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Secondary transitions of aryl-aliphatic polyamides
III. ^{2}H NMR investigation

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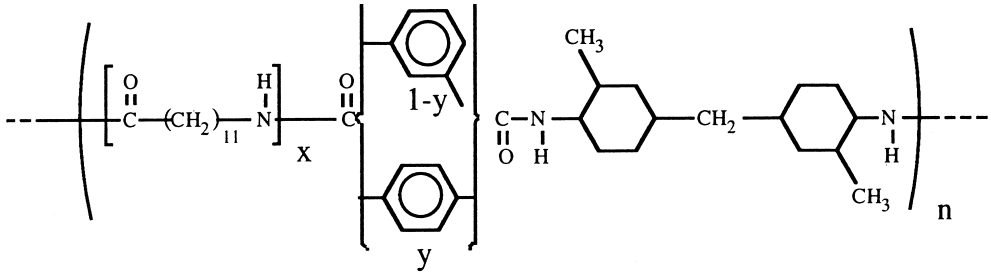
Abstract

^{2}H NMR experiments were performed on a selectively deuterated aryl-aliphatic copolyamide in order to investigate the local dynamics of the phenyl rings as a function of temperature. The activation energy of the phenyl ring flip motion, determined from the ^{2}H NMR experiments, was shown to be identical to the activation energy determined by dielectric relaxation for the β transition. Such a result tends to indicate that the phenyl ring flips are part of the β transition in the aryl-aliphatic copolyamide under study. © 2000 Elsevier Science Ltd. All rights reserved.

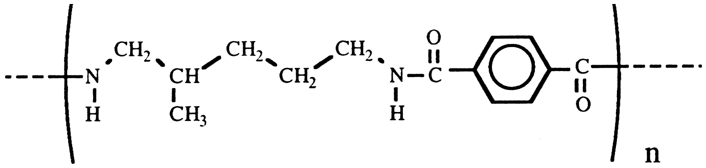
Keywords: Aryl-aliphatic copolyamides; Secondary transitions; ^{2}H NMR

1. Introduction

Dielectric relaxation measurements, performed on the $x\mathrm{T}_y\mathrm{I}_{1-y}$ aryl-aliphatic copolyamides



and MT copolyamide



and reported in the first paper of this series [1], demonstrated the existence of several secondary relaxations which were assigned to motional modes of the carbonyl groups contained in these materials. The motions of non-conjugated C=O groups, C=O groups located between a phenyl ring and a flexible lactam-12 or methylpentane sequence, and C=O groups situated between a phenyl ring and a rigid cycloaliphatic moiety, were shown to be

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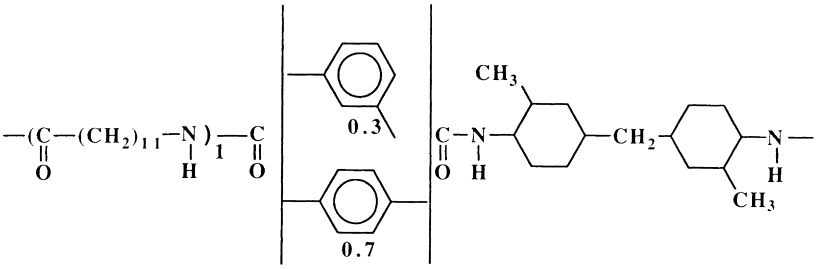

Fig. 1. Chemical structure of the $1T_{0.7}I_{0.3}$ copolyamide.

involved in the γ, β and ω relaxations, respectively. High-resolution solid-state ^{13}C NMR experiments, described in the second paper of this series [2], were carried out on the same series of aryl-aliphatic copolyamides. Results thus obtained corroborated the conclusions of the dielectric analysis. Moreover, they led to a precise description of the motional modes of all the units other than the C=O groups contained in the xT_yI_{1-y} and MT polymers. The lactam-12 units were shown to exhibit local motions in the range of the γ transition, whereas phenyl ring oscillations of both the tere- and isophthalamide rings are simultaneous to oscillations of the adjacent C=O groups and have the same amplitudes. In addition to these ring oscillations that occur in the domain of the β transition, other modes of the *para*-substituted rings were observed and described in terms of π-flips.

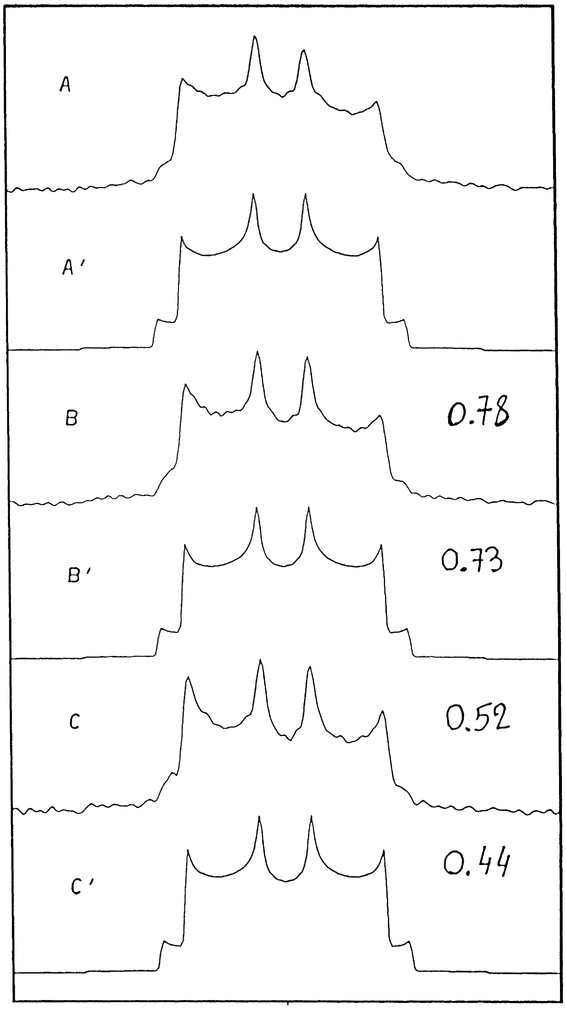

Fig. 2. Experimental and calculated (primed) ^{2}H NMR line shapes at 47°C for different values of the delay τ_1 : (*A*, *A*′) $\tau_1 = 20$ μs; (*B*, *B*′) $\tau_1 = 40$ μs; (*C*, *C*′) $\tau_1 = 80$ μs. The number adjacent to the (*B*, *B*′) and (*C*, *C*′) line shapes is the echo intensity normalized to the $\tau_1 = 20$ μs intensity (*A*, *A*′) with $T_{2d} = 220$ μs. Calculated line shapes are for an inhomogeneous log-Gaussian distribution of correlation times with $\sigma = 2$ decades centered at $\langle\tau_c\rangle = 8 \times 10^{-8}$ s.

^{2}H NMR spectroscopy of selectively deuterated samples is a most powerful technique for studying phenyl ring motions. The quadrupolar interaction is a one-particle tensorial Hamiltonian which is ideally suited to follow orientational dynamics of single molecular bonds [3]. Because of the relatively uncomplicated spin dynamics of an isolated $I = 1$ nucleus, the resonance line shape and the nuclear relaxation rates can be predicted for a wide variety of motional modes [4,5] Reliable deuteron NMR spectra can easily be obtained with the so-called quadrupolar echo pulse sequence [6]. In particular, it has been shown that the deuteron relaxation times T_2, T_1 and T_{1Q} are functions of the orientation of the magnetic field with respect to the molecular coordinate system [7–9]. Since the quadrupolar splitting is also orientation dependent, there is a strong correlation between the relaxation rates and the spectral position along the frequency axis. This correlation, which is almost absent in ^{1}H, ^{19}F and ^{13}C NMR, can serve as an additional source of information concerning the molecular mechanism of the motions [5,10]. Anisotropic T_2 relaxation of ^{2}H NMR line shapes can be observed when a significant part of the signal is in the intermediate exchange domain, i.e. when the rate of the motion $\nu_c = (2\pi\tau_c)^{-1}$ is comparable to the quadrupolar coupling constant ($\nu_Q = e^2qQ/h$) and when the distribution of rates $P(\nu_c)$ is not too broad [11]. When ν_c is much larger than ν_Q, a specific molecular motion leads to a partially averaged electric field gradient tensor and the spin-echo line shape becomes insensitive to ν_c. In this case, ν_c or $P(\nu_c)$ may nevertheless be determined by examining the anisotropic spin–lattice relaxation (T_1 or T_{1Q}) [5,10].

The ring dynamics in an aromatic polyamide, poly(*para*-phenyleneterephthalamide) (PPTA) were recently investigated by using ^{2}H NMR on selectively deuterated samples [12–15]. Results presented in this paper deal with the ^{2}H

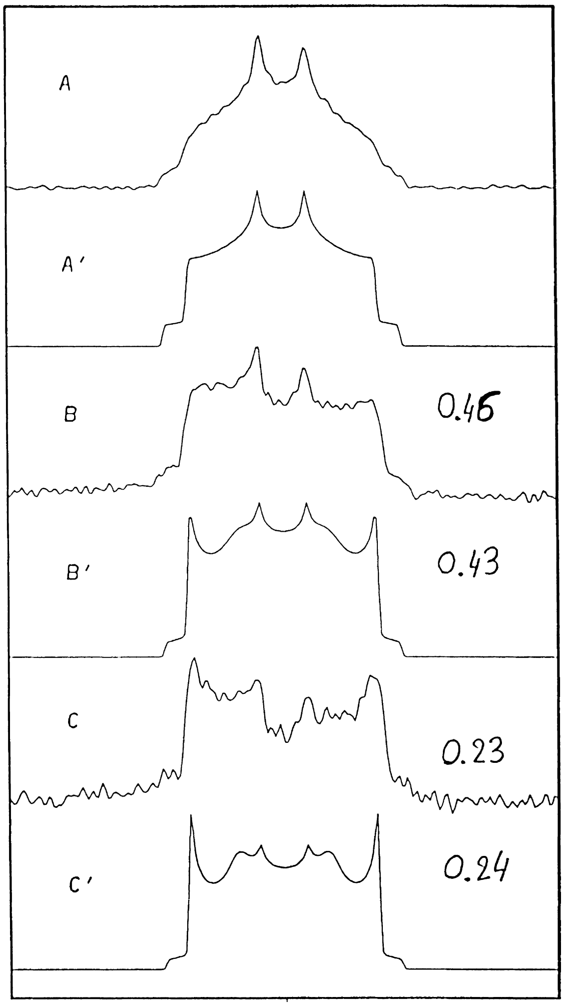

Fig. 3. Experimental and calculated (primed) T_{1Q}-distorted line shapes at 107°C for different values of the delay τ_2 ($\tau_1 = 30$ μs): (A, A') $\tau_2 = 1$ ms; (B, B') $\tau_2 = 10$ ms; (C, C') $\tau_2 = 30$ ms. The number adjacent to the (B, B') and (C, C') line shapes is the echo intensity normalized to the $\tau_1 = 1$ ms intensity (A, A'). Calculated line shapes are for an inhomogeneous log-Gaussian distribution of correlation times with $\sigma = 1$ decade centered at $\langle\tau_c\rangle = 3 \times 10^{-9}$ s.

NMR study of the local dynamics of the terephthalamide rings in the fully amorphous $1T_{0.7}I_{0.3}$ copolyamide. This sample was selectively deuterated on the terephthalamide phenyl rings.

2. Experimental

The chemical formula of the $1T_{0.7}I_{0.3}$ copolyamide is shown in Fig. 1. The sample used was synthesized by P. Blondel at the Elf-Atochem Research Laboratories, France. It was perdeuterated on the terephthalamide phenyl rings. The polymer was carefully dried and sealed under vacuum in a 5-mm tube for future use.

^{2}H NMR measurements were carried out at 46 MHz on a Bruker MSL-300 spectrometer ($B_0 = 7.1$ T) with a standard broad-band Bruker probe. The pulse sequence used was the quadrupolar echo ($\pi/2_x$, τ, $\pi/2_y$, τ, echo) pulse sequence. The $\pi/2$ pulse duration and dwell time were 2 and 0.2 μs, respectively. The data points before the echo maximum were carefully eliminated. Indeed, if the onset of the signal is not exactly set at the echo maximum, spectrum distortions may occur, which may be comparable to the line shape changes induced by local motions [16].

The measurement of T_{1Q}-distorted powder spectra in the fast motion limit was directly obtained by recording the echo decay during the mixing period τ_2 of the Jeener–Broekaert pulse sequence [17].

3. Results and discussion

As an example, Fig. 2 shows the spin-echo line shape of the $1T_{0.7}I_{0.3}$ copolyamide as a function of the delay τ_1 between the two $\pi/2$ pulses at 47°C. It can be seen that the spectra appear to be composites of a rigid Pake-like powder pattern and a fraction exhibiting anisotropic reorientation. The observed splitting between the outermost singularities is characteristic of a relatively rigid phenyl ring with a quadrupolar coupling constant of 176 kHz ($\eta = 0$). The splitting of the two central singularities (31 kHz) is characteristic of π-flips about the 1,4 axis of the phenylene rings [11–13]. On increasing the temperature, the fraction of phenyl rings undergoing π-flips increases to the detriment of phenyl rings with a rigid-lattice behavior. ^{2}H NMR spectra recorded at 87°C show that, at this temperature, all the phenyl rings are involved in π-flips.

The simulated line shapes of Fig. 2 are obtained by considering the π-flip model with an inhomogeneous symmetric log-Gaussian distribution of correlation times with the mean correlation time $\langle\tau_c\rangle$ and the standard deviation σ (in decades) [11]. At 47°C, characteristic line shape changes resulting from anisotropic transverse relaxation (T_2) occur as a function of the delay τ_1 (Fig. 2). The breadth of $P(\nu_c)$ ($\sigma = 2$ decades) is found to be comparable to the one obtained in poly(*para*-phenyleneterephthalamide) [13]. However, with increasing temperature ($T > 47$°C), the T_2 relaxation time due to the fluctuations of the quadrupolar interaction becomes much longer than the contribution due to the nonselective dipolar interactions, $T_{2d} \approx 200$ μs. Hence, the spin-echo line shapes become insensitive to the time scale of the motion and $P(\nu_c)$ can no longer be determined [11]. In this domain of temperature, the motional mechanism may nevertheless be studied via line shape distortions resulting from anisotropic spin–lattice relaxation (T_1 and T_{1Q}), the anisotropy of T_{1Q} being greater and thus favored [5]. Fig. 3 shows the distortions obtained at 107°C for the $1T_{0.7}I_{0.3}$ copolyamide together with the line shape simulations. Note that the T_{1Q} anisotropy is much more pronounced that the T_2 anisotropy (Fig. 2). σ is found to be half the value obtained with the two-pulse spin-echo sequence at lower temperatures (27 and 47°C). Because the measurement of $P(\nu_c)$ from the two-pulse sequence is

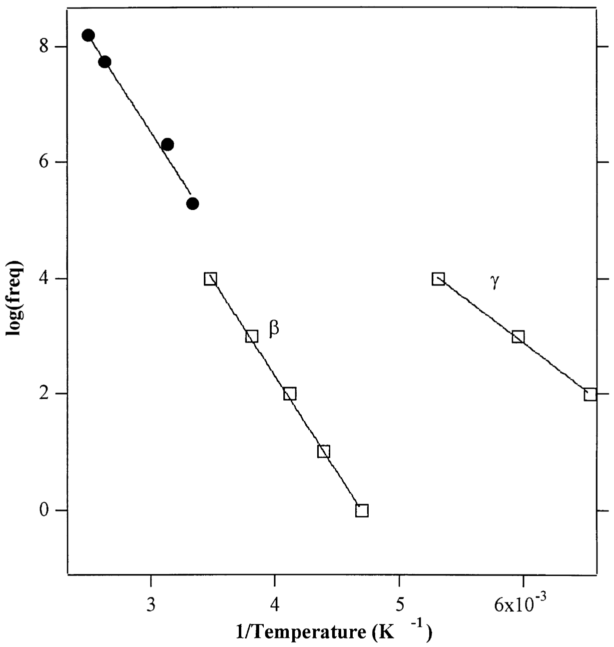

Fig. 4. Relaxation map of the $1T_{0.7}I_{0.3}$ copolyamide: (●) ^{2}H NMR; (□) dielectric relaxation.

affected by the dipolar decay, σ may be overestimated. Indeed, strictly speaking, T_{2d} should be different for fast and slow flipping phenyl rings. On the other hand, the spin-lattice T_{1Q} process is free from such a limitation. Note that an apparent decrease of σ with increasing temperature has also been observed for poly(*para*-phenyleneterephthalamide) [13]. The presence of rapid restricted angle fluctuations (librations or oscillations) in addition to the two-site jump motion is well accounted by a slight decrease of ν_Q with increasing temperature ($\bar{\nu}_Q = 166$ kHz). The fact that the experimental spectra do not exhibit very well defined outermost singularities (Fig. 3) is probably due to the presence of an inhomogeneous distribution of the amplitudes of fluctuations [10,13]. This minor feature is conveniently ignored in the simplified model used here.

The description of the *para*-substituted phenyl ring motions, as obtained from ^{2}H NMR data, in terms of π-flips and ring oscillations or librations, is in very good agreement with the conclusions derived from high-resolution solid-state ^{13}C NMR experiments. More information can be obtained on the motions involved in the β relaxation by comparing ^{2}H NMR and dielectric data on the $1T_{0.7}I_{0.3}$ polymer. The variation of ν_c as a function of temperature is illustrated in Fig. 4 together with the dielectric relaxation data. Results shown in Fig. 4 demonstrate that the temperature dependence of ν_c is in very good agreement with the dielectric relaxation data for the β relaxation. The activation energy determined from the ^{2}H NMR experiments is 63.5 kJ/mol, to be compared to the 63 kJ/mol energy obtained from dielectric relaxation. Although the π-flip motion of the phenylene group itself is not expected to be mechanically active, its characteristics are those monitored for the β dielectric relaxation process, which tends to indicate that phenyl ring flips are part of the β processes in the $1T_{0.7}I_{0.3}$ copolyamide. Moreover, it is seen that ^{2}H NMR nicely complements the dielectric technique towards higher correlation frequencies (Fig. 4). The role of the phenyl ring flips in the β secondary transition of the above aryl-aliphatic copolyamide is very similar to results observed in polyethyleneterephthalate where the phenyl ring flips were shown to be responsible for a part of the β relaxation [18].

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