Molecular Dynamics of Atactic Poly(propylene) Investigated by Broadband Dielectric Spectroscopy

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Broadband dielectric spectroscopy (BDS) has been widely used to characterize the molecular dynamics in polymers and low-molecular-weight glass formers because of its wide dynamic range covering more than 15 frequency decades.[1−3] This experimental technique allows the investigation of molecular motions on various length scales ranging from the fluctuations within a monomeric unit or rotational fluctuations of short side chains to the cooperative glass transition. At much larger length scales, the relaxation dynamics of entire macromolecules take place. A prerequisite for the application of BDS is the presence of dipoles, which provides the link between the molecular motions and the interactions with an external electrical field. Though most of the polymer systems contain at least weakly polar groups in either the main or the side chains, a substantial class of nonpolar polymers, for example polyolefins, do not have dipoles and are thus dielectrically inactive. To overcome this problem, various methods aiming to introduce permanent dipole moments have been proposed.[4] Recently, a convenient method was introduced: the procedure is based on the addition of a small fraction of organic molecules with a high dipole moment μ_{probe}, acting as "dielectric probes"; the doped polymeric matrix becomes dielectrically active. More experimental details can be found in ref 4 and references therein.

In this Communication, the local and cooperative dynamics of atactic poly(propylene) (a-PP) were investigated in a wide range of frequencies and temperatures. So far, molecular motions in a-PP have been studied by NMR,[5−8] light scattering,[7] and dynamics mechanical analysis.[8−10] Preliminary (unpublished) dielectric relaxation spectra by Pakula and co-workers proved that the dielectric relaxation time of the α-process is in good agreement with the segmental dynamics probed by other techniques. In this work, for the first time, the complete relaxation map of atactic polypropylene (a-PP) is presented. The work is based on the analysis of the experimental data collected, above and below T_g, over 8 frequency decades. Both neat and doped a-PP, using (4,4′-(*N,N*-dibutylamino)-(*E*)-nitrostilbene) (DBANS) as "dielectric probe" at low concentration ranging from 0.2% to 1% (m/m), were investigated. The intrinsic dipole moment of DBANS in vacuum is 8 ± 1 D, as estimated from molecular modeling.

The prominent question of any probe technique is the ability of coupling the probe response to molecular motions of the polymer matrix itself. Concerning DBANS, it was already shown[4] that the large angular fluctuations of the probe are exclusively coupled to the structural relaxation, i.e., the cooperative dynamic glass transition, when dispersed in poly(styrene), isotactic poly(propylene), and poly(ethylene). Hence the dielectric probe senses the microviscosity in its close vicinity. In contrast, the dielectric probe response was found essentially not affected by local dynamics (i.e., β-relaxation) or dynamics involving the crystalline phase. No crystalline phase, characteristic of i-PP, was present in a-PP, but a β-relaxation was detected in the glassy state.

Atactic poly(propylene) (a-PP, $M_w = 12\,000$ g/mol, $M_w/M_n = 2.33$, $T_g^{\mathrm{DSC}} = 249.2$ K) was used as received from Scientific Polymer Products. Mixtures of PP and (4,4′-(*N,N*-dibutylamino)-(*E*)-nitrostilbene)[4] were prepared by simultaneously dissolving exact amounts of the two components in *o*-xylene (from Aldrich without further purification) and subsequently mixing to obtain a homogeneous solution. Polymer films were prepared by casting at $T = 110$ °C on circular brass electrodes and annealed for 1 h at 150 °C under a continuous nitrogen flow. Silica fibers were used as spacers between the electrodes, resulting in samples with a well-defined geometry for BDS experiments.

Dielectric spectroscopy measurements were performed isothermally in the frequency range 10^{-2} Hz−10 MHz, using a high-resolution dielectric analyzer (Alpha Analyzer, Novocontrol Technologies) in the temperature range from −160 to 80 °C. In order to determine the relaxation parameters, isothermal dielectric spectra were analyzed by the empirical Havriliak−Negami (HN) function:

$$\epsilon''(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{[1 + (i\omega\tau_{\mathrm{HN}})^a]^b} \tag{1}$$

Here ϵ_∞ is the high-frequency value of the dielectric constant and $\Delta\epsilon$, τ, a, and b indicate the dielectric strength, relaxation time, and shape parameters which characterize the width and the asymmetry of the loss curves, respectively. In order to take into account the contribution due to the conductivity, the term $-i\epsilon_0^{-1}\sigma\omega^{-n}$ (where $\epsilon_0 = 8.854$ pF/m is the vacuum permittivity and $n \leq 1$) was added to eq 1.

Isothermal dielectric relaxation spectra of a-PP doped with 0.2% DBANS at different temperatures are shown in Figure 1. A structural (α-)relaxation process well visible above T_g and a secondary process showing up in the glassy state far below T_g were detected; both processes slowed down upon decrease in the temperature.

To illustrate the effect of the probe concentration on the structural and secondary relaxation, an isochronal representation of the dielectric loss ϵ'' at 13.8 kHz for different concentration of DBANS is shown in Figure 2. At high temperatures ($T = 303$ K) a strong peak corresponding to the α-relaxation, being the dielectric manifestation of the dynamic glass transition, is observed. This process, also discernible for the undoped PP, is amplified upon increase of the concentration of the dielectric probe and is slightly shifted toward higher temperatures. A second peak, labeled as β-relaxation, is present at lower temperatures ($T = 148$ K). This sub-T_g process is not affected by the presence of DBANS, indicating that the dynamics of the dielectric probe solely couples to the cooperative dynamics.

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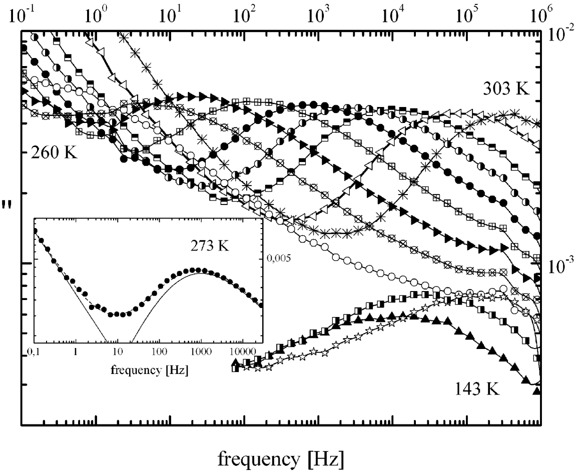

Figure 1. Log−log plot of dielectric loss $\epsilon''(f)$ of a-PP doped with 0.2% of DBANS vs frequency at different temperatures (from right left: 303, 293, 283, 275.5, 273, 268, 263, 260.5, 255, 173, 153, 143 K). In the inset an example of fit for the spectrum at 273 K.

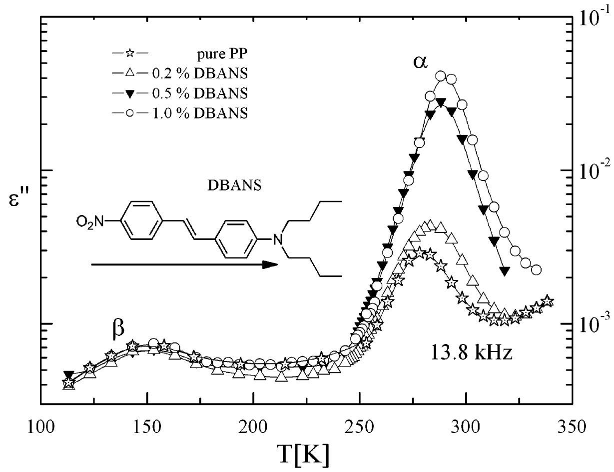

Figure 2. Temperature dependence of the dielectric loss $\epsilon''(T)$ at 13.8 kHz. The continuous lines are guides for the eyes. The structure of the probe and the orientation of the dipole moment within the probe are reported as an inset.

In fact, a linear dependence was found between the intensity of the structural α-relaxation $\Delta\epsilon_\alpha$ and the probe concentration at a fixed temperature (see inset of Figure 3), indicating, first, that the DBANS probes amplify specifically the dynamic dielectric glass transition and, second, that all the dissolved DBANS molecules contribute to the dielectric response. The value of $\Delta\epsilon_\alpha$ extrapolated to a zero concentration of DBANS matches well the dielectric strength obtained for undoped PP. Consequently, a strikingly selective sensitivity of the probe dynamics to the dynamic glass transition is ensured. The secondary β-relaxation observed in the glassy state of a-PP obeys the Arrhenius law $\tau_\beta = \tau_\infty \exp(E_\beta/RT)$, with an activation energy $E_\beta = 23 \pm 2.5$ kJ/mol and $\log(\tau_\infty/\mathrm{s}) = -13 \pm 1$ for all concentrations of DBANS (cf. Figure 4). This β-relaxation can be attributed to specific molecular features of the polymer. In fact, there is a striking coincidence of these parameters with those reported for the β-relaxation of polyisobutylene,[11,12] where the dielectric β-process was attributed to concerted rotations of methyl groups attached to the same atom of carbon of the polymeric backbone[13] or to combined motions of the methyl group and the main chain.[14] It has to be anyway pointed out that the reorientation of the methyl group in PP as measured by NMR[15] occurs on a much shorter time scale and with a lower activation energy (9.7 kJ/mol).

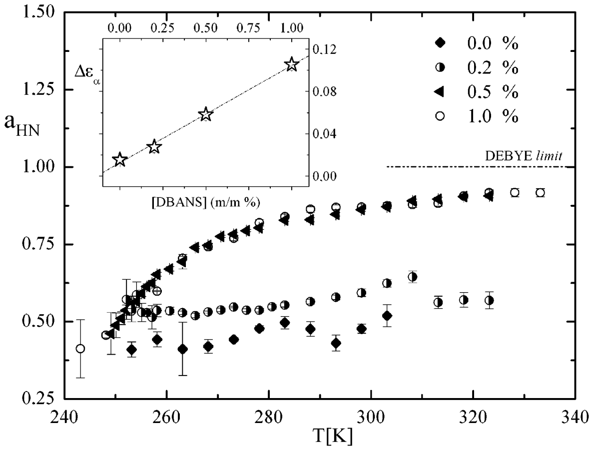

Figure 3. Thermal evolution of the Havriliak−Negami shape parameter a_{HN} of the structural α-relaxation for the undoped and doped a-PP. In the inset, the dielectric strength of the structural relaxation $\Delta\epsilon_a$ as a function of the probe concentration for a-PP at $T = 298$ K; the solid line is a linear fit of the data.

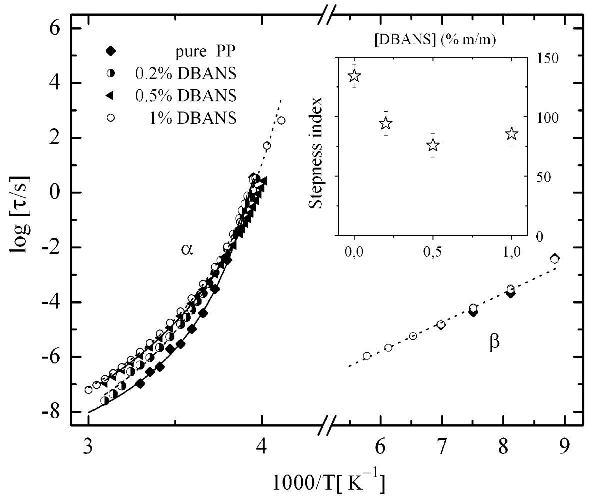

Figure 4. Relaxation map of the structural α-relaxation and secondary β-relaxation for undoped and doped a-PP. The solid lines and dots are VFT fits for the structural α-relaxation and linear Arrhenius fit for the β relaxation. In the inset, the concentration dependence of the steepness index, calculated from the dielectric relaxation measurements, is shown.

The structural α-relaxation times $\tau_\alpha(T)$ follow the usual non-Arrhenius temperature dependence, as shown in Figure 4. The experimental data were fitted in terms of the empirical Vogel−Fulcher−Tammann equation (VFT)

$$\tau_\alpha = \tau_\infty \exp\left[\frac{E_V}{R(T - T_V)}\right] \qquad (2)$$

yielding the three VFT parameters, E_V, τ_∞, and the Vogel temperature T_V, listed in Table 1. The dielectric glass transition temperature T_g, also given in Table 1, was determined using the common convention $\tau(T_g) = 100$ s. A minor T_g reduction upon addition of DBANS is observed (see Table 1), indicating a very weak plasticizing effect. This is due to the presence of aliphatic tail being part of DBANS, as has been discussed in ref 18. However, this little T_g shift is essentially negligible, which implies that the DBANS-containing PP retains the "correct" calorimetric and dielectric T_g of pure PP. Hence, at temperatures close to T_g, the dynamics of a-PP do not depend on the concentration of DBANS, as the structural relaxation times from systems with different concentrations accumulate around the same values.

Table 1. Glass Transition Temperature and the Relevant VFT Parameter for Pure and Doped a-PP at Different Concentration As Determined by Dielectric Relaxation Measurement

[DBANS] (% m/m)	T_V [K]	$\log(\tau_\infty/s)$	E_V [kJ/mol]	$T_g = T(\tau = 100$ s) [K]	T_g (DSC) [K]	steepness index m
0	226.0	−10.91	5.94	250.0	249.2	134.2
0.2	211.2	−11.97	9.84	248.0	250.4	94.2
0.5	199.1	−11.78	11.67	243.3	250.0	75.8
1.0	209.0	−11.13	9.55	247.0	249.3	85.4

On the other hand, at higher temperatures and higher frequencies, the probe dynamics is significantly slower than the α-process of the PP matrix. This effect is an inherent feature of a rotational probe. In fact, its hydrodynamic extension (larger than L, the size of DBANS probe ~1.5 nm[4,16]) exceeds the size $\xi(T)$ of a cooperatively rearranging region (CRR), which is reported around 2 nm[17,18] (at T_g). Consequently, the probe will average over the mobility of several CRR's (for $L \gg \xi(T \gg T_g)$), between which no dynamic correlation exists. For these reasons, in these conditions, the probe relaxation is not affected by the heterogeneous nature of the glass transition dynamics and enters into a hydrodynamic regime.[19,20] This picture is verified by the values assumed by shape parameter a_{HN} of the α-process (see Figure 3), showing an almost Debye-like peak for high DBANS concentrations at high temperatures (short relaxation times).

The different effect of DBANS on the high- and low-frequency dynamics is the natural cause for the changes in the dynamic fragility (or steepness index) m, defined as $d \log(\tau)/d(T_g/T)|_{T=T_g}$:[21] the curves of PP-DBANS are flatter than the pure PP; therefore, m gets reduced from 134 for the pure a-PP to 85 for PP + 1% DBANS. It should be noted that a dynamic fragility of $m = 137$ was found for the segmental dynamics of a-PP by dynamical mechanic spectroscopy,[7,9] a value being in excellent agreement with our data for pure a-PP. For the samples with higher concentration of DBANS, the steepness index reaches a plateau value of nearly 80. Interestingly, the weaker temperature dependence of probe dynamics could be an indication of a strong coupling[20] of the DBANS rotational motions to the host viscosity, for which similar reduced m values ($m \sim 70$) were found.[7,9]

The experimental data reported in this Communication aim to fill the gap in the characterization of atactic poly(propylene), considered as a model system to study the melt dynamics in amorphous polymers. The relatively low value of the intrinsic dipole moment of this polymer does not permit an easy analysis of its dielectric relaxation. Notwithstanding this, it was possible to characterize the glass transition dynamics of a-PP by broadband dielectric spectroscopy using small amounts of DBANS, an organic molecules with a high dipole moment, as "dielectric probe".

From a systematic investigation of the effect of probe concentration on the dielectric relaxation behavior of atactic polypropylene, we can conclude that the addition of DBANS enhances the strength of the α-process, while in the vicinity of T_g, the probe relaxation time resembles the intrinsic cooperative dynamics of the polymer. Finally, at lower temperatures a secondary relaxation process, not affected by the probe concentration, was revealed.

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