the α_2 peak exhibits a slight shift toward lower temperatures with increasing PE content and its area is enhanced with PE ratio, and (3) with increasing PA% wt/wt the α_1 peak shows a shift toward higher temperatures and an increase of its area.

$\tan \phi$ spectra carried out at 0.1 Hz on PEBA samples based on 50%, 70%, and 80% wt/wt PA show another weak peak (β_2 peak) located at -90°C , -100°C , and -80°C respectively.

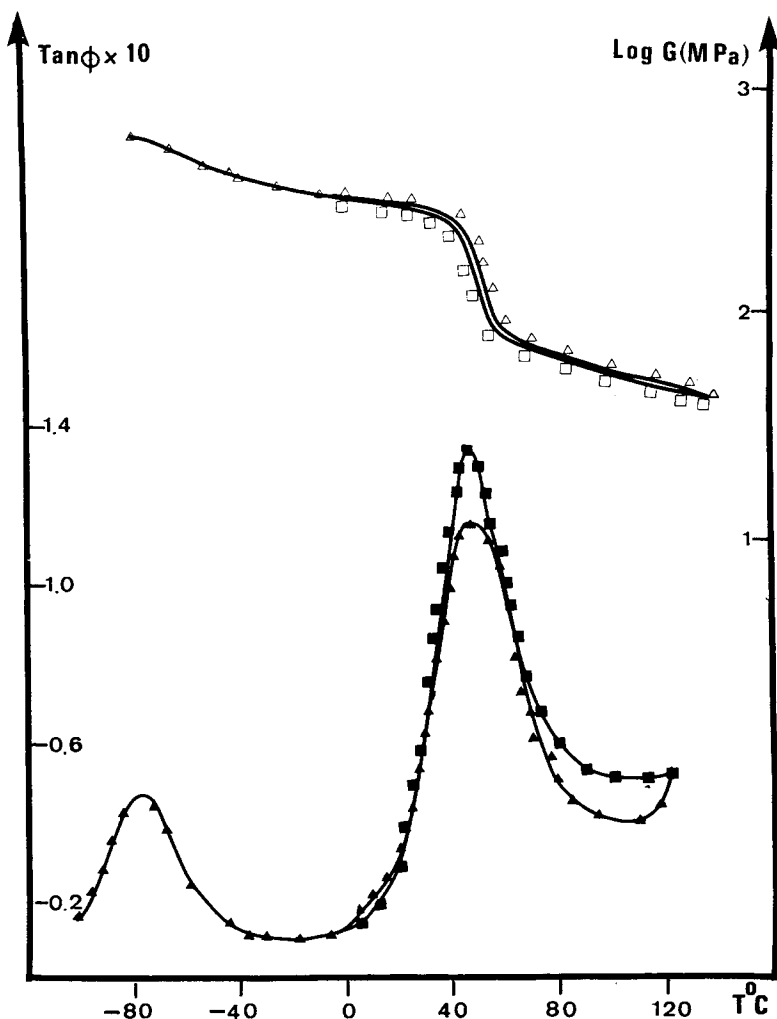


Fig. 2. Storage modulus, G , and dissipation factor, $\tan \phi$ as a function of temperature of polyamide 12 (1 Hz). (Δ, Δ), Material as received, first run carried out on increasing the temperature—material aged at room temperature, fifth run carried out on increasing the temperature. (\blacksquare, \square), Material as received, second run performed on decreasing the temperature from 120 to 0°C .

Thermal Treatments Carried Out on a PEBA Sample (70% wt / wt PA)

Three torsional pendulum runs are performed on a PEBA sample with 70% wt/wt PA at a frequency of 1 Hz. The sequence of the runs is as follows.

First run, material as received. After cooling the specimen from room temperature to -160°C at a rate of about $5^\circ\text{C}/\text{min}$, the first run is made by increasing the temperature up to 110°C . Because of the loss in the specimen stiffness at temperatures above 80°C , measurements could not be performed in the temperature range between 80 and 110°C . $\tan \Phi$ spectrum exhibits the three relaxation peaks, β_1 , α_2 , and α_1 peaks located at -140°C , -56°C , and -12°C , respectively.

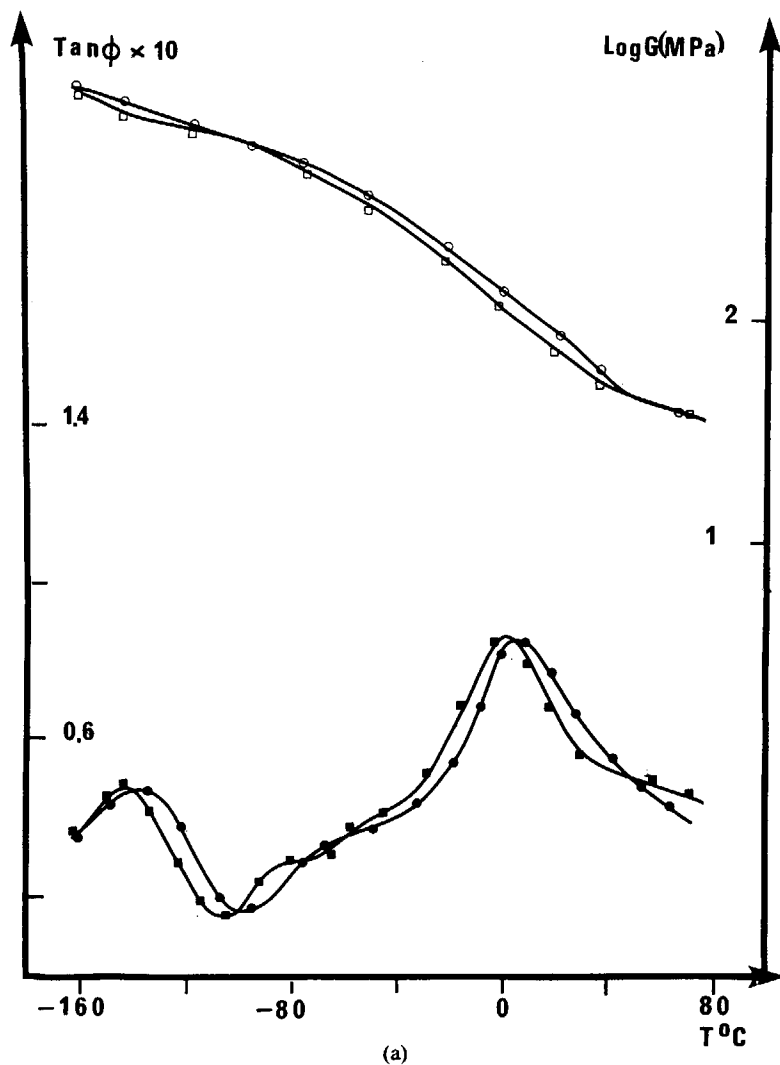


Fig. 3. Storage modulus, G , and dissipation factor, $\tan \phi$ versus temperature of polyether block amide copolymers (PEBA) with varying % wt/wt PA (3a - 80%, 3b - 70%, 3c - 50%, 3d - 30%, 3e - 20%). (\bullet , \circ), 1 Hz, (\blacksquare , \square), 0.1 Hz.

Second run. After the first run, the specimen is quenched from 110°C to 15°C at a rate of about $30^{\circ}\text{C}/\text{min}$, and then, cooled from 15°C to -160°C at a rate of about $5^{\circ}\text{C}/\text{min}$. The second run is made by increasing the temperature from -160°C to 110°C . The second run relaxation spectrum is shifted toward lower temperatures in comparison to the first run. Thus, β_1 , α_2 , and α_1 peaks are located at -143°C , -64°C , and -25°C , respectively.

Third run. After the second run, a third run performed in reverse by decreasing the temperature from 110°C to -160°C at a rate of about $0.5^{\circ}\text{C}/\text{min}$ gives the same results as the second run (no changes in the location and in the magnitude of the relaxation peaks) (Fig. 4).

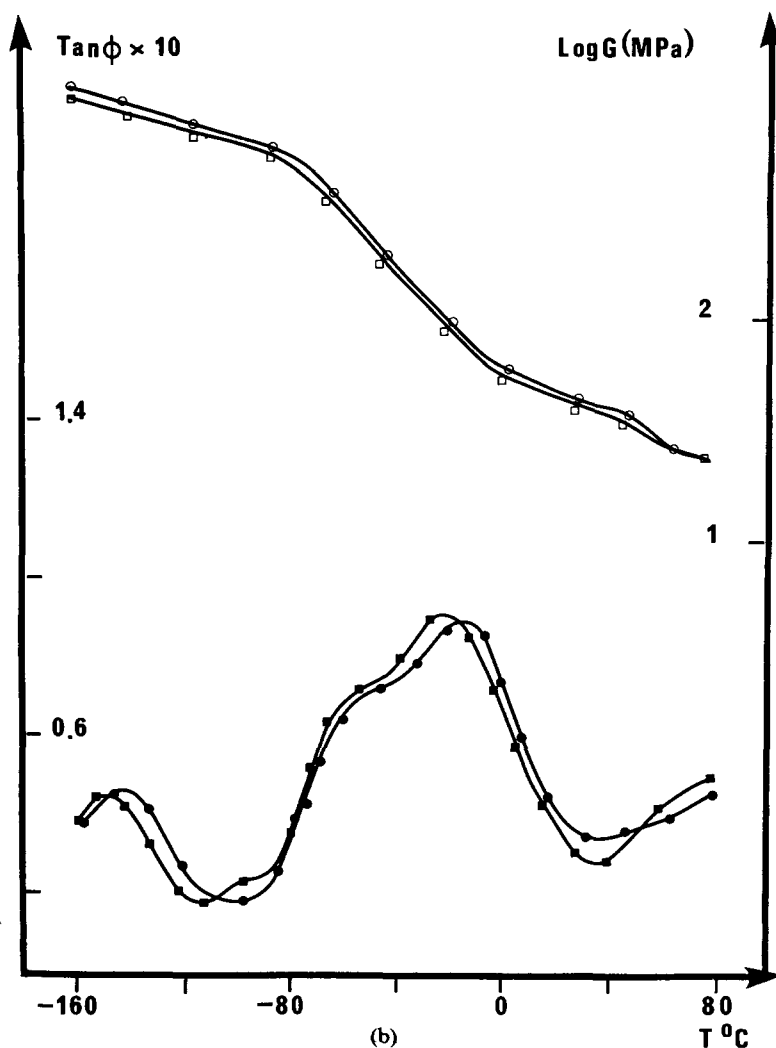


Fig. 3. (Continued from the previous page.)

Differential Scanning Calorimetry

The DSC thermogram of a PA 12 sample carried out at increasing temperature exhibits one endotherm about 180 $^{\circ}\text{C}$ [Fig. 5(a)]. The thermograms performed on the PEBA series at increasing temperature show one endotherm. With increasing PA ratio, endotherm area is enhanced [Fig. 5(b)]. With increasing the block length of the hard segments, endotherm temperature is shifted toward higher temperatures. Experimental data are listed in Table II. The DSC thermogram performed on a PA 12 sample heated from 20 to 120 $^{\circ}\text{C}$ at 0.5 $^{\circ}\text{C}/\text{min}$ then cooled slowly from 120 to 20 $^{\circ}\text{C}$ at 0.5 $^{\circ}\text{C}/\text{min}$ is the same as the "as received" PA 12 sample.

The DSC thermogram performed on a PEBA sample with 70% wt/wt PA quenched from 110 $^{\circ}\text{C}$ to 15 $^{\circ}\text{C}$ is the same as the "as received" PEBA sample.

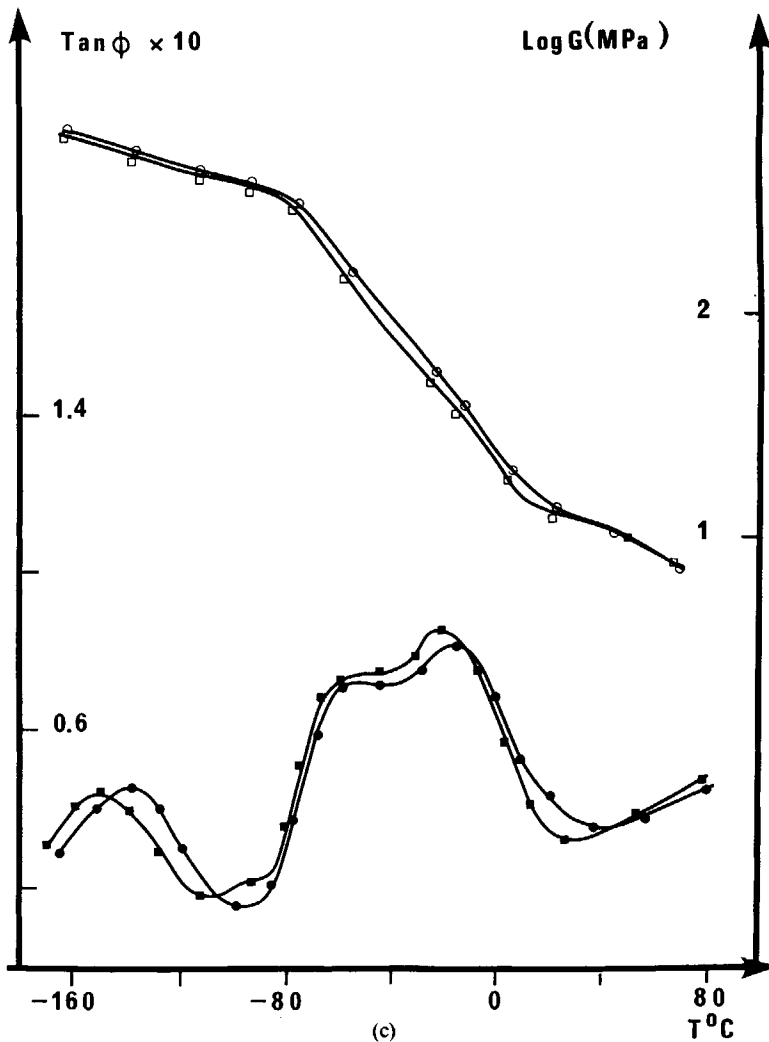


Fig. 3. (Continued from the previous page.)

DISCUSSION

Thermogram Analysis

Materials as received. The endotherm peak exhibited by the PA 12 sample, about 180°C, is related to the melting of the PA 12 crystalline phase. The endotherms exhibited by the PEBA samples are related to the melting of the hard segment crystalline phase.

According to the data (Table II), the melting temperatures of the hard domains depend on the block length of the hard segments. Thus, PEBA samples B and C with different PE/PA weight ratios but based on PA with equal molecular weight (2000) show melting endotherms located at the same temperature (162°C). Moreover, with increasing the block length of the hard segments, melting temperatures are shifted toward higher temperatures as

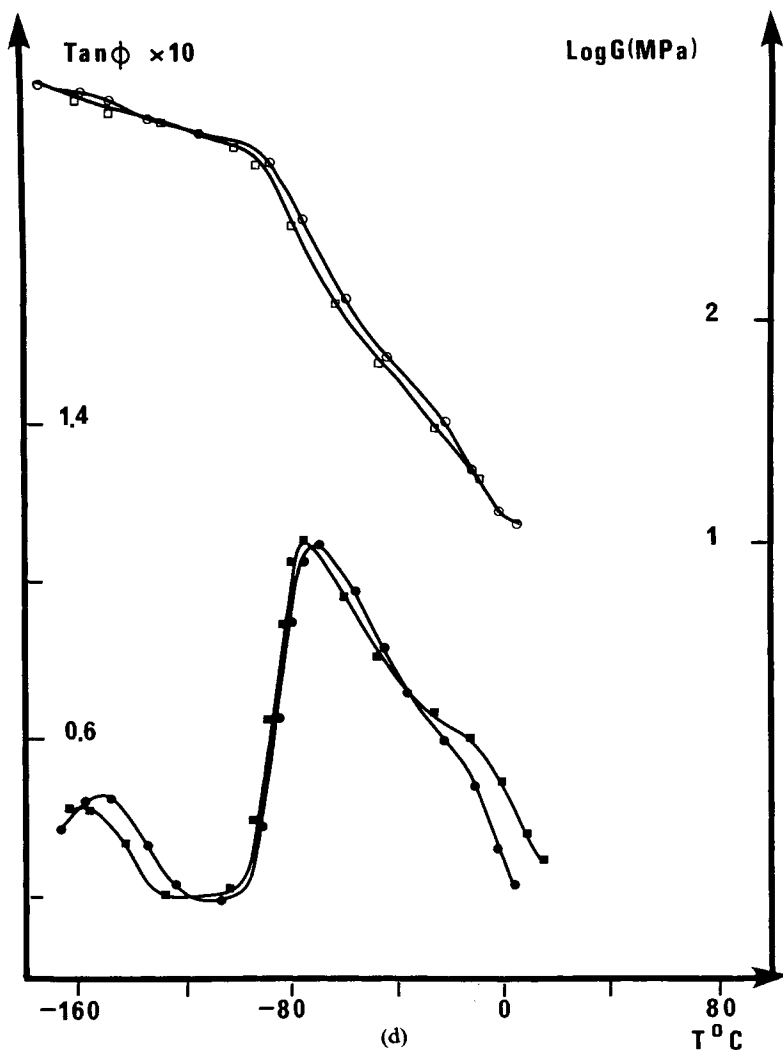


Fig. 3. (Continued from the previous page.)

shown in Table III. It is known that the crystalline domain diameter increases as the square root of molecular weight.⁵ Thus, with increasing the block length of the hard segments, hard domains become larger and more perfect. As a result, melting temperatures of the hard domains are shifted toward higher temperatures with increasing the block length of the hard segments. Moreover, data reported in Table II suggest that microphase separation depends on the block length of the PA segments. Furthermore, according to Figure 5, melting endotherm peak areas, related to melting enthalpies of the hard domains, are enhanced with increasing PA% wt/wt. As a result, the amount of crystalline phase of the hard segments increases with increasing PA content. Calorimetric data carried out on such PEBA samples by Xie and Camberlin³ have shown two melting endotherms of the hard domains. This discrepancy between their results and ours could be due to difference in sample synthesis

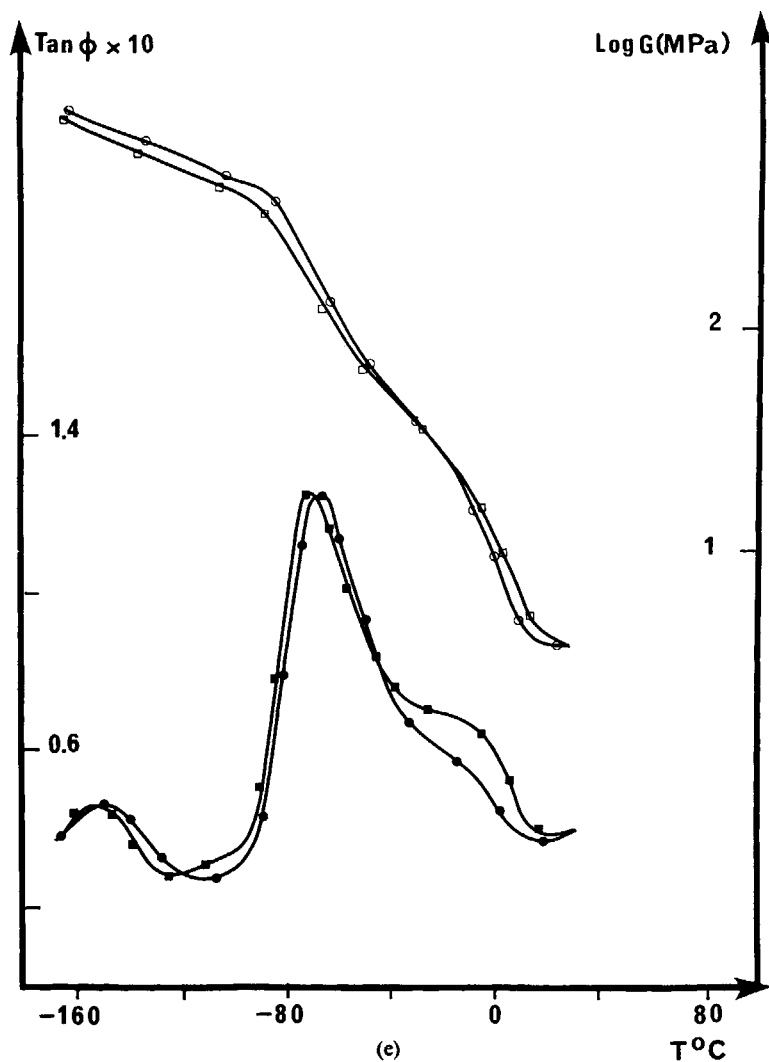


Fig. 3. (Continued from the previous page.)

conditions. Thus, previous work^{6,7} has shown that thermal treatments occurring during sample preparation could induce a double melting endotherm related to the presence of two different crystallographic structures and/or two different crystallite size distributions.

Thermal treatments. The DSC thermogram of the PA 12 slowly heated from 20 to 120°C and then slowly cooled to room temperature is the same as the "as received" sample one. As a result, this thermal treatment does not induce changes in the crystallinity degree and/or in the crystallite size distribution. Furthermore, the DSC thermogram of the PEBA sample with 70% wt/wt PA and quenched from 110 to 15°C is the same as the "as received" PEBA sample. This result suggests that this thermal treatment does not induce changes in the amount of hard crystalline phase and/or in the crystallite size distribution.

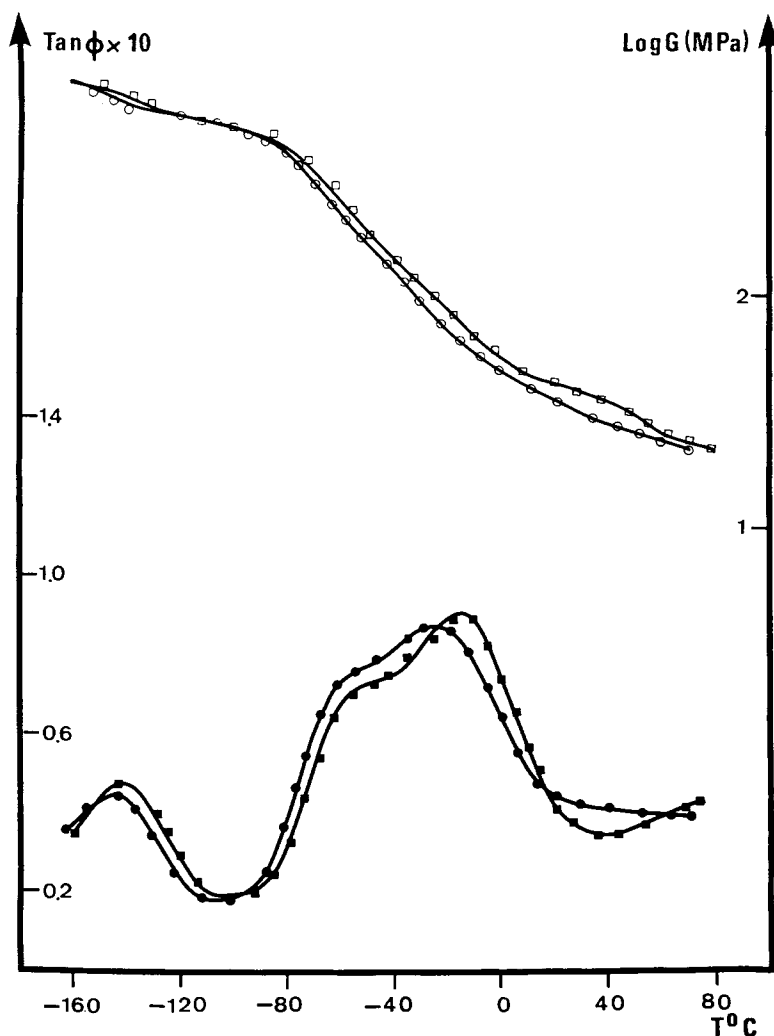


Fig. 4. Storage modulus, G , and dissipation factor $\tan \phi$ versus temperature of a polyether block amide copolymer sample (70% wt/wt PA) performed at 1 Hz. (■, □), Material as received, first run carried out on increasing the temperature from -160 to 110°C (because the loss in the stiffness at temperatures above 80°C , measurements could not be performed in the temperature range between 80 and 110°C). (●, ○), Quenched material from 110 to 15°C , second run performed on increasing the temperature, third run performed on decreasing the temperature from 110° to -160°C at $0.5^\circ\text{C}/\text{min}$.

Dynamic Mechanical Analysis

PA 12 Homopolymer

Material as received. According to Owen and Bonart,⁸ the α relaxation peak about 47°C is related to the glass transition. The β peak is related to a subglass transition.⁹ The glass transition ($T = 47^\circ\text{C}$) has an apparent activation energy of 90 – 94 kcal/mol (Table III). This result is in agreement with

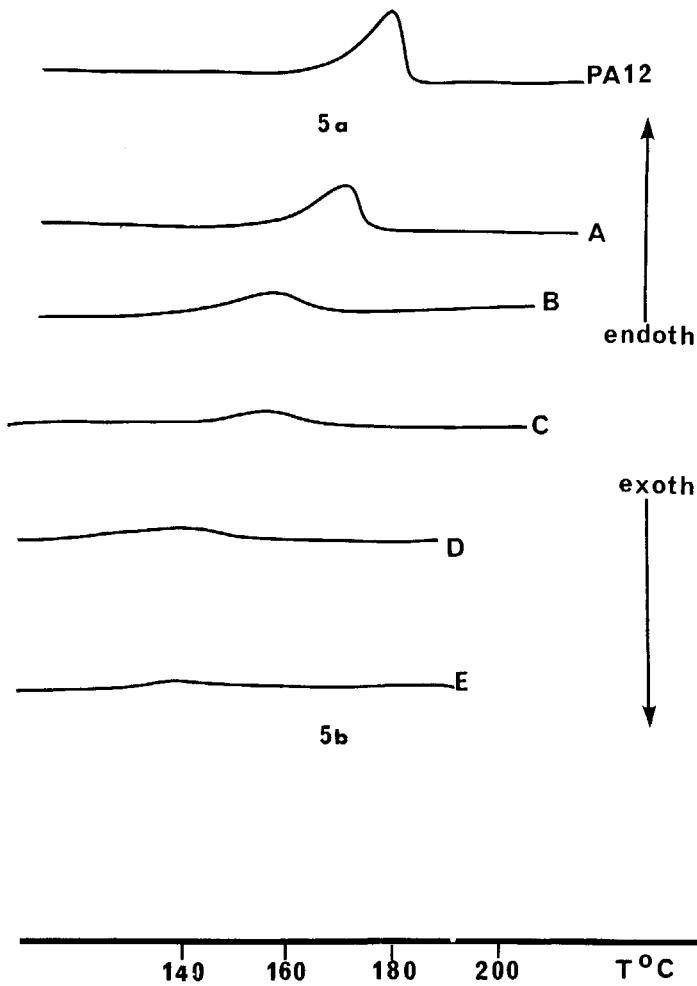


Fig. 5. DSC curves performed on increasing the temperature. (a) PA 12 homopolymer; (b) PEBA copolymers with varying wt/wt PA.

TABLE II
DSC Data Melting Temperatures of the Hard Domains

Sample	% wt/wt PA	M_n (PA 12)	Temperature of peak endotherm (°C)
PA12	100	—	180
A	80	4000	171
B	70	2000	162
C	50	2000	162
D	30	850	143
E	20	600	137

TABLE III
 Temperatures of Relaxation Peak Maxima Displayed at 1 Hz ($T_{1 \text{ Hz}}$) and Apparent Activation Energies, E,
 of These Relaxation Phenomena (E in kcal/mol)

Relaxation peak	Sample											
	PA 12		A		B		C		D		E	
	$T_{1 \text{ Hz}}$ ($^{\circ}\text{C}$)	E	$T_{1 \text{ Hz}}$ ($^{\circ}\text{C}$)	E	$T_{1 \text{ Hz}}$ ($^{\circ}\text{C}$)	E	$T_{1 \text{ Hz}}$ ($^{\circ}\text{C}$)	E	$T_{1 \text{ Hz}}$ ($^{\circ}\text{C}$)	E	$T_{1 \text{ Hz}}$ ($^{\circ}\text{C}$)	E
β	-75	17 ± 1	—	—	—	—	—	—	—	—	—	—
β_1	—	—	-138	8.7 ± 1.5	-140	7.4 ± 1.5	-145	6.9 ± 1.5	-148	6.6 ± 1.5	-150	6.4 ± 1.5
α	+47	92 ± 2	—	—	—	—	—	—	—	—	—	—
α_1	—	—	+4	68.9 ± 1.5	-12	61 ± 5	-15	60 ± 5	-25	55 ± 10	-32	60 ± 15
α_2	—	—	-52	57 ± 15	-56	55 ± 10	-58	61 ± 5	-66	63 ± 5	-71	61 ± 1.5

Apparent activation energies are calculated as follows. $E = R (\ln 1 \text{ Hz} - \ln 0.1 \text{ Hz}) / (1/T_{0.1 \text{ Hz}} - 1/T_{1 \text{ Hz}})$ ($T_{1 \text{ Hz}}$ and $T_{0.1 \text{ Hz}}$ are absolute temperature (K) of the maxima in $\tan \phi$ at 1 Hz and 0.1 Hz respectively).

the value reported by Owen and Bonart.⁸ The subglass transition ($T = -75^{\circ}\text{C}$) has an apparent activation energy of 16–18 kcal/mol.

Thermal treatments. According to the experimental data showing the effects of the thermal histories on the micromechanical properties of a PA 12 sample, we can draw the following set of conclusions. (a) the PA 12 sample allowed to stay at room temperature (i.e., aged at room temperature) exhibits a significant decrease in the α damping peak on one hand and an increase of the storage modulus in the α temperature range on the other; (b) the aging effects are erased by heating the specimen above the glass transition temperature.

Furthermore, as shown by calorimetric data, these thermal treatments performed on PA 12 do not induce changes in the amount of crystallinity and/or in the crystallite size distribution. As a result, physical aging performed at room temperature could produce a collapse in the free volume remaining,¹⁰ which decreases in the molecular segment mobility on one hand, and increases in the storage modulus on the other hand.

PEBA Series

Materials as received. The temperature and the areas of the α_1 and α_2 relaxation peaks, respectively, are plotted versus % wt/wt PA in Figure 6. For all PEBA series, the α_1 and α_2 temperatures are located between the PA 12 homopolymer and the PE homopolymer glass transitions (glass temperature of the polyethers used is about -80°C according to Wang and Cooper¹¹), respectively. In addition, the α_1 and α_2 peak temperatures all increase with the PA ratio. Furthermore, peak areas change with the PE/PA weight ratio rather than peak magnitudes. Thus, we have nearly evaluated the α_1 and α_2 peak areas for all PEBA series. As a result, the α_1 peak area increases because the PA ratio is increased, while the α_2 peak area increases with the PE ratio. These results show that the α_1 and α_2 peaks could be related to the glass transitions of the hard and soft segments, respectively. According to Xie and Camberlin,³ α_1 is related solely to the melting of the PE crystalline phase. Thus, some discrepancy appears between their α_1 peak interpretation and ours. However, the temperature and the area of the α_1 peak all increase with PA ratio. Then, it is not expected that the PE crystalline phase amount increases with the % wt/wt PA. Moreover, calorimetric data reported by Xie and Camberlin³ show the presence of a soft crystalline phase only for PEBA samples with PE of molecular weight 2000. As a result, α_1 peak exhibited by the A and B PEBA samples (PE molecular weight = 1000) cannot occur again and cannot be consistently related to the melting of the PE crystalline phase. The α_1 peak must be consistently related to the glass transition of the hard segments, even if the melting of the PE crystalline phase should contribute as in the case of PEBA samples with PE of 2000 molecular weight (samples C, D, and E). Apparent activation energies of the α_2 and α_1 relaxation peaks are about 55–69 kcal/mol and 55–63 kcal/mol, respectively, for all PEBA series (Table III). Because the locations of the relaxation peaks are not well defined, the estimated errors of the calculated apparent activation energies are great. Despite these great errors, the apparent activation energies of the glass transitions of the soft phase (α_2 peak) for all PEBA series are close to the

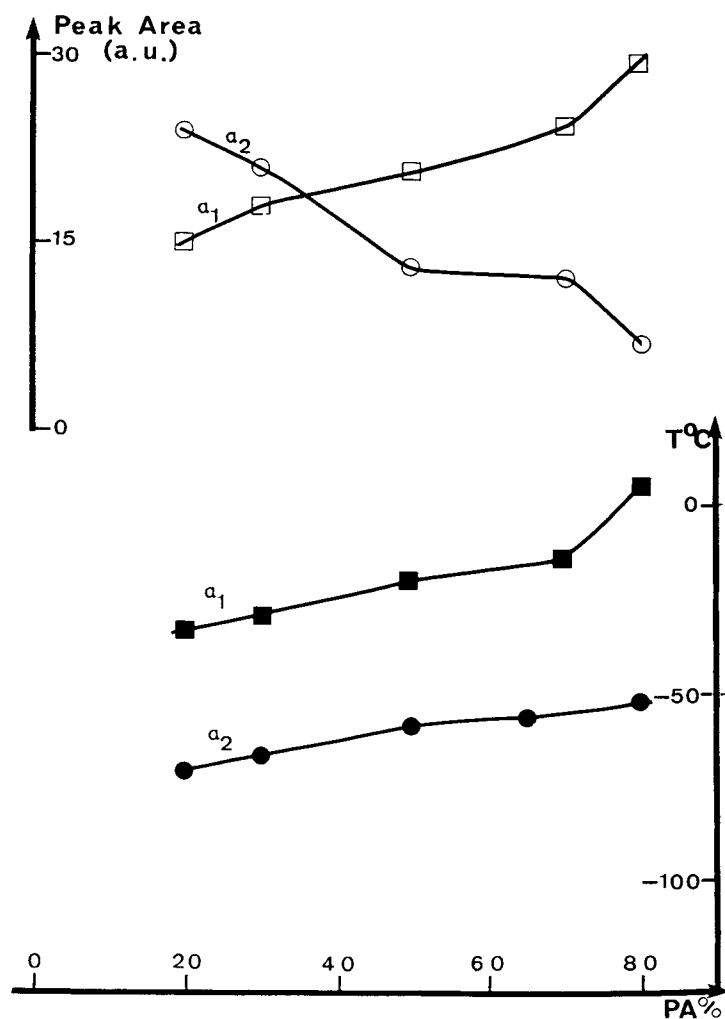


Fig. 6. Temperatures of the α_1 (■) and α_2 (●) relaxation peaks vs. PA content (% wt/wt). Areas (in arbitrary units) of the α_1 (□) and α_2 (○) relaxation peaks vs. PA content (% wt/wt).

value reported by Etienne et al.¹² regarding multisequenced polyurethanes with same polyethers (62 kcal/mol).

The β_1 peak, located between -138°C and -150°C , according to the PE/PA % wt/wt, has been previously observed on multisequenced polyurethanes based on the same polyethers.^{12,13} According to these authors, the β_1 peak could be related to a subglass transition occurring in the PE phase. According to this β_1 peak interpretation, it could be expected that the area and/or the magnitude of the β_1 peak would increase with increasing the PE ratio. However, according to the spectra reported in Figure 3, the β_1 peak magnitude and area appear to be unaffected by the PE/PA% wt/wt. As a result, the β_1 relaxation peak occurring in the PEBA samples possibly could be caused by the same number of moving units in the PE vitreous phase, regardless of the PE amount. Furthermore, apparent activation energies of the

β_1 peaks are about 6.4–8.7 kcal/mol, for all PEBA series (Table III). On increasing the PE content, the β_1 peak activation energy appears to decrease. As a result, it can be suggested that local motions concerned in the β_1 relaxation become easier on increasing the PE amount, that is, on increasing the $M_n(\text{PE})/M_n(\text{PA})$ ratio (Table I). Thus, on decreasing the macromolecular chain stiffness, the mobility of the units concerned in the β_1 process is enhanced.

The β_2 peak exhibited only on the 50%, 70%, and 80% PA PEBA spectra performed at 0.1 Hz is very likely merged in the α_2 peak in the other relaxation spectra. This β_2 peak possibly could be related to a subglass transition in the hard phase as the β peak exhibited by the PA 12 homopolymer.

Thermal Treatments Carried Out on a PEBA Sample (70% wt / wt PA)

Compared to the relaxation spectrum of the as-received specimen, relaxation spectrum of a PEBA sample (70% wt/wt PA) quenched from 110 to 15°C, as described previously, exhibits a shift toward lower temperatures and a decrease in the storage modulus in the (–90°C, +80°C) temperature range. Moreover, after this run, a slow cooling performed on this sample from 110 to 20°C does not erase the effects induced by the quenching treatment. As a result, three hypotheses could explain this. First, the physical state of the amorphous phase would be changed by the quenching treatment. Second, a decrease in the crystalline phase amount would lead to the observed results. Third, physical linkage due to Van Der Waals or hydrogen interactions in hard segment clusters would be destroyed as a consequence of soft segment diffusion at increasing temperature from 20 to 110°C. The first hypothesis is not proved because the PEBA sample was quenched at a higher temperature (15°C) than the highest glass transition (α_1 peak). Therefore, the cooling kinetics could not induce a change in the physical state of the amorphous phase. The second hypothesis is also not proved because the upper temperature (110°C) from which the quenching treatment was carried out is lower than the melting point of the hard domain crystalline phase as shown by calorimetric data. In this way, the thermal treatment does not change the crystallinity degree of the hard phase and/or the crystallite size distribution in the hard phase. Furthermore, this thermal treatment could not, consistently, change the crystallinity amount of the soft phase because the low molecular weight (1000) of the PE used does not allow the presence of a soft crystalline phase.³ As a result, the third hypothesis would be preferred. Thus, physical linkage should be destroyed by increasing the temperature to 110°C and it could lead to the decrease in the storage modulus and to the shift toward lower temperatures in the relaxation spectrum.

CONCLUSIONS

Dynamic mechanical and differential scanning calorimetric experiments were carried out to characterize the properties and the morphology of a series of polyether block amide copolymers (PEBA) with varying PE/PA weight ratios.

The dynamic mechanical spectra, performed at 1 and 0.1 Hz showed three main relaxation peaks, defined on increasing the temperature as, (1) a subglass transition of the soft phase, (2) the glass transition of the soft segments and (3) the glass transition of the hard segments. The calculated apparent activation energies of the subvitreous transition and the glass transition of the soft phase are, about, 6.4–8.7 kcal/mol and 55–69 kcal/mol, respectively. On increasing the PE, the activation energy of the subglass transition appears to decrease. This could be related to an increase in the mobility of the units concerned in this relaxation process with increasing the $M_n(\text{PE})/M_n(\text{PA})$ ratio, that is, with decreasing the macromolecular chain stiffness. Moreover, the magnitude and the area of the subglass transition peak appear to be unaffected by the PE/PA% wt/wt. While it is not expected, this could suggest that the same number of moving units are concerned in the subglass relaxation process, regardless of the PE amount. The apparent activation energy of the glass transition of the hard segments is about 55–63 kcal/mol. Because the locations of the peaks related to the glass transitions of the soft and hard phase are not well defined, the calculated apparent activation energies exhibit great estimated errors. Thus it cannot be concluded that the changes in the apparent activation energy values of the glass transitions result on increasing the PE/PA% wt/wt. Furthermore, compared to the micromechanical data exhibited by the as-received sample, a quenching treatment from 110°C (temperature lower than the melting temperature of the hard crystalline phase) to 15°C (temperature higher than the glass transition of the hard segments) performed on a PEBA sample (70% wt/wt PA) leads to a decrease in the storage modulus and to a relaxation spectrum shift toward higher temperatures. As a result, the heating of the PEBA sample up to 110°C should destroy physical linkage due to Van Der Waals or hydrogen interactions in hard segment clusters as a consequence of soft segment diffusion. The differential scanning calorimetry experiments performed on these PEBA samples show melting endotherms related to the melting of the hard crystalline phase. With increasing block length, melting temperatures are shifted toward higher temperatures showing that hard crystalline domains become larger. With increasing PA content, the amount of hard crystalline phase increases as shown by the endotherm peak areas.

Dynamic mechanical measurements were carried out in the GEMPPM department, INSA, Lyon, France. We thank Dr. Etienne for his technical assistance. We wish to thank Dr. Huet of ATOCHEM Co. for supplying the polymers described in this work.

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