Dynamics of an Amorphous Polymer by an Improved NMR Approach Based on the Simultaneous Analysis of ^{1}H and ^{13}C Relaxation Times

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A new approach to extract quantitative dynamic information from NMR relaxation data of amorphous polymers is presented, consisting of the simultaneous fitting of ^{1}H and ^{13}C T_1 vs temperature curves obtained at different frequencies by means of unified motional models. The reliability of the dynamic parameters obtained by this approach is substantially increased with respect to the single curve analysis because of the possibility of both investigating motions over a wide frequency range and combining relaxation times carrying either global (^{1}H nuclei) or local (^{13}C nuclei) dynamic information. Experimental data were obtained for an amorphous ethylene–propylene random copolymer over a wide temperature range above its glass-transition: ^{1}H spin–lattice relaxation times were measured by wide-line techniques at four Larmor frequencies, while high-resolution MAS techniques were used to get ^{13}C spin–lattice relaxation times at a single frequency. The experimental data were analyzed in terms of segmental main-chain motion, rotation of the methyl groups about their ternary symmetry axes, and librations of C–H bonds, described by suitable models. The results showed good agreement between experimental and calculated data and allowed a detailed characterization of the motions investigated to be obtained.

Introduction

NMR relaxation times have proved to be very useful in investigating the dynamic behavior of polymeric materials in the solid state, which is closely related to their mechanical properties. In fact, NMR gives access to very detailed information on motions over a wide range of characteristic frequencies, up to 10^{12} Hz, thanks to the different nuclei that can be observed (e.g., ^{1}H, ^{13}C, ^{2}H) and to the different NMR measurements that can be performed (exchange, line width, spin–lattice relaxation). 2D- or 3D-exchange techniques[1] have proved to be extremely useful in studying the dynamics of solid polymers, characterized by motions with correlation times in the range 10^{-5}–10^2 s, giving direct detailed information both on the time scale and geometry of segmental reorientations, even though often requiring labeling of the polymer. The dynamic range has been sometimes extended to frequencies up to 10^7 Hz by performing also 1D line shape analysis in deuterated samples.[2] The analysis of relaxation times allows one to extend the dynamic range further; the interpretation of NMR experimental relaxation times in terms of dynamic parameters is however usually not straightforward and requires the use of suitable models of motion. To this end, several models have been developed having either a theoretical or an empirical basis, sometimes originating from different experimental techniques, such as dielectric relaxation.[3]

It is now well-known that an unambiguous quantitative analysis of relaxation times would require experimental data collected at different temperatures and at more than one frequency,[4] even though such a large data set is seldom available. In fact, relaxation curves vs temperature at a single frequency can usually be satisfactorily reproduced by several models, therefore yielding erroneous dynamic information.[5]

Furthermore, it must be borne in mind that relaxation times of different nuclei contain different and complementary dynamic information because of either the different relaxation mechanisms or the influence of spin diffusion, which is strongly dependent on the spin density. Multinuclear ^{13}C and ^{2}H relaxation studies have been performed on specifically labeled components in polymeric blends[6] or in block copolymers[7] in order to obtain a clean separation of component dynamics; however, multinuclear NMR can also be used to increase the experimental data available for the analysis in the case of single-component systems. For instance, ^{1}H spin–lattice relaxation is mainly determined by homonuclear dipolar interactions, and the dynamic information that can be extracted is usually averaged over the whole sample because of both the scarce spectral resolution in the solid state and the strong influence of spin diffusion. On the contrary, ^{13}C spin–lattice relaxation times in natural abundance samples carry local dynamic information; in fact, in this case the main interaction involved is the dipolar interaction with directly bonded protons, a high spectral resolution in the solid state is achievable by suitable techniques, as MAS and high-power decoupling, and the spin diffusion process is substantially negligible. It is therefore clear that in order to get a more complete description of the dynamics in complex systems, such as polymers, the variable-temperature and multifrequency study should be extended to different nuclei.

Although many studies concerning the quantitative analysis of either ^{1}H or ^{13}C relaxation times in solid polymeric systems are reported in the literature, to the best of our knowledge, a simultaneous analysis of variable-temperature multifrequency relaxation data of both these nuclei has never been attempted. Indeed, different models have been proposed and applied for

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the analysis of ^{1}H and ^{13}C relaxation data which take into account the peculiar relaxation behavior of these two nuclei. For example, the Cole−Cole model[8] is often applied in the analysis of ^{1}H spectral densities since it takes into account motional correlation and distribution of correlation times, whereas the DLM model,[9] which considers the influence of librations, is normally used for ^{13}C.

The aim of the present work was the assessment of the possibility of getting detailed dynamic information on polymeric systems, without resorting to specific labeling, by performing a simultaneous analysis of ^{1}H and ^{13}C spin−lattice relaxation times based on the same motional models. To this end, ^{1}H spin−lattice relaxation times were measured at four different Larmor frequencies using low-resolution techniques, and ^{13}C spin−lattice relaxation times were measured at one Larmor frequency by high-resolution techniques on a completely amorphous ethylene−propylene random copolymer, already characterized in a previous paper,[10] in the temperature range from −60 to 100 °C. The experimental data were analyzed taking into account two main dynamic processes, i.e., main-chain segmental motion and methyl group rotation about the ternary symmetry axis. The motional correlation, distribution of correlation times, and influence of librations are considered in the data analysis procedure.

Experimental Section

The sample used was an amorphous ethylene−propylene random copolymer (EPR-V), with an ethylene content of 56.5 wt %, by Enichem Elastomeri (DUTRAL CO054). The glass-transition temperature (T_g), measured by DSC at a scan rate of 10 °C/min, was −52 °C.

The NMR experiments were carried out on three different NMR spectrometers: a Varian InfinityPlus 400 ("Varian"), equipped with a 7.5 mm CP-MAS probe, working at 399.89 MHz for proton; a Bruker AMX-300 WB ("Bruker"), equipped with a 4 mm CP-MAS probe, working at 300.13 MHz for proton and at 75.47 MHz for ^{13}C; a Varian XL-100 interfaced with a Stelar DS−NMR acquisition system ("Stelar"), used for measurements at 20.00 and 25.00 MHz for proton.

The ^{1}H 90° pulse lengths were 4.0, 3.5, and 2.5 μs on the Varian, Bruker, and Stelar spectrometers, respectively, while the ^{13}C 90° pulse length was 3.5 μs on the Bruker spectrometer.

The ^{1}H spin−lattice relaxation times were measured at low resolution by direct proton observation using either inversion−recovery or saturation−recovery pulse sequences followed by a solid echo: relaxation delays of up to 5 s in the inversion−recovery experiments and variable delays ranging from 20 μs to 5 s were used. The ^{13}C spin−lattice relaxation times were measured at high resolution using an inversion−recovery technique with high-power proton decoupling during ^{13}C signal acquisition,[11] spinning the sample at the magic angle with a frequency of 3 kHz; the relaxation delay was 5 s, and the variable delay of the inversion−recovery sequence ranged from 20 μs to 5 s. A minimum number of scans of 32 and 200 was used for proton and carbon experiments, respectively. The measurements were performed in the temperature range from −50 to 80 °C; temperature was controlled with an accuracy of 0.1 °C, except for temperatures below 7 °C, where the accuracy was within 0.4 °C. At least 15 min was allowed for sample temperature stabilization.

The ^{13}C relaxation times were obtained by analyzing the experimental spectra with the "SPORT-NMR" software package, previously developed in our group.[12] This software reproduces all the spectra of a relaxation measurement as a sum of peaks

through nonlinear least-squares minimization procedures, calculating the integrals of each peak in each spectrum, and finally determining the relaxation times by fitting the exponential recovery trend of the integrals for each peak. This allows the biasing effect of peak superpositions to be removed in the relaxation time determination.

The analysis of the relaxation times in terms of motional models was performed using the "Mathematica"[13] software (version 4.0) for a PC; the "Nonlinearfit" package was used for the fitting, and the results were displayed through standard graphic routines.

Theory

For an ensemble of dipolarly coupled protons characterized by the same intrinsic relaxation time, determined by a single motional process, spin−lattice relaxation rates can be written as linear combinations of spectral densities $J(\omega)$ following the equation[14]

$$R_1 = \frac{1}{T_1} = C[J(\omega_0) + 4J(2\omega_0)] \tag{1}$$

where ω_0 is the Larmor frequency and C is a constant related to that fraction of the second moment which corresponds to the dipolar interactions averaged by the motional process under consideration.

When more motions contribute to relaxation, the expression for R_1 may become very complicated.[15] This is reasonably the case in polymeric systems, where several inequivalent sets of protons are usually present and the relaxation times measured are often completely averaged by spin diffusion. If, however, the different motions contributing to the measured T_1 can be assumed independent, the spin−lattice relaxation times can be approximated to the following equation

$$R_1 = \frac{1}{T_1} = C\sum_i a_i[J_i(\omega_0) + 4J_i(2\omega_0)] \tag{2}$$

where the sum runs over the number of motional processes, contributing to the relaxation with a relative weight a_i.

In carbon spin−lattice relaxation measurements, the relaxation time can be expressed as a linear combination of spectral densities, provided that the latter are written for an ensemble of carbon nuclei coupled through dipolar interactions to protons chemically bonded to them; the resulting spectral density function has the following expression[14]

$$R_C = \frac{n}{15} \frac{C_C}{r_{CH}{}^6}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \tag{3}$$

where n is the number of protons bonded to the specific site, r_{CH} is the C−H bond distance, ω_C and ω_H are the Larmor frequencies of ^{13}C and ^{1}H, respectively, and C_C is

$$C_C = \frac{3}{4}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_H{}^2 \gamma_C{}^2 \hbar^2 \tag{4}$$

The spectral densities in eqs 1−3 can be expressed in terms of motional correlation times by means of equations depending on the theoretical or semiempirical model chosen to describe the dynamics. In the present work, the Havriliak−Negami model[16] was chosen since it takes into account a distribution of correlation times in the system but also correlation of motions and therefore is, in principle, particularly suitable for describing
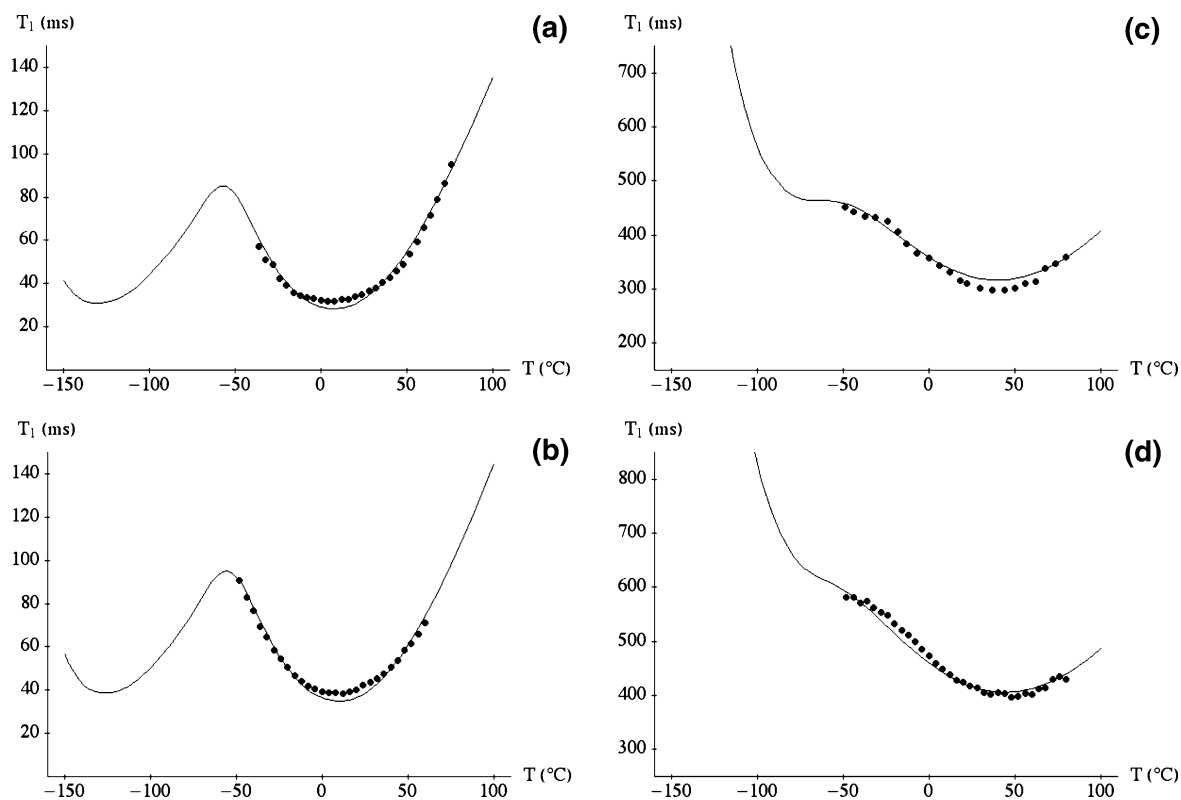
Figure 1. ^{1}H spin−lattice relaxation times vs temperature at the Larmor frequencies of (a) 20.00, (b) 25.00, (c) 300.13, and (d) 399.89 MHz. Symbols and lines indicate experimental and calculated relaxation times, respectively.

the dynamics of polymer chains. On the basis of this model, the following equation for spectral densities can be derived

$$J(\omega) = \frac{2}{\omega}\sin\left[\epsilon \arctan\left(\frac{(\omega\tau)^\delta\sin\left(\frac{\delta\pi}{2}\right)}{1 + (\omega\tau)^\delta\cos\left(\frac{\delta\pi}{2}\right)}\right)\right]\left[1 + (\omega\tau)^{2\delta} + 2(\omega\tau)^\delta\cos\left(\frac{\delta\pi}{2}\right)\right]^{-\epsilon/2} \quad (5)$$

where δ is a parameter giving a measure of the degree of correlation between motions and $\delta\epsilon$ is a measure of the spread in height of the activation barrier of the motional process; δ ranges from 0 to 1, while ϵ ranges from 0 to $1/\delta$. It must be noticed that the HN spectral density reduces to the Cole−Cole,[8] Davidson−Cole,[17] or Bloembergen−Purcell−Pound (BPP)[18] spectral density if $\epsilon = 1$, $\delta = 1$, or ϵ and $\delta = 1$, respectively.

To reproduce the experimental trends of relaxation times with the temperature, it is necessary to express the temperature dependence of the correlation times. In this work we used the well-known Arrhenius expression

$$\tau = \tau_\infty e^{E_a/kT} \quad (6)$$

with E_a being the activation energy of the motion and τ_∞ the correlation time extrapolated to infinite temperature, to describe the trend of the methyl group rotation correlation times vs temperature. The backbone motion correlation time above T_g was analyzed instead using the Vogel−Tamman−Fulcher (VTF) equation[19]

$$\tau = \tau_\infty \exp\left(\frac{B}{T - T_0}\right) \quad (7)$$

where B is a pseudo-activation energy (expressed in temperature units) and T_0 the empirical Vogel temperature.

Results and Discussion

Spin−lattice relaxation times were determined by analyzing the relaxation curves obtained from inversion−recovery experiments in terms of exponential functions. Both ^{1}H and ^{13}C relaxation curves could be well reproduced by means of a single-exponential function at all temperatures and frequencies.

A qualitative analysis of the T_1 experimental curves, reported in Figures 1 and 2, reveals a regular trend characterized by the presence of a minimum between 0 and 50 °C for all curves with the exception of the methyl carbon curve (Figure 2c). The temperature corresponding to the minimum regularly decreases with decreasing Larmor frequency (50 °C for ^{1}H T_1 at 400 MHz, 20−25 °C for ^{13}C T_1 at 75 MHz down to about 5 °C for ^{1}H T_1 at 20 MHz), thus indicating that all relaxation times are mainly affected by the same motional process. Considering the occurrence of T_1 minima some tens of degrees above the glass-transition temperature and the absence of a minimum in the methyl ^{13}C T_1 curve within the temperature range investigated, this motional process must be identified with the segmental main-chain reorientation, whose onset is indeed associated to the glass transition. However, closer inspection of the experimental ^{1}H relaxation times recorded at the highest frequencies (300 and 400 MHz) reveals the tendency to reach a maximum at the lowest temperatures investigated, very close to the glass-transition temperature. This suggests that at lower temperatures another motional process, presumably the methyl rotation about its ternary symmetry axis, becomes relevant, and it must therefore be taken into account in the analysis, not only to describe the ^{13}C methyl T_1 curve, but also the ^{1}H relaxation. This is reasonable considering that the proton spin−lattice relaxation time measured arises from the whole sample because
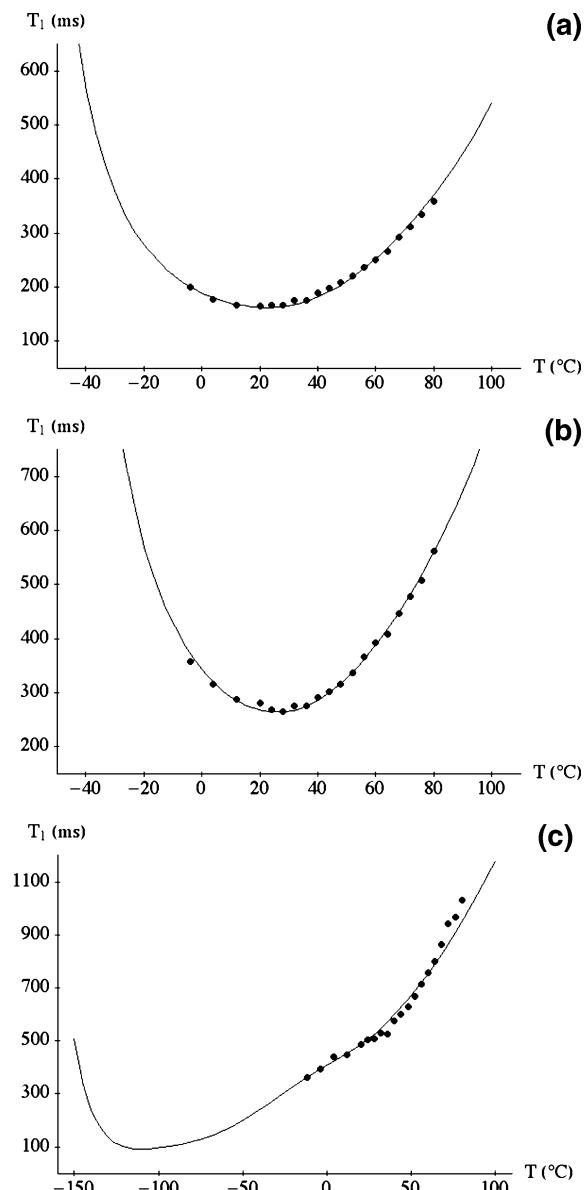
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Figure 2. ^{13}C spin−lattice relaxation times vs temperature at 75.47 MHz for (a) methylene carbons resonating at 38.1 ppm, (b) methine carbons resonating at 33.7 ppm, (c) methyl carbons resonating at 21.0 ppm. Symbols and lines indicate experimental and calculated relaxation times, respectively.

TABLE 1: Motional Parameters Obtained from the Fitting

motion	parameter	value
main-chain segmental motion	δ	0.77 ± 0.02
	ϵ	0.27 ± 0.02
	B	860 ± 50 K
	T_0	183 ± 5 K
	τ_∞	$(4.0 \pm 1.0) \times 10^{-12}$ s
methyl rotation	δ	0.69 ± 0.03
	E_a	10.6 ± 0.5 kJ/mol
	τ_∞	$(6.3 \pm 1.3) \times 10^{-13}$ s

account a possible correlation of motions and/or distribution of correlation times. For the temperature dependence of correlation times, we assumed an Arrhenius trend for the methyl rotation, while in the case of backbone segmental motions, the VTF model, which considers the peculiarity of motional processes responsible for the occurrence of the glass transition, has been applied.

The proton relaxation times at the different frequencies and temperatures were considered to obey eq 2, with the sum running over the two motional processes discussed above considered independent; for the ^{13}C relaxation times of backbone carbons, the methyl motion is clearly irrelevant and the contribution of C−H bond librations is usually taken into account.[9] However, if librations are considered independent from—and much faster than—segmental motions, their contribution to the relaxation rate results in a simple scaling factor,[21] and therefore eq 3 remains valid provided that an additional multiplying factor $(1 - a)$ is introduced, where a $(0 < a < 1)$ is related to the amplitude of the librations, described as anisotropic reorientations within a cone.

The inclusion of the methyl ^{13}C relaxation curve in the set of data used in the fitting procedure revealed to be necessary in order to get a reliable determination of the methyl rotation parameters; in fact, the sole proton relaxation data (where the contribution of methyl rotation is evident at the lowest temperatures at 300 and 400 MHz) allowed only a rough extrapolation to be obtained because of the limited low-temperature range experimentally accessible. However, the results obtained considering the methyl ^{13}C relaxation times in terms of methyl rotation and librations did not give a satisfactory agreement with the corresponding experimental curve, in particular regarding the manifest change in the slope at about 40 °C. This could be due to the fact that the contribution of main-chain segmental motions is relevant or at least nonnegligible also for the relaxation of methyl carbons. The inclusion of this contribution in the calculation of T_1 is by no way simple and is out of the scope of the present work; however, in order to verify this hypothesis and obtain a rough evaluation of this contribution to the methyl carbon relaxation, we assumed that the methyl ^{13}C relaxation rate could be written as a sum of two terms, one arising from methyl rotation and the other from main-chain motions.

The results of the fitting performed as described above are reported in Table 1 and in Figures 1 and 2, where the calculated relaxation curves (extended over a wider temperature range to show the predicted occurrence of relaxation times minima due to the methyl motion) are compared with the experimental ones.

The satisfactory agreement between experimental and calculated curves, despite the diversity of the experimental data sets used in the fitting, constitutes strong evidence of the validity of the approach used and the models chosen for the analysis of the data.

The results obtained from proton relaxation indicate that the segmental main-chain motions are slightly, but not negligibly,
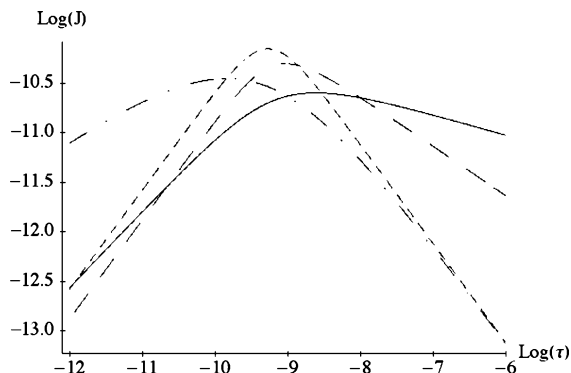
of both the wide-line techniques used and the averaging effect of the spin diffusion process. Moreover, it is well known that in polypropylene-like systems the methyl rotation represents an active relaxation sink below the glass-transition temperature.[20]

A global fitting procedure was applied to the ^{1}H relaxation curves obtained at 20, 25, 300, and 400 MHz as well as to the ^{13}C relaxation curves obtained from the peaks at about 21.0 (CH$_3$), 33.7 (CH belonging to ethylene−propylene−ethylene triads), and 38.1 ppm (CH$_2$ belonging to both propylene−ethylene−propylene and propylene−ethylene−ethylene triads) in the ^{13}C spectrum acquired by high-resolution techniques.[10] The choice of these ^{13}C peaks was determined by their good signal-to-noise ratio and the fact that the value of n in eq 3 is known with certainty ($n = 3$, 1, and 2 for the peaks at 21.0, 33.7, and 38.1 ppm, respectively).

The two motions considered in the fitting procedure, i.e. the backbone segmental motions and the methyl rotation, have been treated within the HN model, since this takes independently into

Figure 3. Logarithm of spectral densities (s^{-1}) calculated from eq 5 as a function of $\log(\tau)$, with τ expressed in s, at a frequency of 300.13 MHz and with $\epsilon = 0.27$, $\delta = 0.77$ (solid line, values obtained from the fitting); $\epsilon = 1$, $\delta = 1$ (short-dashed line); $\epsilon = 0.5$, $\delta = 1$ (long-dashed line); $\epsilon = 2$, $\delta = 0.5$ (dot–dashed line).

Figure 4. Calculated correlation time vs temperature for segmental main-chain motions (solid line) and methyl rotation (dashed line).

correlated ($\delta = 0.77$) and heavily distributed ($\epsilon\delta = 0.21$). Given the complexity of the Havriliak–Negami expression for the spectral density in terms of the parameters ϵ and δ, reported in eq 5, the effect of the parameter values on J cannot be straightforwardly predicted. To this regard, an extensive discussion is present in ref 3. Here, to better understand the extent of correlation and distribution of motions as far as main-chain motions are concerned, the spectral density obtained from the fitting has been compared with those calculated for significant ϵ and δ values (see Figure 3). In particular, curves have been calculated as a function of $\log(\tau)$, fixing $\delta = 1$ and $\epsilon = 0.5$ (i.e., no correlation and intermediate distribution), $\delta = 0.5$ and $\epsilon = 1/\delta = 2$ (i.e., no distribution and intermediate correlation), and $\epsilon = \delta = 1$ (i.e., no distribution and no correlation, corresponding to the Bloembergen–Purcell–Pound model). By comparison with the BPP curve, it is clear that correlation and distribution almost exclusively affect the fast and slow motion sides of the curve, respectively, giving rise in both cases to a decrease of the slope. The curve obtained from the fitting of the experimental data shows a strong deviation with respect to the BPP curve in the slow motion side, which is even stronger than that observed for the curve obtained assuming an intermediate distribution; on the other hand, the deviation from BPP in the fast motion side is sensibly smaller than that given by assuming an intermediate correlation.

A comparison with the same results obtained from carbon relaxation, where the main-chain motions are probed in specific positions of the polymeric chain, is important to understand the nature of this distribution. In this case, a value of 1 for the correlation parameter δ (or, in other terms, the use of the Davidson–Cole model instead of the Havriliak–Negami one) revealed to be the most suitable, as expected because of the local nature of the motions investigated when studying ^{13}C relaxation; for both types of main-chain ^{13}C nuclei the values obtained for ϵ (0.14 and 0.19 for the ^{13}C peaks at 38.1 and 33.7 ppm, respectively) are of the same order of magnitude of the $\epsilon\delta$ value obtained from protons, thus indicating that the distribution of correlation times is homogeneously spread over the different monomeric triads present in the chain. Moreover the best-fitting value of a is on the order of 10^{-3}, indicating that the contribution of librations to the spin–lattice relaxation of main-chain carbon nuclei is fully negligible.

The best-fitting parameters of the VTF equation $T_0 = 183$ K and $B = 860$ K are physically meaningful: T_0, the temperature below which the segmental motions of the main chain are completely absent, is in fact about 40 °C less than T_g, while B
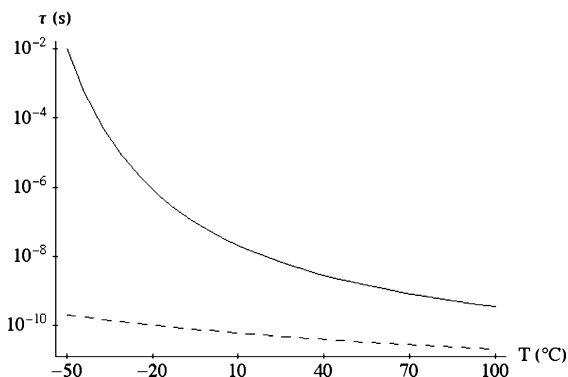
is $4.7 \times T_0$, corresponding to a "fragility" (defined as D^{-1}, being $D = B/T_0$) of 0.21.[22] Studies on polymeric systems often use the Williams–Landel–Ferry (WLF) equation,[23] which is essentially equivalent to the VTF one. The parameters C_1^g and C_2^g, which appear in the WLF equation using the glass-transition temperature as the reference temperature, are related to the VTF parameters through the relations $C_2^g = T_g - T_0$ and $C_1^g = B/(2.303 C_2^g)$. From our VTF parameters we obtained $C_1^g = 9.8$ and $C_2^g = 38$ K. These values are in satisfactory agreement with those reported for a similar ethylene–propylene rubber ($C_1^g = 13$ and $C_2^g = 41$ K)[24] and close to those found for atactic polypropylene ($C_1^g = 10$ and $C_2^g = 56$ K).[4a]

Given the relatively low sensitivity of the overall set of experimental data to the methyl motion, preliminary calculations were performed in order to try to reduce the number of fitting variables; since values very close to 1 were always obtained for the parameter ϵ, this has been fixed to 1 in the final fitting, which is equivalent to applying a Cole–Cole model for this motion instead of the Havriliak–Negami one. A value of 0.69 was found for δ from the fitting, indicating a slight but not negligible correlation and distribution of correlation times; the value obtained for the activation energy of this motion (10.6 kJ/mol) is in very good agreement with values previously reported for polypropylene, ranging from 9.6 to 11.8 kJ/mol.[25,26]

The relative values of the high- and low-temperature T_1 minima in each ^1H relaxation curve, considering the percentage of methyl protons (about 20%), are compatible with results obtained for similar systems, the behavior being intermediate between that observed for polypropylene (with 50% methyl protons)[26,27] and branched polyethylene (with 5% methyl protons).[28]

The fraction of ^{13}C methyl relaxation rate ascribable to the main-chain motions is quite small (12.1%) compared to the fraction due to the rotation of the methyl group about its ternary symmetry axis (87.9%). The constant C_C is reduced by about 50% with respect to its theoretical value, thus suggesting that in this case the contribution of librations is important, although a reliable quantitative determination of the parameter a is prevented by the assumptions made in analyzing the ^{13}C methyl relaxation times and by the limited temperature range experimentally available.

The constant C of eq 2 is 2.9×10^9 s^{-2}, of the expected order of magnitude.[5,29]

The correlation times τ of eqs 6 and 7, calculated for the two dynamic processes, are reported in Figure 4. It is interesting to note that given the very different thermal activation of the two processes, the difference between the two correlation times decreases from 8 to only 1 order of magnitude on passing from the glass-transition temperature to 80 °C.

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Conclusions

The approach proposed here, consisting of a simultaneous analysis of multifrequency ^{1}H and ^{13}C spin−lattice relaxation times of polymers, revealed to be powerful in getting a reliable characterization of the motional processes occurring in an amorphous ethylene−propylene random copolymer. The motions taken into account to describe both ^{1}H and ^{13}C relaxation were the segmental main-chain reorientations, the onset of which is associated with the glass transition, the rotation of side-chain methyl groups about their ternary symmetry axes, as well as C−H bond librations. The main-chain and methyl motions, considered independent, were described by the Havriliak− Negami model, while the contribution of librations was inserted as superimposed in the relaxation expressions within the fast motion limit.

The main-chain segmental motions revealed to exhibit a nonnegligible correlation and a strong distribution of correlation times. In particular, the latter revealed to have a homogeneous nature from the observation of similar distribution coefficients determined for either the whole set of protons or the inequivalent carbons belonging to the main chain. The methyl rotations were also found to be correlated but much less distributed than main-chain motions, obeying the Cole−Cole model ($\epsilon = 1$ in the Havriliak−Negami expression). The influence of methyl motions was substantially negligible in describing low-frequency (20−25 MHz) proton relaxation times above the glass-transition temperature, but this was not the case for the corresponding high-frequency measurements (300−400 MHz), where the difference between the temperatures at which the T_1 minima ascribable to methyl rotation and main-chain segmental motions occur is strongly reduced. The contribution of librations to ^{13}C relaxation is negligible for main-chain carbon nuclei, while it seems relevant in the case of methyl ones. Moreover, to get a good reproduction of the experimental relaxation times of methyl carbons, the contribution of main-chain segmental motions must be taken into account. All the Arrhenius and Vogel−Fulcher− Tamman parameters, describing the trend of correlation times vs temperature, are physically meaningful and/or in good agreement with data previously reported for similar systems.

The method proposed here was successful in the extraction of quantitative dynamic information in polymeric systems from ^{1}H and ^{13}C relaxation data, greatly improving the reliability of the dynamic parameters obtained with respect to single-frequency or single-nucleus analyses. However, even though the agreement between experimental and calculated data is satisfactory, further improvements could be obtained by con-sidering the temperature dependence of some motional parameters, such as those associated with the motional correlation and distribution.

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