Secondary transitions of aryl-aliphatic polyamides
II. High-resolution solid-state ^{13}C NMR investigation

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Abstract

High-resolution solid-state ^{13}C NMR experiments were performed on the two series of aryl-aliphatic copolyamides whose dielectric relaxation investigation is reported in the first paper of this series. The local motions were studied by following the temperature dependence of ^{13}C chemical shift anisotropies and ^{13}C–^{1}H dipolar couplings. In the copolyamides that contain a lactam-12 sequence, the lactam-12 sequences were shown to be involved in significant motions, even at low temperatures. In contrast, in the copolymers whose aliphatic part is a methylpentane sequence, the methylpentane sequences do not exhibit detectable motions at temperatures below 100°C. In all the systems investigated, the aromatic rings were shown to undergo oscillations whose amplitudes and axis depend of the relative *meta-* or *para-* positions of the substituents. In addition to these oscillations, *para*-substituted rings are also involved in π-flips. The motions of the lactam-12 sequences were associated with the γ-relaxation processes whereas both oscillations and π-flips occur in the temperature and frequency ranges of the β-transition observed by dielectric relaxation. © 2000 Elsevier Science Ltd. All rights reserved.
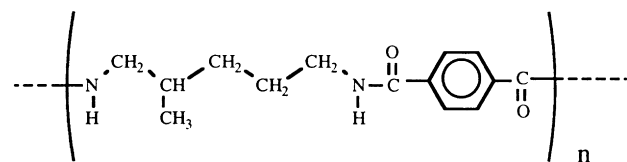
Keywords: Aryl-aliphatic copolyamides; Secondary transitions; High-resolution solid-state ^{13}C NMR

1. Introduction

Dielectric relaxation measurements performed on the xT$_y$I$_{1-y}$ aryl-aliphatic copolyamides
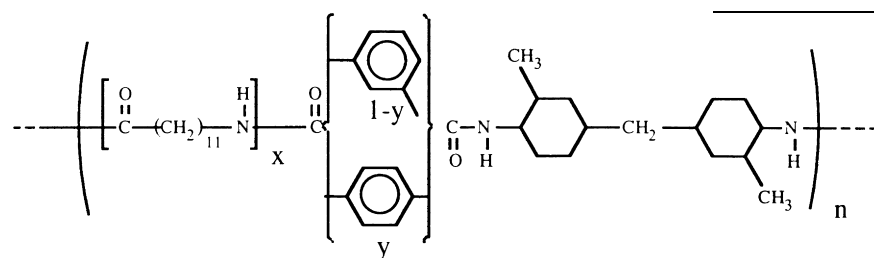
and MT copolyamide

were reported in the first paper of this series [1]. They demonstrated the existence of several secondary relaxations, which were assigned to motional modes of the carbonyl groups contained in these materials. More precisely, the comparison of the results obtained from the xT$_y$I$_{1-y}$ and MT samples permitted to assign the γ, β and ω relaxations, observed by dielectric relaxation, to motions of non-conjugated C=O groups, C=O groups located between a phenyl ring and a flexible lactam-12 or a methylpentane sequence, and C=O groups situated between a phenyl ring and a rigid cycloaliphatic moiety, respectively.

The purpose of the present work is to get a more detailed description of the motions involved in the secondary relaxations of the above aryl-aliphatic polyamides by

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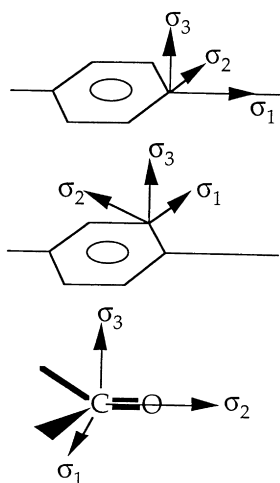*E-mail address:* francoise.laupretre@glvt-cnrs.fr (F. Lauprêtre).

Fig. 1. Directions of the principal axes of the chemical shift tensors used in the paper.

using high-resolution solid-state ^{13}C NMR. In contrast with dielectric relaxation which exclusively focuses on the motions of electric dipoles, high-resolution solid-state ^{13}C NMR provides specific information on the motional behavior of each magnetically inequivalent carbon contained in the repeat unit. Therefore, besides corroborating the conclusions obtained from dielectric data, ^{13}C NMR experiments should also permit to characterize the participation of each part of the constitutive units of the molecule-cycloaliphatic diamine, lactam-12 unit and phenyl rings— to the secondary relaxations of the copolyamides under interest.

The NMR quantities used to derive information on the local motions in the present paper were the ^{13}C chemical shift anisotropies of the unsaturated carbons and the ^{13}C–^{1}H dipolar couplings inside the CH and CH$_2$ groups. The chemical shift anisotropies were determined from the relative intensities of the spinning side bands [2] whereas the measurements of the dipolar couplings, $\langle b^2 \rangle$, were based on the rises of the ^{13}C magnetization in cross-polarization experiments with very short contact times [3]. Indeed, for carbons that are strongly coupled to protons, the rises of polarization, at short contact times, are due to a coherent energy transfer between the carbon and the directly bonded protons, whereas at longer times, this oscillatory transfer is damped by the coupling with the more remote protons, and an incoherent transfer involving spin diffusion then takes place. As a result of the coherent energy transfer which is dominant at short contact times, the contact time necessary to obtain half the maximum of the magnetization, $t_{1/2}$, can be expressed as a function of $\langle b^2 \rangle$ and n, the number of directly bonded protons:

$$t_{1/2} = \pi/(n\langle b^2 \rangle)^{1/2} \qquad (1)$$

For a C–H distance of 1.09 Å and a rigid lattice, $t_{1/2} = 24\ \mu s$ for a CH group and $t_{1/2} = 17\ \mu s$ for a CH$_2$ group. A

reduction in the ^{13}C–^{1}H dipolar coupling by motional processes whose frequency is equal to or higher than a few tens of kHz induces an increase in the $t_{1/2}$ value [3].

Within the accuracy of the data thus obtained, the motional averaging of the chemical shift tensors and ^{13}C–^{1}H dipolar couplings can be interpreted either in terms of rather slow motions with a constant amplitude and with an increasing rate as a function of temperature, or in terms of rapid motions with an increasing amplitude as a function of temperature. The latter assumption was used in the following. The motional model considered for the *para*-substituted phenyl rings was based on (i) rapid oscillations about the *para*-axis of the ring between angles α and $-\alpha$, corresponding to a 2α amplitude of motion, and (ii) fast π-flips of the phenyl rings. In *meta*-substituted phenyl rings, only oscillations occurring about an axis joining the two N atoms were considered. Besides, the copolyamides under study were either entirely or nearly entirely amorphous as a result of their thermal history. Since there was no evidence of dynamic heterogeneity within the accuracy of the experiments, the dynamic heterogeneity of the samples was neglected as a first approximation and the motional behavior of the rings was described at a given temperature in terms of (i) an average oscillation amplitude and (ii) a fraction of phenyl rings undergoing fast π-flips.

From the point of view of its chemical formula, the MT copolyamide is the simplest sample among the copolyamides under study. Therefore, we will first report results obtained on this polymer and carefully describe the data analysis performed on this polymer. Then, we will deal with the xT_yI_{1-y} copolyamides and use the same methodology for the data interpretation.

2. Experimental

The origins and characteristics of the copolyamides used in the present study were described in the first paper of this series [1]. Since we are interested in the secondary relaxations occurring in the amorphous phase, the following procedure was systematically used to strongly inhibit the crystallinity of the semicrystalline MT and 1T polymers: samples were annealed for a few minutes at 320°C under nitrogen atmosphere and then, quenched in liquid nitrogen.

The high-resolution solid-state ^{13}C NMR experiments [4] were conducted at 75.47 MHz with Bruker CXP300, MSL300 and ASX300 spectrometers, with quadrature detection and a single r.f. coil which was double tuned for both ^{13}C and ^{1}H. Proton dipolar decoupling (DD) and magic angle sample spinning (MAS) were used. The spinning speed was in the range from 4500 to 5000 Hz. Its exact value was taken in such a way to avoid the overlap of main lines and spinning side bands. The pulse sequence consisted of a cross-polarization (CP) proton dipolar decoupling sequence. The matched spin-lock cross-polarisation transfers were carried out with ^{13}C and ^{1}H magnetic

Table 1
Principal components of the ^{13}C chemical shift tensors in terephthalic dihydrazide and isophthalamide

Model molecule	C considered	σ_1 (ppm)	σ_2 (ppm)	σ_3 (ppm)
Terephthalic dihydrazide	–C=O–	−80	−5	85
	Aromatic unprotonated C	−97	−17	128
	Aromatic CH	−102	−25	127
Isophthalamide	–C=O–	−69	−20	89
	Aromatic unprotonated C	−89	25	114
	Aromatic CH	−96	−26	122

field strengths of 64 kHz. Unless otherwise specified, the contact duration was 1 ms. The delay time between two successive pulse sequences was taken as 2 s. Spin-temperature inversion techniques allowed the minimization of baseline noise and roll [5]. The variable temperature experiments were made in the temperature range from −150 to 250°C. The temperature calibration was established by using crystalline organic compounds with known melting points in the high temperature range and chemical shift data on samarium acetate [6] in the low temperature range.

The $t_{1/2}$ values were obtained from the variation of the intensities of the different CH and CH$_2$ lines. The maximum magnetization that can be acquired by cross-polarization, S_{max}, was derived by extrapolating, to zero time, the $T_{1\rho}(^1H)$ decrease of the ^{13}C magnetization observed at long contact times. In the rigid lattice, the characteristic times for the coherent and incoherent transfers that participate to the cross-polarization phenomenon are very different. When the $^{13}C–^1H$ dipolar interaction is motionally averaged, the separation between coherent and incoherent transfer may be less clear-cut. To overcome this problem, the time necessary to reach the fourth of the total magnetization, $t_{1/2}$, was determined and transformed into a $t_{1/2}$ value using the following equation:

$$t_{1/4} = 2/3 t_{1/2} \qquad (2)$$

The directions of the principal axes of the chemical shift tensors used in this paper are shown in Fig. 1. They were taken from single-crystal studies of aromatic derivatives [7,8]. As shown in Fig. 1, the least shielded element, σ_1, is in the aromatic plane pointing radially out from the ring whereas the most shielded one, σ_3, is perpendicular to the ring plane. For carbonyl carbons, results reported for acetophenone and benzophenone [9,10], in which the most shielded axis is perpendicular to the sp^2 plane and the intermediate one is along the C=O bond [8] were utilized.

The principal values of the chemical shift tensors, σ_1, σ_2 and σ_3, were derived from the relative intensities of the spinning side bands, using Herzfeld and Berger calculations [2] and the MAS_sb_analysis.m computer program from Levitt [11]. Their values obey the relationship: $\sigma_1 + \sigma_2 + \sigma_3 = 0$ with the convention that: $\sigma_1 < \sigma_2 < \sigma_3$.

The interpretation of σ_1, σ_2 and σ_3 values in terms of motional averaging requires the knowledge of the rigid-lattice σ_1, σ_2 and σ_3 parameters. In order to check that the low-temperature measurements can indeed be
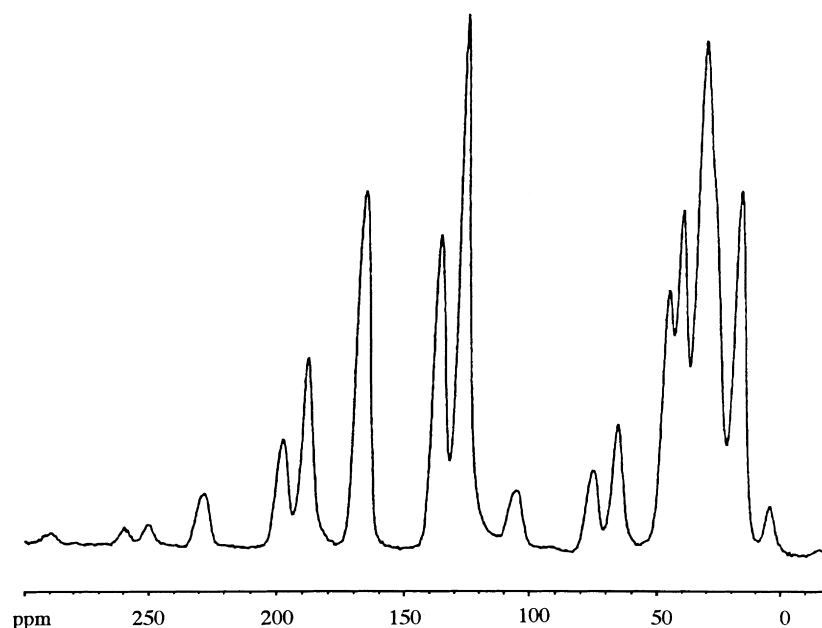

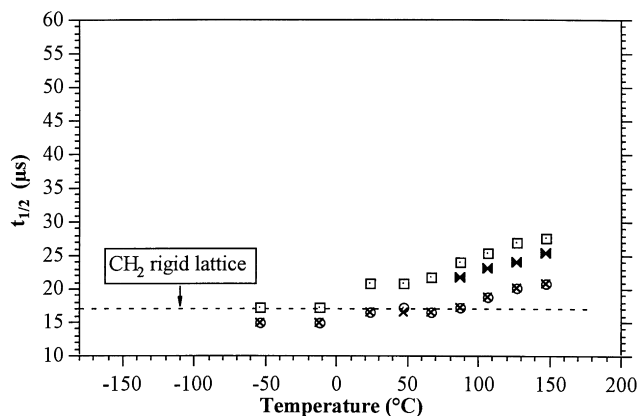Fig. 2. ^{13}C DD/CP/MAS NMR spectrum of the MT sample at 23°C, obtained with a spinning speed of 4620 Hz.

Fig. 3. Temperature dependence of the $t_{1/2}$ values, measured for all the lines of the aliphatic carbons in the MT sample. (×), 46.3 ppm; (○), 40.7 ppm; (□), 32.3 ppm; (▻◅), 27.4 ppm.

considered as rigid lattice parameters, they were compared with data obtained on small crystalline model molecules, such as terephthalic dihydrazide and isophthalamide, and listed in Table 1. The oscillation amplitudes and fraction of flipping rings were derived from the $\sigma_3 - \sigma_1$ difference
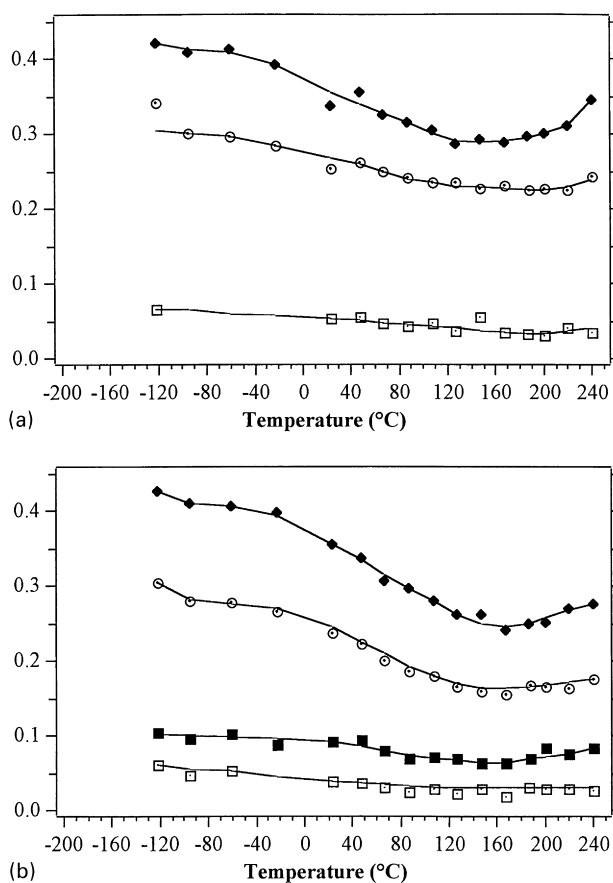

(a)

(b)

Fig. 4. Temperature dependence of the spinning side band intensities for (a) the unprotonated aromatic carbons of the MT copolyamide (b) the protonated aromatic carbons of the MT copolyamide. (◆), I_{+1}/I_0; (○), I_{-1}/I_0; (□), I_{+2}/I_0; (■), I_{-2}/I_0.

whose determination is more precise than the determination of the individual σ_i components. It must be noticed that the experimental accuracy on the chemical shift tensor determination strongly decreases from the MT to the xT_yI_{1-y} copolyamides, following the decreasing proportion of *tere*- or *iso*phthalamide units in the systems. In the xT_yI_{1-y} copolyamides, the accuracy for each determination of the oscillation amplitude is of the order of ±10°.

3. Results and discussion

3.1. MT copolyamide

Fig. 2 shows the ^{13}C DD/CP/MAS NMR spectrum of the MT sample at 23°C. The 166.9, 136.8, 127.3 and 17.4 ppm lines correspond to the C=O carbons, unprotonated and protonated aromatic carbons, and methyl carbons, respectively. The detailed assignment of the 27.4–46.3 ppm region to aliphatic CH and CH$_2$ carbons cannot be performed on the basis of chemical shifts only.

3.1.1. Dynamics of the methylpentane units

The temperature dependence of the $t_{1/2}$ values, measured for all the lines of the aliphatic carbons is shown in Fig. 3. It points out two different behaviors: the first one is associated with the 32.3 and 27.4 ppm lines and the latter corresponds to the 40.7 and 46.3 ppm lines. The 32.3 ppm line exhibits a constant $t_{1/2}$ value, equal to the 17-μs rigid-lattice $t_{1/2}$ of CH$_2$ carbons, below room temperature, which shows that the corresponding part of the aliphatic sequence of the MT copolyamide does not undergo any local motions at a frequency equal to or higher than 10^5 Hz in this temperature range. Then, at temperatures equal to or higher than 20°C, a progressive increase in $t_{1/2}$ is observed for the 32.3 ppm line. The $t_{1/2}$ associated with the 27.4 ppm line exhibits an identical behavior in the temperature range where the 27.4 ppm line is clearly resolved. These $t_{1/2}$ increases are a clear indication of the existence of motional processes of the aliphatic sequence in the tens of kHz region at high temperature.

The $t_{1/2}$ values obtained for the 40.7 and 46.3 ppm lines at temperatures below 100°C are constant and equal to the 17-μs rigid-lattice $t_{1/2}$ of CH$_2$ carbons. Then, at temperatures higher than 100°C, a progressive increase in $t_{1/2}$ is observed for both the 40.7 and 46.3 ppm lines.

The onset of motions, which occurs at a higher temperature for the carbon atoms associated with the 40.7 and 46.3 ppm lines, can be related to the position of these carbons along the aliphatic sequence. Since the terephthalamide unit is the most rigid part of the MT copolyamide, the 40.7 and 46.3 ppm lines should correspond to the CH$_2$ carbons in α position with respect to the amide groups. The 27.4 and 32.3 ppm lines, whose mobility is observed at a lower temperature, should then be associated with the central CH$_2$ carbons of the aliphatic sequence.
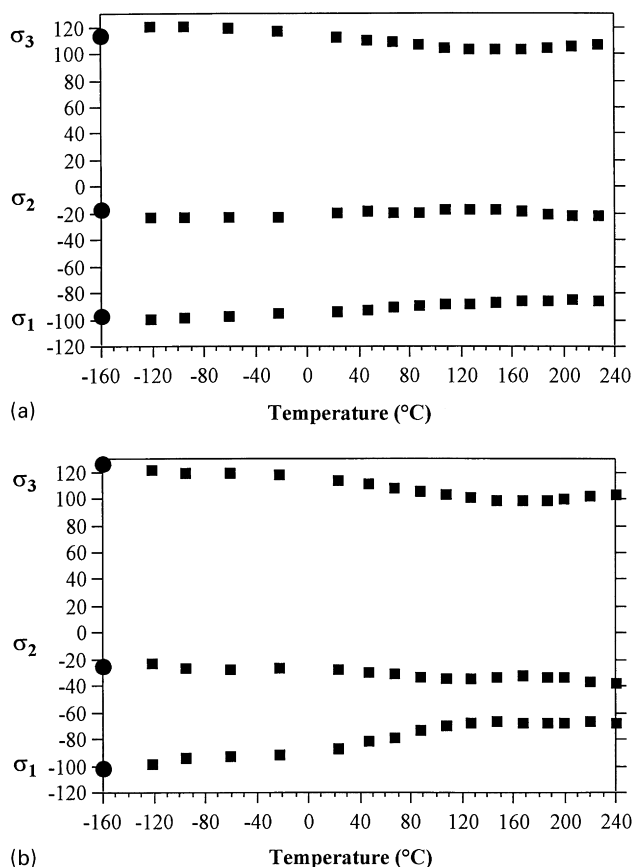
Fig. 5. (a) Principal values of the chemical shift tensor, σ_1, σ_2 and σ_3, derived from data reported in Fig. 4(a). (b) Principal values of the chemical shift tensor, σ_1, σ_2 and σ_3, derived from data reported in Fig. 4(b). (●), σ_1, σ_2 and σ_3 parameters for the unprotonated and protonated aromatic carbons of crystalline terephthalic dihydrazide.

3.1.2. Dynamics of the aromatic rings

The temperature dependence of the spinning side band intensities is plotted in Fig. 4(a) and (b) for the unprotonated and protonated aromatic carbons of the MT copolyamide,
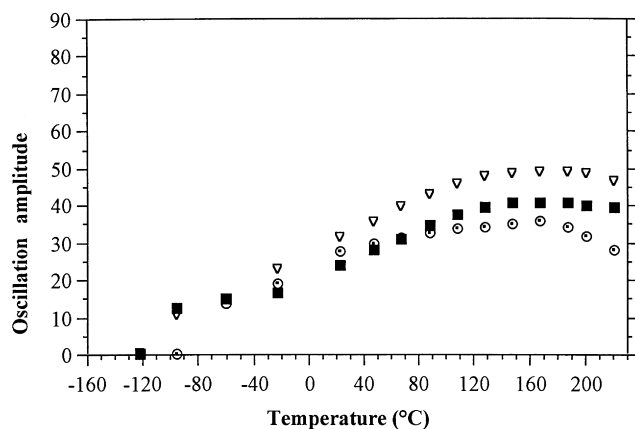

Fig. 6. Oscillation amplitudes (°) derived from the $\sigma_3 - \sigma_1$ difference determined for protonated aromatic carbons (■), unprotonated aromatic carbons (▽) and carbonyl carbons (⊙) of the MT copolyamide.

respectively. Whatever the carbon considered, the decrease of the spinning side band intensities, observed on increasing temperature up to 160°C, indicates a progressive averaging of the chemical shift tensors, and as a consequence, the occurrence of local motions. However, at temperatures higher than 160°C, there happens an increase in the spinning side band intensities which corresponds to a less efficient motional modulation of the chemical shift anisotropy. As clearly demonstrated by the crystallization exotherm exhibited by the DSC trace of the MT sample precisely in the 160°C region, this very unusual behavior is due to a partial crystallization.

The principal values of the chemical shift tensor, σ_1, σ_2 and σ_3, derived from data reported in Fig. 4(a) and (b) are shown in Fig. 5(a) and (b). It is of interest to notice that the σ_1, σ_2 and σ_3 values determined for the MT polymer at $-122°C$, which is the lowest temperature investigated, are very close to the σ_1, σ_2 and σ_3 values of terephthalic hydrazide listed in Table 1 [12]. Since the local electronic environment of the carbons of terephthalic hydrazide and aromatic unit of the MT copolyamide are very similar, terephthalic hydrazide, which is a crystalline molecule at room temperature, can be considered as a model molecule for the chemical shift tensors of the aromatic carbons of MT in the rigid lattice. Therefore, the similarity of the two sets of data indicates that the MT polymer has a rigid lattice behavior at $-122°C$.

Assuming that the orientations of the principal axes of the chemical shift tensor of the unprotonated carbons of the MT copolyamide are those drawn in Fig. 1, results reported in Fig. 5(a) at temperatures up to 0°C are consistent with the existence of motions about the *para* axis of the ring. Indeed, processes about the *para* axis of the ring lead to a partial averaging of the σ_2 and σ_3 components, which are perpendicular to the axis of rotation, while leaving the σ_1 principal value, that is parallel to the axis of rotation, unchanged. Above 0°C, results reported in Fig. 5(a) show a slight averaging of σ_1, which corresponds to a very limited reorientation of the *para* axis of the ring below the glass transition temperature.

As indicated in Section 1, the data analysis associated to the aromatic carbons was performed in terms of ring oscillations and π-flips. However, π-flips do not average the chemical shift anisotropy of unprotonated carbons of *para*-substituted rings since the principal components of their chemical shift tensor are exactly at the same position before and after the π-flip. Besides, π-flips have a very small influence on the chemical shift anisotropy of protonated carbons in *para*-substituted rings [12]. Therefore, the oscillations of the phenyl rings are the only processes involved in the motional modulation observed for the unprotonated aromatic carbons in Fig. 5(a). They should also be the dominant processes responsible for the results observed for the protonated aromatic carbons in Fig. 5(b). Therefore, the role of π-flips in the modulation of the chemical shift anisotropy of aromatic carbons can be neglected as a first
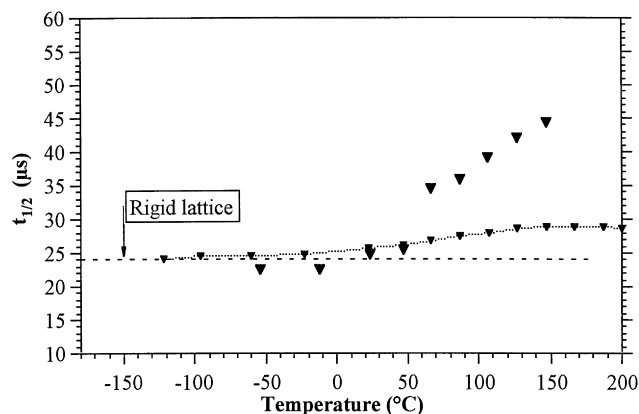
Fig. 7. Temperature dependence of the $t_{1/2}$ values, measured for the protonated aromatic carbons of the MT copolyamide ($\blacktriangledown$) and $t_{1/2}$ values calculated by assuming oscillations of the phenyl rings with amplitudes equal to data reported in Fig. 6 (- - -).

approximation. Within this assumption, the oscillation amplitudes derived from the $\sigma_3 - \sigma_1$ difference for both protonated and unprotonated carbons are shown in Fig. 6. The agreement between the two sets of data is very good, which supports the above approximation and shows that the existence of π-flips cannot be demonstrated by these experiments.

The temperature dependence of the $t_{1/2}$ values, measured for the protonated aromatic carbons is shown in Fig. 7. At temperature higher than 50°C, the $t_{1/2}$ values are much longer than the rigid-lattice $t_{1/2}$. They are indicative of a noticeable mobility. It is of interest to compare these experimental $t_{1/2}$ values to $t_{1/2}$ values calculated by assuming oscillations of the phenyl rings with amplitudes equal to data reported in Fig. 6. Such a comparison is shown in Fig. 7. The significant difference observed between calculated and experimental data demonstrates the existence of additional motions. These additional motions are such that they do not significantly modify the chemical shift anisotropy whereas they average the ^{13}C–^1H dipolar coupling in an efficient way. π-flips meet these two criteria. The fraction of phenyl rings undergoing rapid π-flips is shown in Fig. 8. At
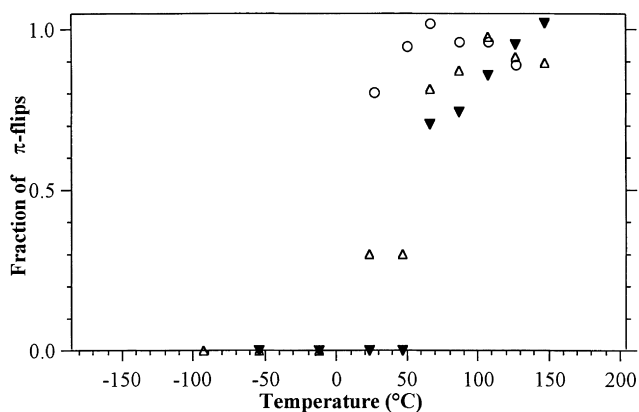

Fig. 8. Fraction of phenyl rings undergoing rapid π-flips in the MT ($\blacktriangledown$), 1T ($\triangle$) and 1.8T ($\bigcirc$) copolyamides.
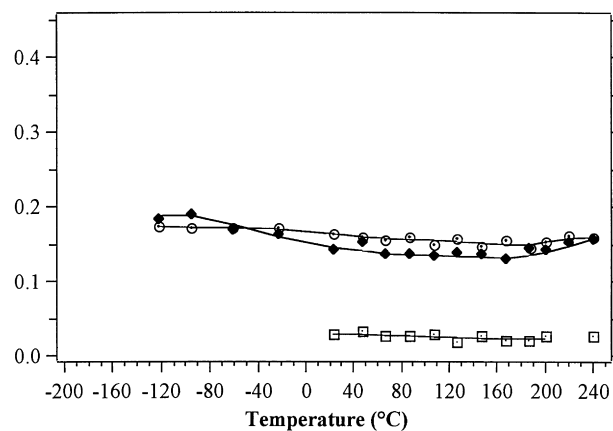

Fig. 9. Temperature dependence of the spinning side band intensities for the carbonyl carbon of the MT copolyamide. ($\blacklozenge$), I_{+1}/I_0; ($\odot$), I_{-1}/I_0; ($\boxdot$), I_{+2}/I_0.

temperatures higher than 60°C, an increasingly large part of the phenyl rings take part in π-flips until all phenyl rings are involved just below the crystallization. ^2H NMR investigations supporting the above analysis of ^{13}C NMR data in terms of oscillations and π-flips will be published in the next paper of this series [13].

3.1.3. Dynamics of the carbonyl groups

The temperature dependence of the spinning side band intensities is plotted in Fig. 9 for the carbonyl carbon. Below the crystallization temperature, the progressive decrease of the spinning side band intensities indicates the existence of local motions with increasing frequency and/or amplitude on increasing temperature. The principal components of the chemical shift tensor of the carbonyl carbon, derived from these data are plotted in Fig. 10. As for the aromatic carbons, values determined at -122°C, which is the lowest temperature investigated, are in very good agreement with those measured on the carbonyl carbon of terephthalic
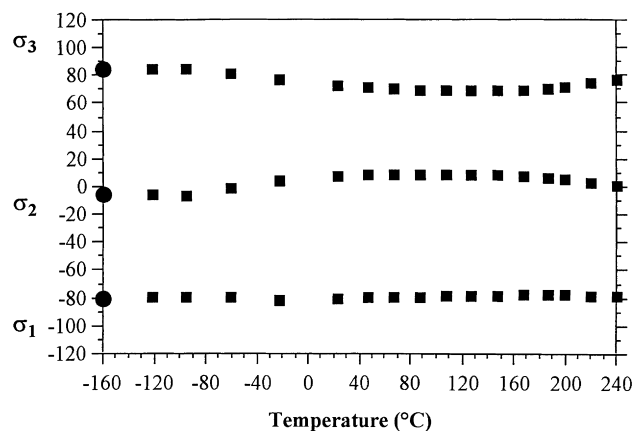

Fig. 10. Principal components of the chemical shift tensor of the carbonyl carbon, derived from data plotted on Fig. 9. ($\bullet$), σ_1, σ_2 and σ_3 parameters for the carbonyl carbons of crystalline terephthalic dihydrazide.
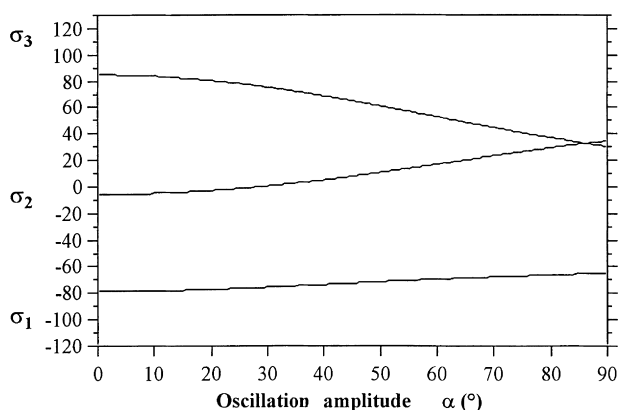
Fig. 11. Effect of oscillations of amplitude $\pm\alpha$ (°) about the *para* axis on the σ_1, σ_2 and σ_3 principal values of the carbonyl carbon.

hydrazide [12] and listed in Table 1. As such, they can be considered as representative of the rigid-lattice behavior of the C=O groups of the MT copolyamide.

As a first approximation, data relative to the carbonyl carbons can be interpreted in terms of oscillations of amplitude $\pm\alpha$ about the *para* axis:
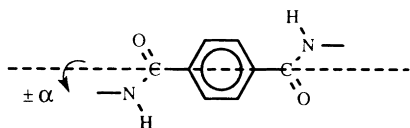
The consequences of such a motion on the σ_1, σ_2 and σ_3 principal values are shown in Fig. 11. It must be noticed that the α dependence of these calculated values is very similar to the temperature dependence of the experimental values. The temperature dependence of the oscillation amplitudes

associated with the carbonyl groups is shown in Fig. 6. Within experimental accuracy, oscillation amplitudes calculated for the carbonyl and aromatic carbons are very similar, which tends to indicate that the C=O groups and adjacent phenyl rings are involved in correlated motions. This conclusion is consistent with the quasi-conjugated character exhibited by the phenyl–amide bond.

3.1.4. Conclusion on the local dynamics of the MT copolyamide

The analysis of the motional averaging of the ^{13}C chemical shift tensors and ^{13}C–^{1}H dipolar couplings has pointed out the onset of correlated oscillations of the phenyl rings and adjacent C=O groups at very low temperatures (around $-100°$C). At higher temperatures, above 50°C, π-flips of the phenyl rings can be clearly detected. Then, at temperatures higher than 80°C, significant motions of the methylpentane unit are observed.

It is of interest to compare these conclusions with results deduced from the analysis of dielectric relaxation experiments on the same copolyamide [1]. The MT copolymer exhibits a β relaxation which can be unambiguously assigned to the motions of its C=O groups. If we extrapolate the relaxation map of the β dielectric transition to a frequency of 10^5 Hz, which corresponds to processes that are able to significantly average the chemical shift anisotropy, the temperature of the maximum of the loss peak thus obtained is 58°C. Indeed, as shown by the NMR experiments, at 58°C, the C=O groups undergo oscillations with an amplitude, $\pm\alpha$, of 30°C. Therefore, there is a satisfying qualitative agreement between ^{13}C NMR and dielectric data. However, the description of motions, as derived from the analysis of high-resolution solid-state ^{13}C NMR
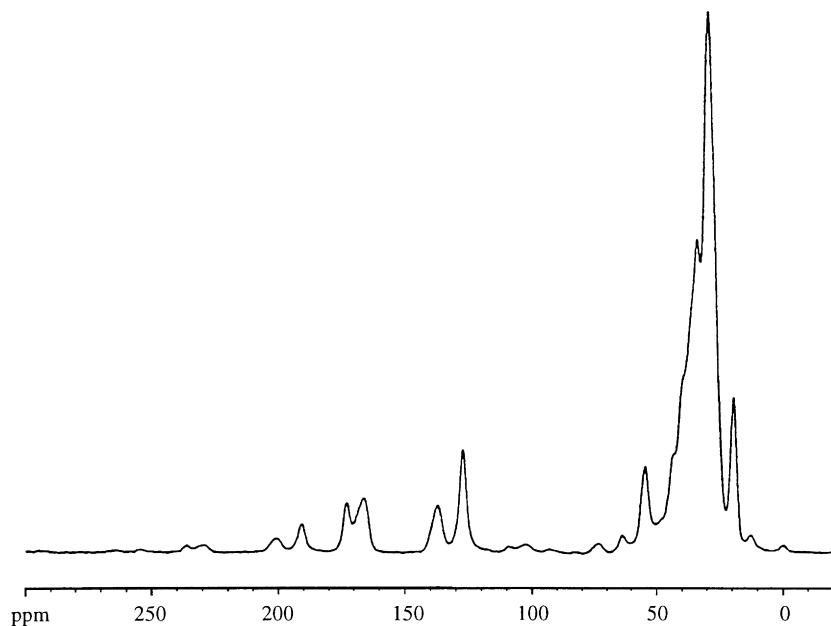

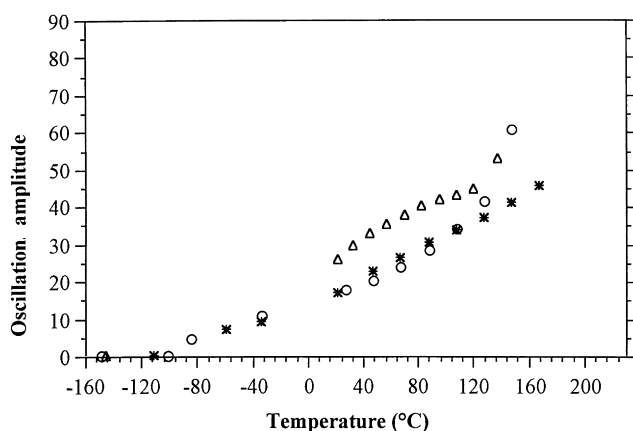Fig. 12. ^{13}C DD/CP/MAS NMR spectrum of the 1T sample at 32°C, obtained with a spinning speed of 4700 Hz.

Fig. 13. Temperature dependence of the oscillation amplitudes (°) of the aliphatic C=O groups in the 1T ($\triangle$), 1.8T ($\bigcirc$) and 1I ($*$) polymers.

experiments, in terms of oscillations of the terephthalamide unit and ring flips that all occur in the domain of the β transition, is much more detailed.

3.2. xT_yI_{1-y} copolyamides

As an example, the ^{13}C DD/CP/MAS NMR spectrum of the 1T sample at 32°C is shown in Fig. 12. The 137.1 and 127.3 ppm lines correspond to the unprotonated and protonated aromatic carbons, the 54.6, 34.0 and 19.4 ppm lines are assigned to CH, CH$_2$ and CH$_3$ carbons of the cycloaliphatic units, respectively. The lactam-12 carbon line is observed at 29.7 ppm. It is interesting to notice that the C=O groups in an entirely aliphatic environment resonate at 172.9 ppm whereas the two C=O groups adjacent to the phenyl rings share the same resonance line at 166.1 ppm. While the dielectric relaxation experiments have shown that the latter C=O groups exhibit a different behavior depending on the nature, i.e. lactam-12 or 3,3$'$-dimethyldicyclohexylmethane unit, of their other neighbor, the NMR technique is not able to distinguish the contribution of each group.
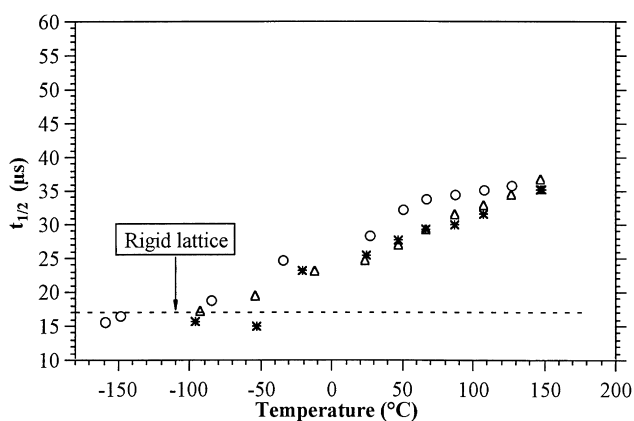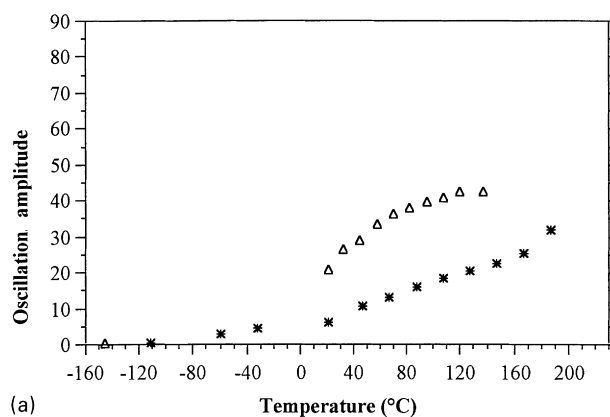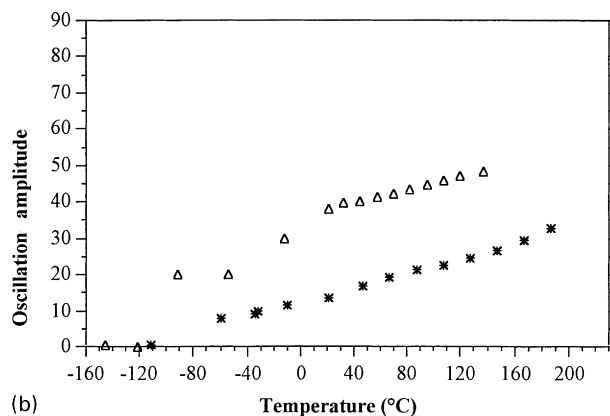

Fig. 14. $t_{1/2}$ values, measured for the lactam-12 methylene carbons of the 1T ($\triangle$), 1.8T ($\bigcirc$) and 1I ($*$) polymers.


(a)

(b)

Fig. 15. (a) amplitudes of oscillations (°) of the iso- and terephthalamide C=O groups vs temperature in the 1I ($*$) and 1T ($\triangle$) polymers. (b) amplitudes of oscillations (°) of the phenyl rings vs temperature in the 1I ($*$) and 1T ($\triangle$) polymers.

3.2.1. Dynamics of the lactam-12 units

The amplitudes of the oscillations undergone by the C=O carbons resonating at 172.9 ppm, which are the C=O groups next to the lactam-12 units, were derived from the spinning side band intensities by assuming oscillations about an axis joining the N atom to the cycloaliphatic ring, which is the most likely motion to occur in the neighborhood of an amide group:
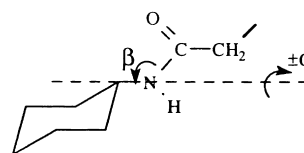
These oscillation amplitudes are plotted as a function of temperature in Fig. 13 for the 1T, 1.8T and 1I polymers. The onset of oscillations is detected at very low temperatures, around −80°C. Below room temperature, their amplitude is of the order of 10°, which is at the very limit of experimental accuracy. At higher temperatures, the oscillation amplitudes take on more significant values which increase on increasing temperature and do not depend on the exact chemical nature

of the xT_yI_{1-y} polymer within experimental accuracy. It is interesting to note that the transition temperature, determined at 10^5 Hz by extrapolating the dielectric data on the γ transition is around −60°C, indicating that there is a satisfying agreement between NMR observations and assignment of the γ transition to modes of the C=O groups in an aliphatic environment.

In contrast with the lines of the carbonyl carbons which have a small intensity, the 29.7 ppm line corresponding to the lactam-12 methylene carbons is intense, which allows a precise $t_{1/2}$ determination. The $t_{1/2}$ values, determined from the dependence of the intensity of the 29.7 ppm line as a function of the contact time are displayed in Fig. 14 as a function of temperature for the 1.8T, 1T and 1I polymers. They point out the existence of low temperature motions in the very temperature range where small oscillations of the C=O groups in an aliphatic environment are observed, which tends to indicate that the oscillations of the C=O groups are accompanied by simultaneous motions of the lactam-12 sequence. It is interesting to note that the $t_{1/2}$ values obtained for the 1.8T polymer are systematically longer than those measured in the 1T and 1I samples. This result is consistent with the higher amount of aliphatic flexible units contained in the 1.8T copolyamide.

3.2.2. Dynamics of the iso- and terephthalamide units

The amplitudes of oscillations of the iso- and terephthalamide C=O groups and phenyl rings, about an axis parallel to the local symmetry axis of the phenyl ring, are plotted as a function of temperature in Fig. 15(a) and (b) for the 1I and 1T polymers.

In the 1I copolyamide, data obtained for isophthalamide C=O groups and phenyl rings indicate the existence of small oscillations, with similar amplitude for both groups, over the whole temperature range. This result shows that the isophthalamide C=O groups and phenyl rings of the 1I copolyamide are involved in small correlated motions. It is consistent with the expected restricted mobility of *meta*-substituted phenyl rings. It is of interest to note that the $t_{1/2}$ values, determined for the protonated aromatic carbons of the 1I polymer, are entirely accounted for by data reported in Fig. 15(b), in agreement with the fact that *meta*-substituted rings do not undergo π-flips.

In the 1T copolyamide, within the experimental accuracy, which is quite poor for these groups, C=O groups do not exhibit oscillations of noticeable amplitude below room temperature. Above room temperature, the oscillation amplitude of the C=O groups is much larger in the 1T than in the 1I polymer, in agreement with the higher mobility of *para*-substituted rings and attached C=O groups. Data reported in Fig. 15(a) permit to check that, at 35°C, which is the temperature of the β dielectric relaxation extrapolated at 10^5 Hz, the terephthalamide C=O groups exhibit a significant mobility, with oscillation amplitudes of ±30°. Results displayed for the phenyl groups are qualitatively

similar to those observed for the C=O groups, with low amplitude motions below room temperature and large oscillations with the same amplitude as the oscillations of the C=O carbons above room temperature, which indicates that the motions of the C=O groups and adjacent phenyl rings are likely to be correlated in this temperature range. As for the MT copolyamide, $t_{1/2}$ measurements for the protonated aromatic carbons of the 1T and 1.8T polymers indicate that a fraction of *para*-substituted phenyl rings are undergoing π-flips. The temperature dependence of this fraction of phenyl rings is shown in Fig. 8. The onset of π-flips of the phenyl rings occurs at a relatively lower temperature in the 1.8T copolyamide than in the 1T and MT polymers.

3.2.3. Dynamics of the cycloaliphatic units

Whatever the copolyamide xT_yI_{1-y} studied, $t_{1/2}$ values determined from the intensity variation of the lines associated with the CH and CH$_2$ carbons of the 3,3′-dimethyldicyclohexylmethane units are equal to the rigid-lattice $t_{1/2}$ over the whole temperature range investigated, i.e. up to 150°C. This result implies that the 3,3′-dimethyldicyclohexylmethane units do not undergo local motions in the 10^5 Hz range in the temperature domain considered.

4. Conclusions

High-resolution solid-state ^{13}C NMR experiments leads to a detailed description of the local dynamics of the aryl-aliphatic copolyamides under study. As observed from NMR measurements, the behavior of the carbonyl carbons is in qualitative agreement with results derived from the dielectric relaxation study of these compounds [1]. Indeed, at the temperatures which characterize the γ and β transitions at the frequency of the NMR experiment, a noticeable mobility of the corresponding C=O groups was pointed out whenever the experimental accuracy or the temperature range investigated permitted to observe it.

The MT and xT_yI_{1-y} copolyamides differ by the nature of their aliphatic units. In the MT polymer, the methylpentane sequences do not exhibit detectable motions at temperatures below 100°C. The xT_yI_{1-y} polymers contain two different aliphatic units. Whatever the nature of the acid or the lactam-12 amount, the cycloaliphatic units are immobile at temperatures below the glass-transition temperature. On the contrary, the lactam-12 sequences are involved in significant motions, even at low temperatures, independently of the iso- or terephthalic environment. The higher the lactam-12 content, the higher the mobility of the lactam-12 sequence.

In all the systems investigated, the aromatic rings undergo oscillations about an axis, which depends on the geometry of the mobile unit. At a given temperature, all the *para*-substituted rings exhibit similar oscillation amplitudes,

which are much larger than those observed in the *meta*-substituted units. Besides, *para*-substituted rings are involved in π-flips. It is of interest to notice that these occur in the temperature and frequency ranges of the β transition. Their onset is detected at a lower temperature in the 1.8T polymer than in the 1T and MT polymers. The ^{2}H NMR investigation of these ring flips will be described in the next paper of this series [13].

Acknowledgements

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