

## Secondary transitions of aryl-aliphatic polyamides IV. Dynamic mechanical analysis

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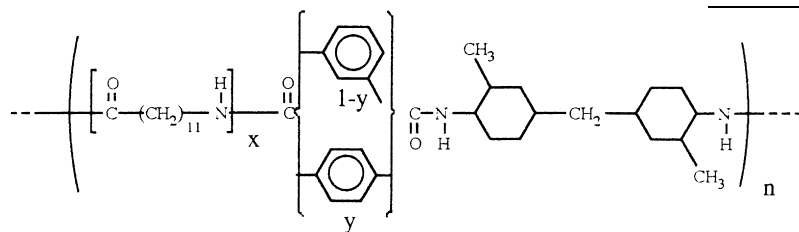
### Abstract

Dynamic mechanical analysis was performed on the aryl-aliphatic copolyamides, based on lactam-12 sequences, a tere- or iso-phthalic moiety, and a 3,3'-dimethyldicyclohexylmethane unit in regular order, whose dielectric relaxation,  $^{13}\text{C}$  NMR and  $^2\text{H}$  NMR investigations are reported in the preceding papers of this series. It demonstrates the existence of three secondary relaxations,  $\gamma$ ,  $\beta$  and  $\omega$ , which occur in the temperature and frequency ranges where similar secondary relaxations are observed by dielectric relaxation. Comparison of the results obtained in the present paper with those derived from the whole set of experiments carried out on these materials leads to a precise description of the local motions that are responsible for the observed secondary relaxations. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Aryl-aliphatic copolyamides; Secondary transitions; Dynamic mechanical analysis

### 1. Introduction

The secondary relaxations of the  $x\text{T}_y\text{I}_{1-y}$  aryl-aliphatic copolyamides:



were already investigated by several techniques. Dielectric relaxation measurements, reported in the first paper of this series [1], demonstrated the existence of several secondary relaxations  $\gamma$ ,  $\beta$  and  $\omega$ , which were assigned to motions of non-conjugated C=O groups, C=O groups located between a phenyl ring and a flexible lactam-12 sequence, and C=O groups situated between a phenyl ring and a rigid cycloaliphatic moiety, respectively. High-resolution solid-state  $^{13}\text{C}$  NMR experiments, as well as  $^2\text{H}$  NMR experiments performed on a selectively deuterated sample, corroborated the conclusions of the dielectric analysis [2,3]. Moreover, they led to a precise description of the motional behavior of

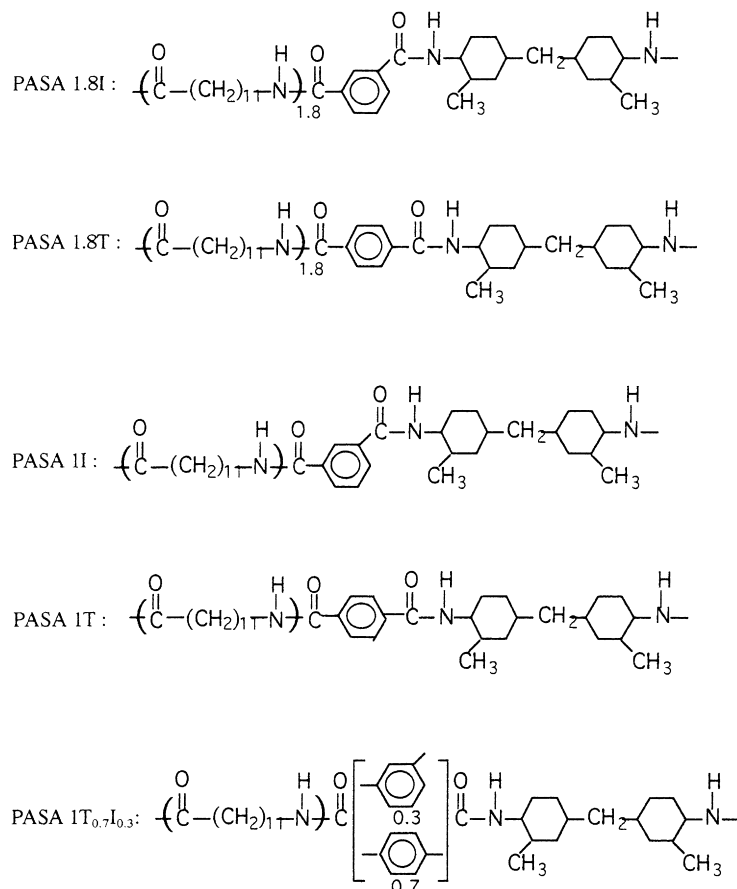
all the units, other than the C=O groups, contained in the  $x\text{T}_y\text{I}_{1-y}$  polymers. The lactam-12 methylene carbons were shown to exhibit local motions in the range of the  $\gamma$

transition, which indicates that there is a coupling of the motions of the lactam-12 C=O groups and methylene units. At higher temperatures, phenyl ring oscillations of both the tere- and iso-phthalamide rings are simultaneous to oscillations of the adjacent C=O groups and have the same amplitudes. This result demonstrates the existence of a significant coupling between the phthalamide rings and adjacent C=O groups which move in a correlated way. In addition to these ring oscillations,  $\pi$ -flips of the *para*-substituted rings were also shown to occur in the temperature and frequency domain of the  $\beta$  dielectric transition. It must be noticed that, as long as the C=O oscillations occur between states that exhibit energy differences, due for example to differences in the local packing and intermolecular interactions, they take part in the dielectric relaxations [4,5].

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Table 1

Chemical formulas of the repeat units of the  $xT_yI_{1-y}$  aryl-aliphatic copolyamides under study

Secondary relaxations can also be investigated by dynamic mechanical analysis. The comparison of data obtained from dielectric relaxation and dynamic mechanical analysis is particularly informative since the two techniques are sensitive to different parameters. In dielectric spectroscopy, only relaxation processes of dipolar groups are detected, whereas motions that are active in dynamic mechanical analysis are motions that modify the environment of the units considered.

The purpose of the present paper is the characterization of the dynamic mechanical behavior of the  $xT_yI_{1-y}$  copolyamides, the comparison of the results thus obtained with the dielectric relaxation data reported in Ref. [1] and the identification of the local motions that are responsible for the secondary transitions observed in this series of compounds.

## 2. Experimental

The chemical formulas of the copolyamides under study are shown in Table 1. The samples used in the dynamic mechanical experiments were obtained by compression

molding. This method includes a relatively slow cooling which favors the development of a noticeable crystallinity in the crystallizable 1T sample [1].

Since the dynamic mechanical behavior of polyamides is known to depend on the amount of residual water, all the samples were carefully annealed under vacuum at  $T_g + 20^\circ$  for two days at least to remove residual water. The absence of water was checked by thermal gravimetric analysis, which did not detect any loss weight at temperatures below the degradation temperature of  $450^\circ\text{C}$  in the annealed films.

The glass transition temperatures were measured using a differential scanning calorimeter (DSC) (Du Pont 1090) operating at 10 K/min. The glass transition temperature,  $T_g$ , was estimated from the intersection between the initial base line and the sloping portion of the base line due to the glass transition phenomenon.

The dynamic mechanical properties of the copolyamides under study were determined by using two different machines:

1. A servohydraulic testing machine MTS 831.10 operating in tensile mode. A sinusoidal deformation (strain

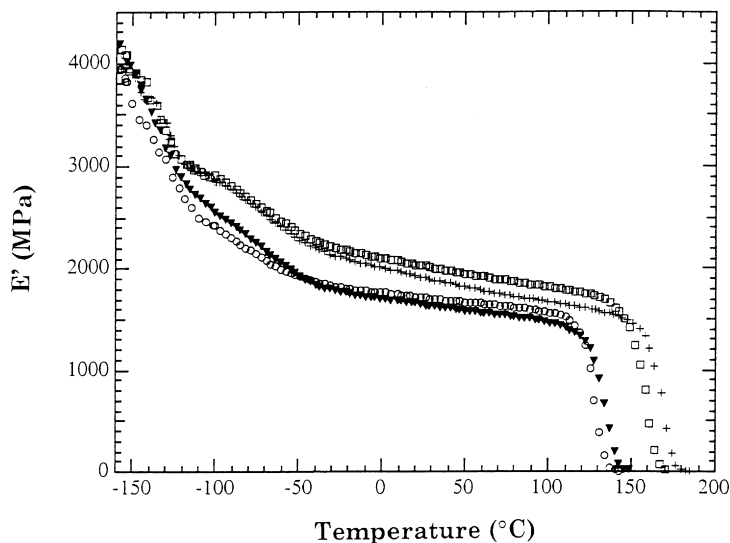


Fig. 1. Temperature dependences of  $E'$  as determined at 1 Hz for the different copolyamides under study. (○): 1.8I; (▼): 1.8T; (□): 1I; (+): 1T<sub>0.7</sub>I<sub>0.3</sub>.

amplitude as small as 0.1%) was superimposed on a static deformation of about 0.1%. The frequency domain covered by the experiments ranged from 0.03 to 80 Hz. Measurements were performed from  $-90$  to  $190^\circ\text{C}$ . The sample size was  $3 \times 15 \times 40 \text{ mm}^3$ .

2. A dynamic mechanical analyzer Dupont DMA 983. Experiments covered the frequency range from 0.1 to 2 Hz and temperatures from  $-150$  to  $190^\circ\text{C}$ . The applied strain was 0.15% in flexural mode. Samples of about  $2 \times 10 \times 40 \text{ mm}^3$  were used.

The accuracy on the determination of the temperature at which the maximum of  $E''$  or  $\tan \delta$  is observed for the  $\beta$  peak is of the order of  $3^\circ\text{C}$ , due to the natural width of the  $\beta$  peak.

Viscoelastic experiments performed in the tensile mode yield directly the storage modulus,  $E'$ , loss modulus,  $E''$ ,

damping,  $\tan \delta = E''/E'$ , and loss compliance,  $J'' = E''/[E'^2 + E''^2]$ . The flexural data were transformed into  $E'$  and  $E''$  by using a routine available on the Dupont DMA 983 and a Poisson ratio equal to 0.33 in the glassy state.

The choice of the viscoelastic function that should be used for a quantitative comparison of the mechanical behavior of different materials is still an open question. However, results obtained by Charlesworth [6] on epoxy-amine networks, as well as data obtained in our laboratory on MMA-based copolymers [7] and epoxy-amine networks [8], indicate that the loss compliance can be considered as the most relevant parameter, at least for additive purposes. Therefore, in the following, the semi-quantitative analysis and the comparison of the viscoelastic data determined for the different systems will be performed

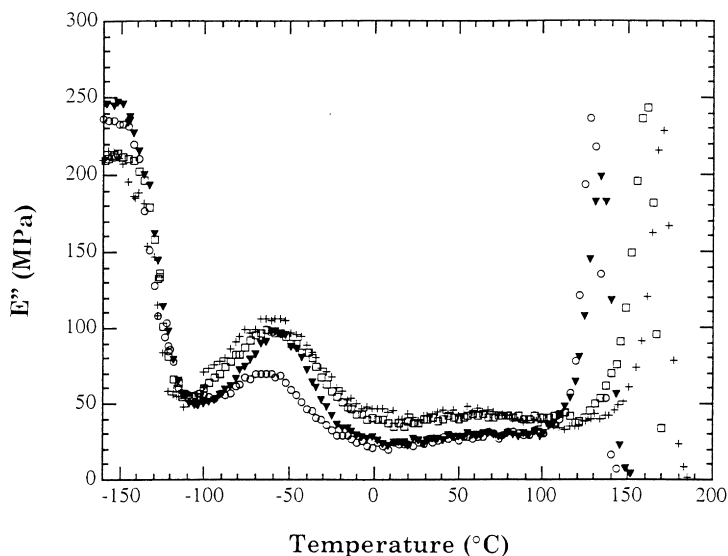


Fig. 2. Temperature dependences of  $E''$  as determined at 1 Hz for the different copolyamides under study. (○): 1.8I; (▼): 1.8T; (□): 1I; (+): 1T<sub>0.7</sub>I<sub>0.3</sub>.

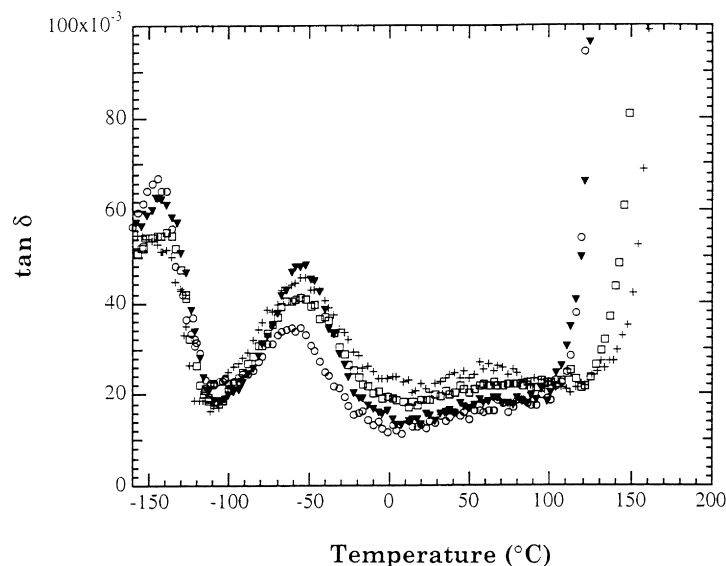


Fig. 3. Temperature dependences of  $\tan \delta$  as determined at 1 Hz for the different copolyamides under study. Note that only a small part of the transition associated to the glass transition phenomenon is shown in the figure since its amplitude is about 30 times larger than the amplitude of the secondary transitions. (○): 1.8I; (▼): 1.8T; (□): 1I; (+): 1T<sub>0.7</sub>I<sub>0.3</sub>.

in terms of  $J''$ . Such a description in terms of compliance corresponds to deformation of viscoelastic elements in series and implies the strain additivity, in agreement with the very simple idea of a stress applied, at the molecular level, on the chain extremities and inducing a series deformation of the different constitutive units.

### 3. Results and discussion

The temperature dependences of  $E'$ ,  $E''$ ,  $\tan \delta$ , as determined at 1 Hz for the different copolyamides under study, are shown in Figs. 1–3, respectively. They point out the existence of the glass transition phenomenon at high temperature and, at lower temperatures, the presence of three secondary transitions  $\gamma$ ,  $\beta$  and  $\omega$ .

#### 3.1. The glass transition

The temperatures,  $T_{\alpha}(E'')$  and  $T_{\alpha}(\tan \delta)$ , at which  $E''$  and  $\tan \delta$  are maximum at 1 Hz, in the region of the glass transition phenomenon, are listed in Table 2 for the different samples, together with the glass transition temperature,  $T_g$ , derived from DSC experiments. Whatever the copolyamide

Table 2  
Values of  $T_{\alpha}(E'')$  and  $T_{\alpha}(\tan \delta)$ , (°C), determined at 1 Hz, and  $T_g$  (DSC), (°C), for the different copolyamides under study

Copolyamide	$T_{\alpha}(E'')$	$T_{\alpha}(\tan \delta)$	$T_g$ (DSC)
1.8I	130	140	118
1.8T	137	146	124
1I	161	170	151
1T <sub>0.7</sub> I <sub>0.3</sub>	171	180	159

composition, the  $T_{\alpha}(\tan \delta) - T_{\alpha}(E'')$  difference has the 9–10° usual value. In the following,  $T_{\alpha}(E'')$  will be denoted as  $T_{\alpha}$ .  $T_g$  and  $T_{\alpha}$  exhibit a systematic difference of the order of 10°C.

As shown by the data displayed in Table 2, the increase in the lactam-12 amount (from 1 to 1.8 moles in the repeat unit) is accompanied by a strong decrease, of the order of 30° in  $T_{\alpha}$ , in agreement with the flexible character of the lactam-12 moiety. Besides, for a given lactam-12 content, the replacement of terephthalic acid by isophthalic acid induces a slight  $T_{\alpha}$  decrease of the order of 6 and 10° for the 1.8T<sub>y</sub>I<sub>1-y</sub> and 1T<sub>y</sub>I<sub>1-y</sub> polymers, respectively. A similar behavior was observed for other polyamides [9], as well as for polysulfones [10], polyesters [11] and polyimides [12,13].

#### 3.2. The $\gamma$ secondary transition

As shown in Figs. 2 and 3, the  $\gamma$  transition, observed from dynamic mechanical analysis at 1 Hz, is centered around -150°C, in the temperature region of the  $\gamma$  transition observed by dielectric relaxation [1]. In both cases, the temperature range available experimentally does not permit to observe the whole  $\gamma$  relaxation. However, the agreement between the two techniques is qualitatively good in the investigated domain, which suggests that the aliphatic C=O groups, responsible for the  $\gamma$  dielectric relaxation, take part also in the  $\gamma$  mechanical process.

The determinant rôle of the lactam-12 units in the  $\gamma$  transition is clearly demonstrated by the following approach, based on the loss compliance,  $J''$  (Fig. 4). The ratios of the  $J''$  value, determined at -135° and 1 Hz (i.e. in the region of the  $\gamma$  transition) for the considered sample, to

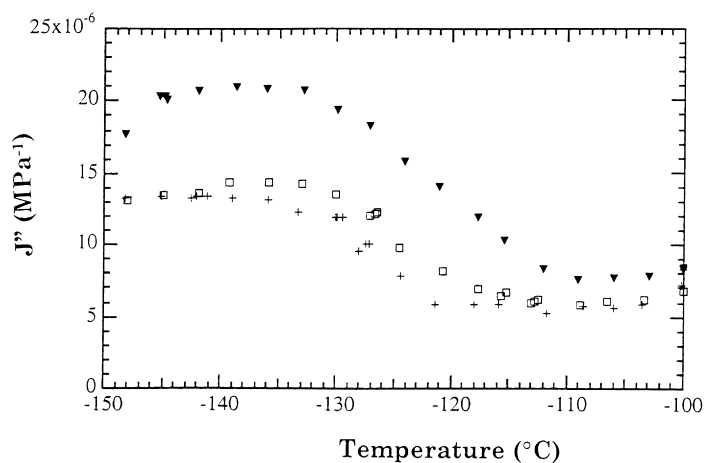


Fig. 4. Temperature dependences of  $J''$  as determined at 1 Hz for the copolyamides under study in the region of the  $\gamma$  relaxation. ( $\blacktriangledown$ ): 1.8T; ( $\square$ ): II; (+): 1T<sub>0.7</sub>I<sub>0.3</sub>.

the  $J''$  value measured under the same conditions for the II polymer, taken as a reference, are listed in Table 3. Within experimental accuracy, these ratios are very close to the  $x$  parameter, which defines the number of lactam sequences in the repeat unit of the  $xT_yI_{1-y}$  copolyamides. This result indicates that the intensity of the  $\gamma$  peak is mostly determined by the amount of lactam-12 units. It does not depend on the nature, tere- or iso-, of the phthalic acid.

It is also important to notice that the temperature region of the  $\gamma$  process of the  $xT_yI_{1-y}$  aryl-aliphatic polyamides under study is close to the temperature domain of the  $\gamma$  mechanical relaxation observed in aliphatic polyamides. In aliphatic polyamides [14–16], the intensity of the  $\gamma$  peak in  $\omega$ -amino acid-based polyamides is an increasing function of the number of methylene carbons in the repeat unit. As a consequence, the  $\gamma$  transition was assigned to local motions involving the  $-(CH_2)_n-$  sequences and the adjacent amide groups. This interpretation of the  $\gamma$  transition in aliphatic polyamides is consistent with the above observations derived from the dynamic mechanical analysis of the  $xT_yI_{1-y}$  aryl-aliphatic polyamides. It is also in agreement with NMR data [2], which pointed out the existence of local motions of the lactam-12  $CH_2$  carbons in the region of the  $\gamma$  process. Therefore, in the  $xT_yI_{1-y}$  aryl-aliphatic polyamides, the  $\gamma$  transition is very likely to originate from motions localized in the  $(CH_2)_n$  sequences of the lactam-12 units and adjacent amide groups. It is of interest to note that the  $\gamma$  relaxation in polyethylene, which is also due to motions

of  $(CH_2)_n$  sequences, is observed around  $-100^\circ\text{C}$  at 1 Hz [14,17], i.e. at a somewhat higher temperature than the temperature of the  $\gamma$  transition of aryl-aliphatic polyamides.

### 3.3. The $\beta$ secondary transition

In contrast to the  $\gamma$  transition, the  $\beta$  relaxation is observed in its entirety in the temperature range available. As shown in Figs. 5 and 6, the  $\beta$  transition occurs in the temperature range from  $-100$  to  $0^\circ\text{C}$  at 1 Hz. It exhibits very similar characteristics in the II, 1T<sub>0.7</sub>I<sub>0.3</sub> and 1.8T samples. With respect to these polymers, the position of the  $\beta$  peak in the 1.8I copolyamide is shifted to lower temperature and the intensity of the transition is lower. As shown by reproducibility experiments plotted in Fig. 6, the difference between the viscoelastic behaviors of the 1.8I and 1.8T polymers in the region of the maximum of the  $\beta$  peak is much larger than the experimental uncertainty.

### 3.4. Influence of the nature of the acid in the 1.8I and 1.8T samples

As shown in Fig. 6, the low temperature part of the  $\beta$  transition is identical in the 1.8I and 1.8T sample. In the high temperature region of this transition, an additional contribution is observed for the 1.8T copolyamide. From results obtained by dielectric [1] and  $^{13}\text{C}$  and  $^2\text{H}$  NMR investigations [2,3], the  $\beta$  transition was assigned to motions of the aromatic rings and amide groups located between the phenyl ring and the lactam-12 unit. Moreover,  $\pi$ -flips of the phenyl rings were also observed in the region of the  $\beta$  transition. Since  $\pi$ -flips occur in *para*-substituted rings only, the comparison of the  $\beta$  peak in the 1.8I and 1.8T samples tends to indicate that the high temperature contribution present in the 1.8T polyamide and absent in the 1.8I polymer is due to  $\pi$ -flips of the phenyl rings. In contrast, the low temperature region of the  $\beta$  transition, which is identical in the two polymers, is likely to arise from oscillations of the phenyl rings and adjacent amide groups.

Table 3

Ratios of the  $J''$  value, determined at  $-135^\circ$  and 1 Hz for the considered sample, to the  $J''(II)$  value measured under the same conditions for the II polymer, taken as a reference

Copolyamide	$J''/J''(II)$	$x$
1T <sub>0.7</sub> I <sub>0.3</sub>	0.9	1
II	1	1
1.8T	1.45	1.8

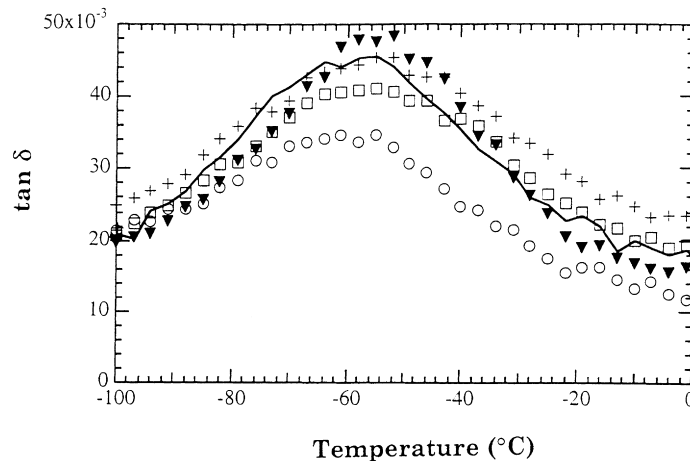


Fig. 5. Temperature dependences of  $\tan \delta$  as determined at 1 Hz for the different copolyamides under study in the region of the  $\beta$  relaxation. (O): 1.8I; ( $\blacktriangledown$ ): 1.8T; ( $\square$ ): II; (+): 1T<sub>0.7</sub>I<sub>0.3</sub>; (-): 1T.

Since these oscillations are mechanically active, they should be accompanied by a local reorganization of the environment of the mobile unit. It is of interest to compare the present interpretation of the  $\beta$  transition in aryl-aliphatic copolyamides with conclusions reached by Maxwell et al. [5] on polyethyleneterephthalate whose  $\beta$  relaxation has a position and extent very comparable to those observed in the present copolyamides. In polyethyleneterephthalate, the low temperature part of the  $\beta$  transition was associated to local motions of the ester groups whereas the high temperature region was assigned to  $\pi$ -flips of the phenyl rings [5], just as in the copolyamides under study.

### 3.5. Influence of the nature of the acid in the II, 1T<sub>0.7</sub>I<sub>0.3</sub> and 1T samples

The amplitudes of the  $\beta$  transition are very similar in the II, 1T and 1T<sub>0.7</sub>I<sub>0.3</sub> copolyamides. Based on the above assignment of the high temperature part of the  $\beta$  transition to  $\pi$ -flips of the phenyl rings, a larger amplitude should be expected for an entirely amorphous 1T polymer. However, since the 1T sample is semi-crystalline and  $\pi$ -flips of the

phenyl rings occur in the amorphous phase only, no quantitative comparison can be made for this polymer. The behavior of the 1T<sub>0.7</sub>I<sub>0.3</sub> sample will be discussed at the end of the next section.

### 3.6. Influence of the lactam-12 content

As shown in Fig. 5, the intensity of the  $\beta$  transition is higher in the II than in the 1.8I polymer. In these samples, the increase of the lactam-12 content from 1 to 1.8 induces a change in the density of the phenyl rings and amide groups that are active in the  $\beta$  transition. This density can be estimated by using the following formula:

$$N_{\beta} = n\rho N_{Av}/M_0$$

where  $N_{\beta}$  is the number of active groups per volume unit at the  $\beta$  transition,  $n$  the number of CO–NH– $\Phi$  groups, associated to the  $\beta$  transition, per repeat unit,  $\rho$  the mass of the volume unit of the polymer,  $N_{Av}$  the Avogadro number and  $M_0$  the molar mass of the repeat unit. The values of  $n$ ,  $\rho$ ,  $M_0$  and  $N_{\beta}$  are listed in Table 4 for the II and 1.8I polymers. The ratio of the  $N_{\beta}$  value in the II polymer,  $N_{\beta}$

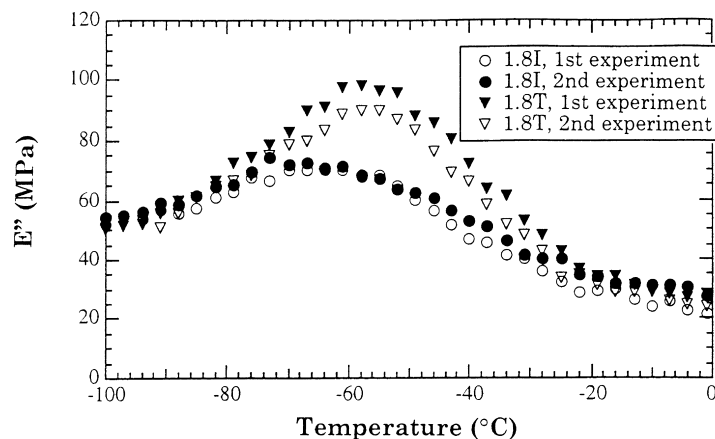


Fig. 6. Reproducibility of viscoelastic data in the region of the  $\beta$  relaxation, as obtained by using the MTS 831.10 testing machine.

Table 4  
Characteristics of the 1I and 1.8I samples

Copolyamide	<i>n</i>	$\rho$ (g cm <sup>-3</sup> )	$M_0$ (g mol <sup>-1</sup> )	$N_\beta$ (cm <sup>-3</sup> )
1I	1	1.055	565	$1.13 \times 10^{21}$
1.8I	1	1.042	722.6	$0.87 \times 10^{21}$

(1I), to the  $N_\beta$  value in the 1.8I polymer,  $N_\beta$  (1.8I), is equal to 1.30. The ratio of the respective areas of the  $\beta$  transition as determined from the plots of  $J''$  vs temperature in these two polymers is equal to 1.31. The equality of these two ratios indicates that the intensity decrease observed for the  $\beta$  transition in the 1.8I polymer is due to the dilution of the mechanically active groups which results from the increase in the lactam-12 content.

### 3.7. Analysis of the cooperativity of local motions

Table 5 shows the activation energies,  $E_{a_{\max}}$  and  $E_{a_{\text{end}}}$ , and entropies,  $\Delta S_{\max}$  and  $\Delta S_{\text{end}}$ , determined at the maximum and end of the  $\beta$  transition, respectively, by using Starkweather analysis [18–20]. Whatever the polymer considered, except the 1.8T copolyamide, the  $E_{a_{\max}}$  and  $\Delta S_{\max}$  values are in the range from 55 to 60 kJ mol<sup>-1</sup> and from 30 to 40 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. In the 1.8T sample,  $E_{a_{\max}}$  and  $\Delta S_{\max}$  are equal to 65 and 60 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. At the end of the  $\beta$  transition, the activation energies are 10–15 kJ mol<sup>-1</sup> higher than the  $E_{a_{\text{end}}}$  values in the 1.8I, 1I and 1T<sub>0.7</sub>I<sub>0.3</sub> polymers, whereas, in the 1T and 1.8T samples, the increase from  $E_{a_{\max}}$  to  $E_{a_{\text{end}}}$  is of the order of 25–30 kJ mol<sup>-1</sup>. The same tendencies are observed for the activation entropies: the  $\Delta S_{\max}$  and  $\Delta S_{\text{end}}$  values are equal in the 1.8I, 1I and 1T<sub>0.7</sub>I<sub>0.3</sub> polymers within experimental accuracy. The rather small values of  $\Delta S_{\max}$  and  $\Delta S_{\text{end}}$  in these samples indicate that the motions that are responsible for the  $\beta$  transition are very localized modes [9]. On the other hand, in the polymers based on terephthalic acid only,  $\Delta S_{\text{end}}$  is approximately twice the value of  $\Delta S_{\max}$ , which implies that the motional cooperativity is higher in the high temperature part of the  $\beta$  transition than around the temperature of the maximum of the  $\beta$  peak. Using the above interpretation of the  $\beta$  transition, the more cooperative motions are straightforwardly identified as motions involving the  $\pi$ -flips of the phenyl rings whereas the localized modes that occur in the lower temperature region are oscillations of the phenyl rings and adjacent amide groups. This result is in perfect agreement with the conclusions

Table 5  
Activation energies and entropies determined at the maximum and end of the  $\beta$  transition, using Starkweather analysis

Copolyamide	$E_{a_{\max}}$ (kJ mol <sup>-1</sup> )	$\Delta S_{\max}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$E_{a_{\text{end}}}$ (kJ mol <sup>-1</sup> )	$\Delta S_{\text{end}}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
1.8I	55	30	70	35
1.8T	65	60	95	120
1I	55	30	70	25
1T <sub>0.7</sub> I <sub>0.3</sub>	60	40	70	30
1T	60	40	85	85

derived by Maxwell et al. [5] on polyethyleneterephthalate who associated the low and high temperature regions of the  $\beta$  transition to localized modes of the ester groups and more cooperative motions involving  $\pi$ -flips of the phenyl rings, respectively.

As shown by the  $\Delta S_{\max}$  and  $\Delta S_{\text{end}}$  values reported in Table 5, there is no indication of the existence of cooperative  $\beta$  motions in the 1T<sub>0.7</sub>I<sub>0.3</sub> sample. This result indicates that the cooperative motions that involve  $\pi$ -flips of the phenyl rings in the high temperature region of the  $\beta$  transition cannot occur without a high density of *para*-substituted rings in a given site.

### 3.8. The $\omega$ transition

The  $\omega$  transition is a weak and wide transition centered around 60°C, in the temperature range of the  $\omega$  secondary relaxation observed by dielectric relaxation [1]. As observed also by dielectric relaxation, the position and width of the  $\omega$  mechanical peak are independent of the copolyamide composition, within experimental accuracy.

The common features shared by the  $\omega$  mechanical and dielectric transitions tend to indicate that these two phenomena have the same origin, i.e. they arise from motions that involve the conjugated amide groups situated between the aromatic ring and aliphatic cyclodiamine.

### 3.9. The temperature dependence of the storage modulus

The temperature dependence of the storage modulus,  $E'$ , is shown in Fig. 1 for the various samples under study.

The values of the storage moduli,  $E'_{-155^\circ\text{C}}$  and  $E'_{-105^\circ\text{C}}$ , determined at  $-155$  and  $-105^\circ\text{C}$ , respectively, for the different copolyamides, as well as the  $E'_{-155^\circ\text{C}} - E'_{-105^\circ\text{C}}$  differences, are listed in Table 6. At low temperatures, the storage moduli tend to a common value, independently of their chemical composition. In contrast, at  $-105^\circ\text{C}$ , which can be considered as the end of the  $\gamma$  transition, the moduli of the 1.8T and 1.8I compounds are 300 MPa lower than the modulus of the 1I and 1T<sub>0.7</sub>I<sub>0.3</sub> materials. As shown by the data reported in Table 6, the  $E'_{-155^\circ\text{C}} - E'_{-105^\circ\text{C}}$  difference does not depend on the nature of the acid (tere- or isophthalic acid). It increases on increasing the lactam-12 content. These results are consistent with the above assignment of the  $\gamma$  transition to motions involving parts of the lactam-12 moieties.

The values of the storage moduli,  $E'_{-100^\circ\text{C}}$  and  $E'_{0^\circ\text{C}}$ ,

Table 6

Storage moduli (MPa) at  $T = -155^{\circ}\text{C}$ ,  $T = -105^{\circ}\text{C}$  and decrease of the storage modulus between  $-155$  and  $-105^{\circ}\text{C}$  for the copolyamides under study

Copolyamide	$E'_{-155^{\circ}\text{C}}$	$E'_{-105^{\circ}\text{C}}$	$E'_{-155^{\circ}\text{C}} - E'_{-105^{\circ}\text{C}}$
1.8I	3950	2450	1500
1.8T	4190	2640	1550
II	4120	2920	1200
1T <sub>0.7</sub> I <sub>0.3</sub>	3960	2910	1050

determined at  $-100$  and  $0^{\circ}\text{C}$ , respectively, on each side of the  $\beta$  transition, for the different copolyamides, as well as the  $E'_{-100^{\circ}\text{C}} - E'_{0^{\circ}\text{C}}$  differences, are listed in Table 7. The  $\beta$  transition is accompanied by a 800 MPa decrease of the storage modulus for the 1.8T, II and 1T<sub>0.7</sub>I<sub>0.3</sub> samples and a 650 MPa decrease for the 1.8I copolyamide, whose  $\beta$  transition is of relatively lower intensity. It must be noticed that the storage modulus decrease induced by the  $\beta$  transition is lower than the storage modulus decrease induced by the  $\gamma$  transition.

The values of the storage moduli,  $E'_{20^{\circ}\text{C}}$  and  $E'_{80^{\circ}\text{C}}$ , determined at 20 and  $80^{\circ}\text{C}$ , respectively, on each side of the  $\omega$  transition, for the different copolyamides, as well as the  $E'_{20^{\circ}\text{C}} - E'_{80^{\circ}\text{C}}$  differences, are listed in Table 8. The  $\omega$  transition only induces a weak decrease in the storage modulus. The  $E'_{20^{\circ}\text{C}} - E'_{80^{\circ}\text{C}}$  difference is an increasing function of the terephthalic acid content and a decreasing function of the lactam-12 content. The latter units act as a diluent for the groups that are mechanically active in the  $\omega$  transition.

#### 4. Conclusions

The dynamic mechanical analysis of the aryl-aliphatic copolyamides under study demonstrates the existence of three secondary relaxations,  $\gamma$ ,  $\beta$  and  $\omega$ , which occur in the temperature and frequency ranges where similar secondary relaxations are observed by dielectric relaxation.

The lactam-12 units, whose non-conjugated amide groups and methylene carbons undergo motions in a low temperature range, are responsible for the  $\gamma$  transition. This origin of the  $\gamma$  transition is comparable to the one observed in aliphatic polyamides. The amplitude of the  $\gamma$  peak, as estimated from the loss compliance,  $J''$ , is largely determined by the lactam-12 content in the repeat unit of

Table 7

Storage moduli (MPa) at  $T = -100^{\circ}\text{C}$ ,  $T = 0^{\circ}\text{C}$  and decrease of the storage modulus between  $-100$  and  $0^{\circ}\text{C}$  for the copolyamides under study

Copolyamide	$E'_{-100^{\circ}\text{C}}$	$E'_{0^{\circ}\text{C}}$	$E'_{-100^{\circ}\text{C}} - E'_{0^{\circ}\text{C}}$
1.8I	2420	1770	650
1.8T	2600	1700	900
II	2900	2100	800
1T <sub>0.7</sub> I <sub>0.3</sub>	2900	2000	900

Table 8

Storage moduli (MPa) at  $T = 20^{\circ}\text{C}$ ,  $T = 80^{\circ}\text{C}$  and decrease of the storage modulus between 20 and  $80^{\circ}\text{C}$  for the copolyamides under study

Copolyamide	$E'_{20^{\circ}\text{C}}$	$E'_{80^{\circ}\text{C}}$	$E'_{20^{\circ}\text{C}} - E'_{80^{\circ}\text{C}}$
1.8I	1710	1610	100
1.8T	1650	1510	140
II	2030	1860	170
1T <sub>0.7</sub> I <sub>0.3</sub>	1920	1710	210

the copolyamide. As a consequence, the storage modulus of copolyamides containing 1.8 lactam-12 units in the repeat unit is lower than the modulus of compounds containing 1 lactam-12 unit in the repeat unit at temperatures higher than  $-120^{\circ}\text{C}$ .

The  $\beta$  transition involves the conjugated  $\Phi$ -CONH sequence, where the relevant amide group is situated between the aromatic ring and the lactam-12 moiety. The mechanical response is closely related to the ring motions. Whereas the lower temperature part of the  $\beta$  transition can be assigned to localized motions of amide groups and isophthalic or terephthalic rings, the higher temperature range of the  $\beta$  transition is associated with intra- or intermolecular cooperative motions involving  $\pi$ -flips of the terephthalic rings.

The characteristics of the  $\omega$  transition are very similar, whatever the investigation technique, which tends to show that the mechanical and dielectric  $\omega$  relaxations are both due to motions that involve the amide groups located between the phenyl rings and cycloaliphatic moiety. The replacement of terephthalic rings by isophthalic rings induces a decrease in the intensity of the  $\omega$  transition and, as a consequence, a higher storage modulus in the temperature range delimited by the  $\omega$  relaxation and the glass transition.

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#### References

- [1] Beaume F, Lauprêtre F, Monnerie L, Maxwell A, Davies GR. *Polymer* 2000;41:2677.
- [2] Beaume F, Lauprêtre F, Monnerie L. *Polymer* 2000;41:2989.
- [3] Garin N, Hirschinger J, Beaume F, Lauprêtre F. *Polymer* 20:41; in press.
- [4] Nicholson TM, Davies GR. In preparation.
- [5] Maxwell AS, Monnerie L, Ward IM. *Polymer* 1998;39:6851.
- [6] Charlesworth JM. *J Mater Sci* 1993;28:399.
- [7] Tézé L. Thèse de l'Université Paris 6, 1995.
- [8] Heux L, Halary JL, Lauprêtre F, Monnerie L. *Polymer* 1997;38:1767.
- [9] Park Y, Ko J, Ahn T, Choe S. *J Polym Sci, Polym Phys Ed* 1997;35:807.
- [10] Aitken CL, McHattie JS, Paul DR. *Macromolecules* 1992;25:2910.
- [11] Sheu FR, Chern RT. *J Polym Sci, Polym Phys Ed* 1989;27:1121.



- [12] Stern SA, Mi Y, Ymamamoto H, Clair A. *J Polym Sci, Polym Phys Ed* 1989;27:1887.
- [13] Coleman MR, Koros WJ. *J Memb Sci* 1990;50:285.
- [14] McCrum NG, Read BE, Williams G. *Anelastic and dielectric effects in polymeric solids*, London: Wiley, 1967.
- [15] Varlet J, Cavaillé JY, Perez J. *J Polym Sci, Polym Phys Ed* 1990;28:2691.
- [16] Pathmanathan K, Cavaillé JY, Johari GP. *J Polym Sci, Polym Phys Ed* 1992;30:341.
- [17] Willbourn AH. *Trans Faraday Soc* 1958;54:717.
- [18] Starkweather HW. *Polymer* 1991;32:2443.
- [19] Starkweather HW. *Macromolecules* 1988;21:1798.
- [20] Starkweather HW. *Macromolecules* 1981;14:1277.