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Segmental Dynamics in Poly(vinylethylene)/Polyisoprene Miscible Blends Revisited. A Neutron Scattering and Broad-Band Dielectric Spectroscopy Investigation

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ABSTRACT: Despite the great experimental effort carried out over the past years by means of different techniques, the segmental dynamics in the model blend system poly(vinylethylene)/polyisoprene (PVE/PI) is still a topic of strong debate. One of the most controversial questions is the possibility of a bimodal distribution of segmental relaxation times for polyisoprene in the blend. In this work, we have combined a microscopic technique, quasielastic neutron scattering (QENS), with molecular isotopic labeling and broad-band dielectric spectroscopy. The measurements have been carried out on the same samples and at the same temperature (270 K). By means of this combination, we have shown that all the PI in the miscible blend sample PVE/PI (50 wt % PVE−50 wt % PI) dynamically behaves very close to pure PI. In contrast, the α-relaxation of PVE component in the blend is drastically "plasticized". In addition, it has been shown for the first time by QENS that the secondary β-like processes seem not to be modified by blending, at least for the blend component displaying the higher T_g. These experimental facts contradict many of the results previously published about the dynamics of the PI/PVE system, and as far as our knowledge, they cannot be explained in the frame of the models presently available for polymer blends dynamics.

I. Introduction

The study of the thermodynamics of polymer blends has been a very active field in polymer physics during the past 10 years. Recently, also dynamic aspects such as the so-called "dynamic miscibility", i.e., the question concerning how the dynamics of each component is modified in the blend, came into focus. In an ideal two-component molecular miscible system we could expect a completely homogeneous dynamic behavior, in the meaning that the time scale as well as the relaxation function of each component becomes similar in the blend. However, it is well-known that polymers are complicated systems from a molecular point of view, displaying a rich variety of dynamic processes that extend over more than 15 decades in time/frequency scales and that also show different spatial scales. Apart from vibrations and torsional librational modes, polymers usually show very localized and fast side-group motions (e.g., methyl group rotation), localized motions involved in the secondary β-relaxation, the molecular origin of which is still to be unveiled, and the so-called segmental motions involved in the glass transition (α-relaxation) which are diffusive in nature (i.e., without a defined spatial scale). It is generally believed that the faster and the more localized a molecular motion takes place, the less it would be affected by blending. For example, it has recently been shown by quasielastic neutron scattering[1] that the methyl group rotation in the poly(vinyl methyl ether)/polystyrene (PVME/PS) system is hardly sensitive to blending. Moreover, the dielectric β-relaxation of PVME also seems to be unaffected by blending with PS.[2] On the contrary, it has been found that the slower dynamic processes such as the α-relaxation and the so-called terminal relaxation are strongly changed by blending.[3−6]

It is worth emphasizing that the miscibility of polymer systems was from the early times implicitly defined in terms of segmental dynamics through the old criterion that a miscible blend should display only one glass transition temperature, T_g (i.e., only one α-relaxation), intermediate between the T_g's of the two components of the blend. However, differential scanning calorimetric (DSC) scans of miscible blends in the T_g range show a very broad step which starts almost at the glass transition of the blend component showing the lowest T_g. This broad glass transition has usually been associated with the existence of concentration fluctuations in the blend, which would imply a broad distribution of T_g's. However, the DSC technique does not allow in general to distinguish whether two separated and broad glass transition ranges (i.e., two different segmental mobilities) are still present in the experimental scan.

Over the past years this question has been investigated by different spectroscopic methods, mainly dielectric spectroscopy and NMR, at $T > T_g$. Among the different polymer blend systems investigated, the system poly(vinylethylene) (PVE) and polyisoprene (PI) can be considered as a model miscible polymer blend because PVE and PI form nearly athermal blends (i.e.,

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segment–segment interaction parameter $\chi \approx 0$) over the entire compositional range. The system PVE/PI has been investigated by dielectric spectroscopy,[7,8] mechanical spectroscopy,[7,9] and two-dimensional deuteron exchange nuclear magnetic resonance (2D-NMR).[10,11] However, it is worthy of remark that not all measurements were carried out on comparable samples. In particular, dielectric and mechanical measurements reported by Alegría et al.[7] correspond to blends in which the PI component was *cis*-1,4-polyisoprene, while in the case of 2D-NMR measurements the PI component had a microstructure of about 78% *cis*-1,4, 16% *trans*-1,4, and 6% 3,4. The molecular weights were also different, and in the case of some mechanical measurements[9] the materials were lightly cross-linked in order to minimize creep phenomena. In addition, a diblock copolymer of PVE and PI has also been investigated by dielectric and mechanical spectroscopy, dynamic light scattering,[12] and quasielastic neutron scattering.[13] In this case, the characteristics of the polymer components, PI and PVE, were similar to those of the polymers forming the blends measured by 2D-NMR.

Despite this experimental effort, the segmental dynamics in the PVE/PI system is poorly understood, and the question of dynamic miscibility in this "model system" is still a topic of strong controversy. Two different segmental modes (α-relaxation) have clearly been observed by dielectric spectroscopy and 2D-NMR in PVE/PI blends. A qualitatively similar behavior has also been observed in the copolymer samples by dielectric spectroscopy. However, while the characteristic time scale of the faster mode observed by dielectric spectroscopy is close to that of pure PI, the corresponding time scale measured by 2D-NMR is slower by about 2 orders of magnitude. On the other hand, the incoherent quasielastic neutron data obtained in the copolymer sample 50PVE/50PI at 280 K were also analyzed[13] in terms of two segmental contributions. Thereby, the slower one was considered as purely elastic in the time window ($\approx 10^{-10}$– 10^{-8} s) covered by the spectrometer used. Under such conditions, the characteristic time of the faster mode obtained by this analysis was also close to that of pure PI. On the other hand, the analysis of the dielectric data reported by Alvarez et al.,[8] which took into account that the dielectric strength of PVE is by a factor of 2 larger than that of PI, revealed the astonishing result that the relaxation times of PI in the blend were distributed according to a bimodal distribution. Thereby, the faster component of this distribution was centered close to the pure PI relaxations. The existence of this bimodal distribution would imply that part of the PI in the blend (it was estimated ≈40% for the 50PVE/50PI composition) dynamically behaves as pure PI and the rest as the PVE in the blend.

The picture of concentration fluctuations, where the probability of their occurrence is described by a Gaussian distribution around the average composition,[14] cannot account for such a behavior. Recently, two theoretical models were brought forward. On the basis of a nonlocal χ parameter, Khokhlov et al.[15] have formulated a thermodynamic theory of microphase separation in polymer blends predicting local demixing in overall miscible polymers. Such a microphase separation on small scales would be very difficult to observe in a static experiment but could have profound effects on the local chain dynamics. On the other hand, starting from the concept of cooperativity volumes which depend on the local composition, Kumar et al.[16] proposed a theory of concentration fluctuations that predicts a bimodal distribution of local environments, one centered around the average composition and the other close to the pure component with the lower T_g.

With these ideas in mind and trying to shed new light on the open questions discussed above, in this work we have used quasielastic neutron scattering (QENS) combined with selective isotopic labeling of PVE/PI samples. This experimental technique is very suitable to face the question of polymer blends dynamics in general. First of all, QENS is a microscopic technique that provides space-time information about the geometry and speed of the molecular motions involved through the momentum (Q) and energy ($\hbar\omega$) transfer dependence of the experimental magnitudes. Second, due to the very different scattering cross sections of hydrogen and deuterium, it is possible to highlight the dynamic response of one of the components in the blend by protonation. In this case, the neutron scattering intensity is dominated by the incoherent scattering of the hydrogen atoms. Therefore, the dynamics of the protonated polymer in the blend determines neutron scattering spectra, and in this way, the dynamic response of each of the two components of the blend can experimentally be isolated. In addition to QENS measurements, we have carried out new broad-band dielectric spectroscopy measurements which enlarge the frequency range previously used[7,8] by almost 5 orders of magnitude. Moreover, it is worth emphasizing that these new measurements were performed on the same samples investigated by QENS.

In this paper we will report on QENS measurements performed at $T = 270$ K. This temperature was chosen for different reasons. First, according to the available data on PVE/PI system, this temperature should be low enough to avoid the contribution of the α-relaxation of PVE component in the blend. On the other hand, this temperature should be high enough to allow the observation of the α-relaxation response of the PI component within the experimental window (≈ 0.5–$13\ \mu$eV) covered by high-resolution QENS techniques. In addition, at 270 K not only the dielectric α-peak of the blend sample PVE/PI but also the corresponding peaks of the two homopolymer components can be observed in the frequency range (10^{-3}–2×10^{8} Hz) covered now.

II. Experimental Section

II.1. Samples. The system investigated in this work is a well-known miscible blend of PVE and PI with a composition of 50 wt % PVE–50 wt % PI. The two pure homopolymer components of the blend were also measured for comparison. To experimentally highlight by quasielastic neutron scattering the dynamics of each of the components of the blend, we have used blend samples with selective deuteration of one of the two components. Moreover, in the case of PI, the methyl group was always deuterated in order to avoid the "contamination" of the scattering function from the fast methyl group rotation.

The samples studied were hPId$_3$ (protonated polyisoprene with the methyl group deuterated), hPVE [protonated poly(vinylethylene)], and the two blends hPId$_3$/dPVE and hPVE/dPI, where dPVE and dPI refer to fully deuterated PVE and fully deuterated PI, respectively. The scattering is always dominated by the incoherent contribution of the protonated compound: the scattering cross section of the protonated compound, $\sigma_s = \sigma_{inc} + \sigma_{coh}$, relative to the total scattering cross section of the sample, σ_s^{total}, is $\sigma_s/\sigma_s^{total} = 0.85$ for hPId$_3$/dPVE and $\sigma_s/\sigma_s^{total} = 0.89$ for hPVE/dPI. From these contributions, the incoherent part amounts to $\sigma_{inc}/\sigma_s = 0.88$ for hPId$_3$ in hPId$_3$/

dPVE and $\sigma_{inc}/\sigma_s = 0.93$ for hPVE in hPVE/dPI. The same samples used for neutron scattering were also used for dielectric spectroscopy measurements.

The polymers were prepared by anionic polymerization. The initiator was *sec*-butyllithium and benzene the polymerization solvent. The polyisoprene samples were made from isoprene-d_8 (d > 98%) or isoprene-methyl-d_3 (d > 99%) monomer. The reaction conditions lead to a microstructure with 70% *cis*-1,4, 24% *trans*-1,4, and 6% 3,4. The polybutadiene polymers were synthesized from butadiene or butadiene-d_6 (d > 97%), respectively, in the presence of dipiperidinoethane. Thus, polymers with mainly (99%) 1,2 addition are obtained. The molecular weights of the samples (hPId$_3$, 2.3 × 10^4; dPI, 4.2 × 10^4; hPVE, 2 × 10^4; dPVE, 2.3 × 10^4) were determined by membrane osmometry in toluene at 37 °C. The molecular weight distributions, M_w/M_n, were less than 1.02, as determined by size exclusion chromatography. With differential scanning calorimetry (DSC) at a heating rate of 10 K/min, the values of T_g determined from the middle point of the step in the specific heat resulted to be 272 K for PVE, 213 K for PI, and 228 K for the blend. In this case, the DSC trace is rather broad, extending from almost the T_g of PI over roughly 35 K.[11]

Homogeneous polymer blends were prepared by dissolving in benzene. To increase the stability, 0.1% of 2,6-di-*tert*-butyl-4-methylphenol as antioxidant was added. The solvent was removed under high vacuum until a constant weight was achieved.

II.2. Neutron Scattering Measurements. Quasielastic neutron scattering (QENS) measurements were carried out by means of the high-resolution backscattering spectrometer BSS at the Institut für Festkörperforschung (IFF), Forschungszentrum Jülich, Germany. The wavelength of the incident neutrons was set to $\lambda = 6.28$ Å, resulting in an energy resolution of 1 μeV (full width at half-maximum). The range of momentum transfer, Q, covered was 0.2 Å^{-1} < Q < 2 Å^{-1}. The thickness of the sample films ranged between 0.2 and 0.6 mm depending on the cross section, yielding transmissions in the range 81−92%. Flat Al sample holders were used. The resolution of the spectrometer was determined by taking spectra from the samples at 4 K, where the scattering, within the observation window of the instrument, is entirely elastic. The efficiency of the detectors was determined by measuring a standard vanadium sample. The measurements were carried out at $T = 270$ K. The raw data were corrected for detector efficiency, sample container, and absorption using standard programs. After these corrections the magnitude obtained is the experimental scattering function *S(Q,ω)*. The multiple scattering effects from the proposed model scattering function were determined using the DISCUS program.[17]

II.3. Dielectric Relaxation Measurements. Dielectric measurements were performed in the frequency domain from 10^{-3} to 10^9 Hz with a Novocontrol System by means of two different equipments. In the low-frequency range, a Solartron-Schlumberger gain/phase analyzer SI1260 supplemented with a broad dielectric converter allowed to measure from 10^{-3} up to 10^7 Hz. For high frequencies (10^6−10^9 Hz), a Hewlett-Packard impedance analyzer HP4191A based on the principle of a reflectometer was used. The error in the determination of the loss tangent of the dielectric constant was around 10^{-4} for the first setup. In the second setup the error amounts to around 10^{-3} in the range 10^6−10^8 Hz and substantially increases in the highest frequency decade. Overlapping of the spectra at the same temperature was possible by means of the common decade of both pieces of equipment (10^6−10^7 Hz). Measurements were made at isothermal conditions with temperature stability better than 0.1 K. The sample holders used were parallel-plate capacitors of 20 mm diameter for the low-frequency setup and 5 mm diameter for the high-frequency one. The distances between the electrodes were kept constant by insertion of Teflon spacers in the first case and quartz glass fibers in the second one. The measurements obtained with the high-frequency setup, which resolution is more limited, are affected by the contribution of the measuring cell to the loss tangent. To correct the data, a careful evaluation of this contribution was carried out by a measurement performed at very low temperature, where the sample does not show dielectric dispersion.

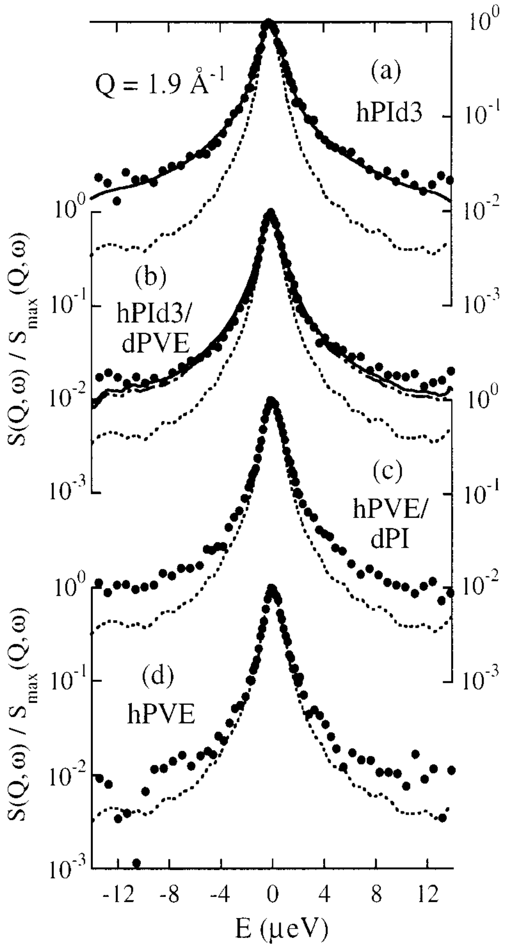

Figure 1. Scattering function of hPId$_3$ (a), hPId$_3$/dPVE (b), hPVE/dPI (c), and hPVE (d) as measured at the Jülich backscattering spectrometer at 270 K for $Q = 1.9$ Å^{-1} in a logarithmic representation. Dotted lines are the instrumental resolution. All spectra have been normalized to the respective intensity maximum. Fit results corresponding to a single KWW law are shown for the pure homopolymer hPId$_3$ [solid line in (a)] and for the blend hPId$_3$/dPVE in (b): the solid line is the fit result if the contribution of the deuterated component is also taken into account, the dashed−dotted line represents the fit without considering the deuterated compound.

III. Results

III.1. Quasielastic Neutron Scattering. Figures 1 and 2 show the normalized quasielastic neutron scattering spectra at $T = 270$ K and at two different values of Q (1.9 and 0.9 Å^{-1}) for all the samples investigated. In the case of pure polyisoprene, hPId$_3$ sample, the measured *S(Q,ω)* displays a clear quasielastic broadening. This broadening increases as the Q value increases. Figure 2 indicates that a considerable broadening of the elastic line is still present at $Q \cong 0.9$ Å^{-1}. This is the behavior expected for the α-relaxation process,[18] taking into account that the experimental temperature in this case is about 60 K above the calorimetric glass transition temperature of polyisoprene. In the case of the hPId$_3$/dPVE sample, the measured *S(Q,ω)* mainly corresponds to the incoherent scattering of the hPId$_3$ component, as was discussed in the Introduction. Figures 1 and 2 also show that the quasielastic broadening observed for hPId$_3$/dPVE is in fact not very different from that observed in the case of the pure polyisoprene

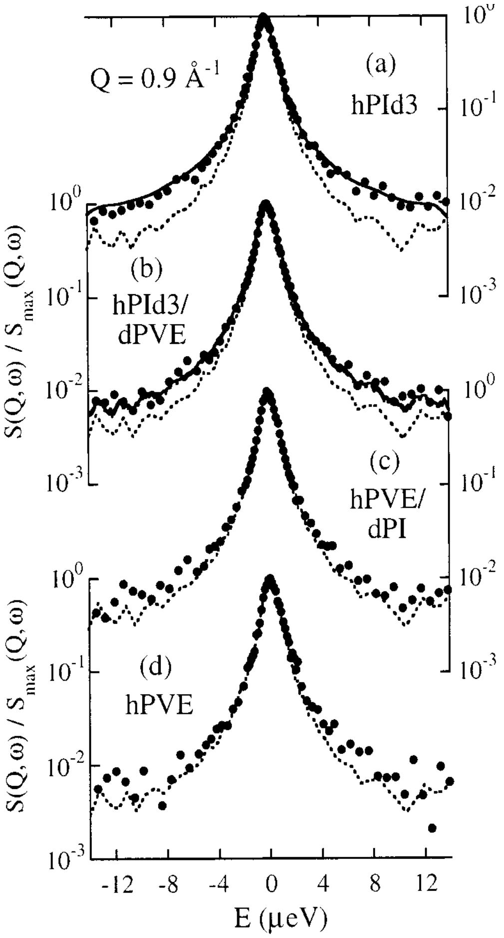

Figure 2. Same quantities as represented in Figure 1 for $Q = 0.9$ Å^{-1}.

sample. From this first qualitative comparison it seems that the polyisoprene α-relaxation dynamics is not strongly affected by blending with PVE, at least in the measured temperature range.

In the case of the pure hPVE sample, unexpectedly, we also observe some quasielastic broadening, which cannot be related to the α-relaxation because the measuring temperature corresponds to the glass transition range of pure hPVE. In this temperature range the α-relaxation is too slow to be detected in the frequency window of a neutron backscattering instrument. Therefore, the measured broadening of the elastic line must originate from a localized secondary process like the Johari–Goldstein β-relaxation, which has previously been observed by QENS in the neighborhood of the glass transition in other polymers.[19,20] This idea is also suggested by the appreciable reduction of the broadening at low *Q* (see Figure 2). On the other hand, Figure 3 shows that the normalized scattering functions in the case of hPVE and hPVE/dPI nearly superimpose. Taking into account the weak contribution to the scattering of the dPI component in the blend, this would indicate that the molecular motions giving rise to this quasielastic scattering are not affected by blending. This result once again supports the idea that these molecular motions correspond to a secondary β-like process. In fact, it has recently been reported[2] that the dielectric β-relaxation of poly(vinyl methyl ether) is not modified by blending with polystyrene. The results reported here for PVE can be considered as the first microscopic evidence by QENS techniques of this dynamic behavior.

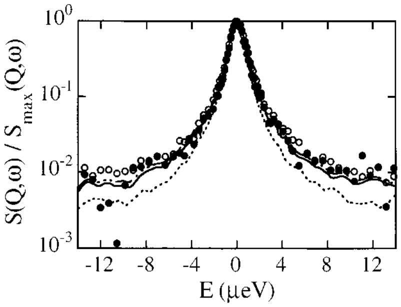

Figure 3. Comparison between the normalized scattering functions of hPVE (●) and hPVE/dPI (○) at 270 K and $Q = 1.9$ Å^{-1} in a logarithmic representation. Dotted line represents the instrumental resolution. Solid line shows the fit with the scattering law corresponding to the β-process of hPVE (eq 4), and dashed–dotted line displays the weighted addition of the contributions of both components in the blend to the total scattering.

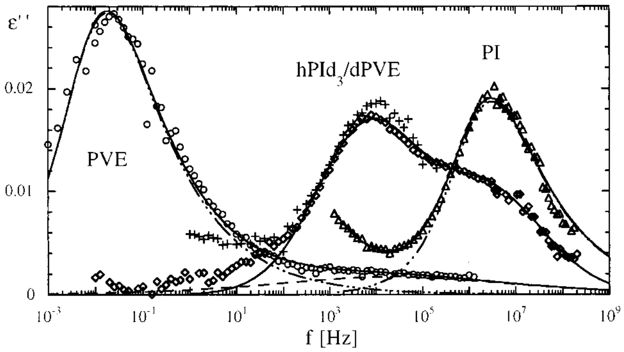

Figure 4. Frequency dependence of the dielectric loss at 270 K for the homopolymers hPVE (○) and hPId$_3$ (△) and for the blend hPId$_3$/dPVE (◇). Experimental results reported on another blend sample[7,8] are plotted for comparison (+). Lines correspond to fit results: in PVE, the dashed–dotted line corresponds to the α-relaxation, the dashed line corresponds to the β-process, and the solid line is the addition of both. In the blend, the solid line is the result of the superposition of processes with the distribution of relaxation times shown in Figure 6. In PI, the dashed–dotted line corresponds to the α-relaxation, and the solid line is the addition of the contributions of the α-process and the normal mode.

III.2. Dielectric Spectroscopy. Figure 4 shows the frequency dependence of the dielectric loss peak $\epsilon''(\omega)$ obtained a $T = 270$ K for the blend sample hPId$_3$/dPVE, as well as for the two homopolymer components, on an absolute scale. In addition, the $\epsilon''(\omega)$ previously published data[7,8] corresponding to the same blend composition, but consisting of homopolymer components with different molecular weight, microstructure, and other molecular characteristics, are also included in the figure for comparison. Note that, as has been mentioned above, the current measurements cover a much wider frequency range (10^{-2}–2×10^8 Hz) than those previously reported.

The dielectric response of pure PVE at 270 K in the frequency range covered shows not only the α-relaxation but also the secondary β-process. As was previously reported,[21] the dielectric strength of the β-process is much lower (around 10%) than that of the α-process. The dielectric loss peak of the α-contribution is centered in the low-frequency range at a frequency of about 2×10^{-2} Hz, which roughly corresponds to a relaxation time of 8 s. It is evident that this low-frequency process cannot be accessed by QENS spectroscopy. However, Figure 4 shows that the β-relaxation is a very broad process that extends toward the high-frequency range explored by QENS. This supports the suggestion that the PVE dynamics observed by QENS at 270 K has to be related to a localized secondary process other than the α-relaxation.

At the experimental temperature, in the case of the pure PI, the α-peak is centered in the high-frequency range at a frequency of about 3×10^6 Hz. This frequency corresponds to a relaxation time of 5×10^{-8} s, which lies in the range covered by the neutron backscattering spectrometer used by us. On the other hand, it is worthy of remark that the so-called "dielectric normal mode" also contributes to the low-frequency dielectric spectrum.[22] The overlap between this mode and the dielectric loss peak corresponding to the segmental α-relaxation depends to a large extent on the molecular weight of the PI component.[22] In the case of the PI investigated here, these two processes are well separated in frequency. This can be seen in Figure 4, where the tail from the normal mode has been represented to show this separation. A similar behavior is observed in the case of the blend sample hPId$_3$/dPVE, although a softening of the normal mode is also present as a consequence of blending. The results corresponding to the effect of blending on the dielectric normal mode of polyisoprene are beyond the scope of this paper and will be published elsewhere.

To focus the attention on the segmental α-relaxation and the comparison with QENS results, we have subtracted from the raw $\epsilon''(\omega)$ data of hPId$_3$/dPVE the normal mode contribution. The subtraction was carried out after first fitting the normal mode contribution to a Cole−Davidson relaxation function[22] and then subtracting the fit curve from the experimental $\epsilon''(\omega)$ data. In this way, the $\epsilon''(\omega)$ data for hPId$_3$/dPVE sample shown in Figure 4 mainly correspond to the segmental α-relaxation (the β-relaxation contribution would only amount roughly 5% of the signal). To check whether all relaxation processes (apart from the normal mode) taking place in the homopolymers are present in the blend response, we have compared the experimental dielectric strength of the blend sample $\Delta\epsilon'_{\mathrm{blend}}$ with that expected starting from the strengths of the relaxations in the pure polymers $\Delta\epsilon'_{\mathrm{PI}}$ and $\Delta\epsilon'_{\mathrm{PVE}}$ for PI and PVE, respectively. The values found for these strengths from the measurements are $\Delta\epsilon'_{\mathrm{blend}} = 0.11$, $\Delta\epsilon'_{\mathrm{PI}} = 0.078$, and $\Delta\epsilon'_{\mathrm{PVE}} = 0.13$. An uncertainty of 10% has to be taken into account in the determination of these quantities. The calculated value of $\Delta\epsilon'_{\mathrm{blend}}$ starting from the homopolymer values and taking into account the blend composition ranges between 0.0975 and 0.104. These two values are obtained under two different simple assumptions for the addition of the contributions in the blend: capacitors in series and in parallel. Therefore, the blend response shown in Figure 4 would contain the dielectric relaxation signal originating from the α- and β-processes of PVE and the α-process of PI.

On the other hand, we emphasize that, in the dielectric measurements on this system previously reported,[7,8] the separation between the normal and segmental modes was not possible. Because of the characteristics of the polyisoprene used at that time, the dielectric normal mode was seen in neither the pure PI loss peak spectrum nor that of the blend. This can be realized in Figure 4 where the normal mode response shows up as an almost flat background overlapping with the segmental contribution.

Finally, Figure 4 also shows that the double-peak structure of the dielectric loss peak from the blend sample hPId$_3$/dPVE is now more clearly visible compared to the old data. The high-frequency component of this double-peak structure is rather close to the loss peak corresponding to the pure polyisoprene. This result, which is in qualitative agreement with the QENS results described above, suggests that the segmental dynamics of PI is hardly modified by blending. On the other hand, the low-frequency component of the double loss peak of the blend hPId$_3$/dPVE sample should correspond mainly to the α-relaxation of PVE modified by blending. As was already commented, the dielectric contribution of the β-process in PVE is very weak. Therefore, from a qualitative point of view, Figure 4 shows that, in contrast to PI, blending seems to strongly affect the α-relaxation of PVE. A shift of more than 5 decades in frequency can be deduced easily from the data of Figure 4. We note that the relaxation time corresponding to the peak of the PVE contribution in the blend sample is about $\tau \sim 2 \times 10^{-5}$ s, still too long to be observable by QENS. This again underlines our interpretation that the contribution from the PVE dynamics observed by QENS, either in pure PVE or in the blend, corresponds to a localized β-process.

IV. Data Evaluation

IV.1. Quasielastic Neutron Scattering Data. Pure Homopolymers. The QENS data taken on the hPId$_3$ sample were analyzed by following the well-established procedure for the α-relaxation in glass-forming polymers.[23] The model scattering function $S(Q,\omega)$ is taken as the Fourier transform (FT) of the intermediate scattering function $S(Q,t)$ given by the following expression:

$$S(Q,t) = \exp\left[-\frac{\langle u^2\rangle}{3}Q^2\right]\exp\left[-\left(\frac{t}{\tau_{\mathrm{W}}}\right)^{\beta}\right] \qquad (1)$$

where the prefactor is the Debye−Waller factor (DWF) with $\langle u^2\rangle$ the mean-squared displacement, and the time dependence is given by the well-known Kohlrausch−Williams−Watts (KWW) function. The stretching parameter β ranges between 0 and 1 and in the case of polymer systems usually takes values in the range 0.4−0.5. The KWW relaxation time τ_{W} depends on both temperature and Q and is taken as

$$\tau_{\mathrm{W}} = \tau_0(T)\left(1 + \frac{1}{Q^2 {l_0}^2}\right)^{1/\beta} \qquad (2)$$

which corresponds to a sublinear diffusion process with an intrinsic jump length distribution for the diffusive jumps given by $f_0(l) = l l_0^{-2} \exp(-l/l_0)$. Equation 2 exhibits an asymptotic low-Q limit $\tau_{\mathrm{W}} \propto Q^{-2/\beta}$, which in fact implies the Gaussian approximation for $S(Q,t)$.[24]

To fit the experimental $S(Q,\omega)$ data, the FT of eq 1 is convoluted with the instrumental resolution, and a flat instrumental background is also allowed which finally turns out to be almost negligible. The β value was fixed to the value determined by dielectric spectroscopy and neutron spin echo $\beta \cong 0.4$[18] (see below). The fitting routine also included multiple scattering corrections which are essential in the low-Q regime. For this purpose, the Monte Carlo program DISCUS[17] was employed.

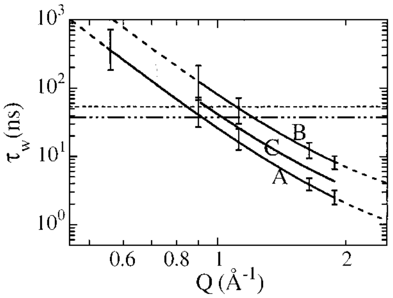

Figure 5. Momentum transfer dependence of the KWW relaxation times obtained from the fit to the scattering function of the homopolymer $hPId_3$ and the blend sample $hPId_3/dPVE$ at 270 K (solid lines A and B, respectively). The error bars are located at the *Q* points where experimental data exist, and dashed lines show the corresponding extrapolations to higher and lower *Q* values beyond the instrumental limitations. The solid line C corresponds to the result obtained for the relaxation times corresponding to the $hPId_3$ contribution in the blend when the dPVE contribution is taken into account. Horizontal lines correspond to the KWW characteristic times obtained by dielectric measurements for the homopolymer $hPId_3$ (dashed−dotted) and the fast component in the blend (dotted) at the same temperature.

DISCUS calculates the multiple scattering contributions arising from the model scattering function considered and yields frequency-dependent correction factors for the single scattering cross section. The approximate complete cross section obtained by application of this factor is then fitted again to the experimental data. After an iteration of four to five steps convergence was achieved, and stable values (within some uncertainty limits) of the fitting parameters τ_0, l_0, and $\langle u^2\rangle$ were obtained: $\tau_0 = 0.23$ ns, $l_0 = 0.42$ Å, and $\langle u^2\rangle = 0.45$ Å^2. The corresponding fitting curves are included in Figures 1 and 2. The resulting $\tau_W(Q)$ is shown in Figure 5. The solid line indicates the *Q* range where some quasielastic broadening can actually be analyzed. Dashed lines are extrapolations of the *Q* law found. Estimated error bars are also included in the figure. They become larger in the low-*Q* range where the quasielastic broadening is weaker. It is worth emphasizing that the results obtained here for the α-relaxation of $hPId_3$ at 270 K are in good agreement with those previously obtained at higher temperatures.[23]

In the case of hPVE, the observed quasielastic scattering should be related to a localized process like the Johari−Goldstein β-relaxation. The QENS data could be analyzed following the same procedure that was used for other polybutadiene, 1,4-PB,[19] and for polyisobutylene, PIB.[20] For a detailed description of this procedure, we refer to those works, and here we will outline the basis of such framework and summarize the results found for the hPVE spectra presented in this paper. The β-process is considered as due to local thermally activated two sites jump processes over a distance *d* with characteristic times defined as

$$\tau_\beta(T) = \tau_0^{\beta} \exp\left(\frac{E}{k_B T}\right) \qquad (3)$$

(k_B = Boltzmann constant). The disorder inherent to glassy polymers gives rise to a broad distribution of activation energies *E*. The assumption of a Gaussian distribution of activation energies, characterized by the average E_0 and the width σ_β, leads to a log-Gaussian distribution of relaxation times $g_\beta(\log \tau_\beta)$. The values of the characteristic parameters can be determined from the dielectric measurements[21] ($E_0 = 0.42$ eV and $\sigma_\beta = 0.187$ eV). In this framework, the incoherent model scattering function reads as

$$S^{\beta}(Q,\omega) = \int_{-\infty}^{+\infty} g_\beta(\log \tau_\beta) S(Q,\omega)_{\tau_\beta}\, \mathrm{d}(\log \tau_\beta) \qquad (4)$$

where $S(Q,\omega)_{\tau_\beta}$ is the scattering function for two sites jumps.[19,20]

The experimental $S(Q,\omega)$ of hPVE could be well described by this model with values similar to that obtained for 1,4-PB[19] ($d \approx 1.5$ Å and $\tau_0^{\beta} \approx 10^{-15}$ s) and a reasonable value for the allowed flat background (0.2% of the intensity at the maximum), as can be seen in Figure 3. A complete characterization of this process on hPVE would need however the input from high-temperature measurements, where the quasielastic scattering can be observed at different *Q* values. This work, which is now in progress, is beyond the main goal of this paper, i.e., the effect of blending on the $hPId_3$ and dPVE dynamics, and will be published elsewhere.

Dynamics of $hPId_3$ and hPVE in the Blend. As has already been discussed, the scattering from the sample $hPId_3/dPVE$ is dominated by the incoherent contribution from the protonated $hPId_3$ component. Therefore, in a first step we have followed the same analysis as that used in the case of pure $hPId_3$. The value of the KWW β-parameter was also fixed to 0.4. In principle, we could expect a lower value of β due to the broadening effect of concentration fluctuations on the α-relaxation of polymer blends.[2] However, it is well-known that this effect diminishes as the temperature increases above the T_g of the blend and in the temperature range covered by QENS seems to be almost negligible.[2] Furthermore, the analysis of the dielectric results also justifies the value of β used (see below). From the fitting procedure we obtain the following values of the fitting parameters: $\tau_0 = 0.95$ ns, $l_0 = 0.45$ Å, and $\langle u^2\rangle = 0.42$ Å^2. The corresponding fitting curves are included in Figures 1 and 2 as dashed−dotted lines. The resulting $\tau_W(Q)$ is shown in Figure 5 (upper curve). As can be seen, the τ_W values are close to those of pure $hPId_3$. For example, at $Q = 1.9$ Å^{-1} they are 2.4 ns ($hPId_3$) and 8.2 ns ($hPId_3/dPVE$), i.e., less than a factor of 4 of difference. We note that also the values of l_0 and $\langle u^2\rangle$ within the experimental uncertainties are essentially the same as those obtained for $hPId_3$.

In a second step of the analysis, we have taken into account the correction due to the contribution from the dPVE in the sample. As mentioned in the Experimental Section, this contribution amounts to about 15% of the total scattering. Taking into account that the PVE local dynamics seems to be hardly affected by blending (see Figure 3), we have modelized this contribution in a pure incoherent approximation by means of eq 4 with the values of the model parameters obtained for pure hPVE. With this, the model scattering function now is given by the following expression

$$S(Q,\omega) = \exp\left[-\frac{\langle u^2\rangle}{3}Q^2\right][0.85 S^{\mathrm{PI}}(Q,\omega) + 0.15 S^{\mathrm{PVE}}(Q,\omega)] \qquad (5)$$

where $S^{\mathrm{PI}}(Q,\omega)$ represents the FT of the normalized KWW function and $S^{\mathrm{PVE}}(Q,\omega)$ is given by eq 4. The values of $\langle u^2\rangle$ and l_0 were fixed to those obtained in the first step of the analysis procedure, which, on the other hand, are similar to those obtained for pure hPId$_3$. Thus, the only fitting parameter now is τ_0, which turns to be $\tau_0 \cong 0.49$ ns. The corresponding fitting curves are shown in Figures 1 and 2 as solid lines. The agreement with the experimental curves is even better after this refinement. The resulting $\tau_W(Q)$ is also shown in Figure 5. As can be seen, after the refinement of the analysis procedure the $\tau_W(Q)$ is slightly modified and becomes even more similar to that of pure hPId$_3$. In fact, we can say that within the uncertainty limits they could just be the same.

In the case of the sample hPVE/dPI, the scattering is dominated by the incoherent contribution from hPVE component. Figure 3 shows that in this case the fitting curve obtained for pure hPVE is also a good description of the $S(Q,\omega)$ corresponding to the hPVE/dPI sample. The slight differences can be accounted for by taking into account the correction due to the scattering from the dPI component in the sample. In this case, the contribution from the dPI component can be estimated to 11% of the total scattering and was modelized in a pure incoherent approximation by means of the FT of the KWW intermediate scattering function with the parameters corresponding to pure hPId$_3$. Now, a new model scattering function was constructed by the superposition of the scattering functions of hPVE and hPId$_3$ weighted by a factor 0.89 and 0.11, respectively. No fitting procedure was followed. The constructed scattering function convoluted with the resolution is shown in Figure 3. The agreement with the experimental data is very good.

As a conclusion, we can say that a careful quantitative analysis of the quasielastic neutron data confirms the results suggested by a qualitative comparison of the data. The β-like local process of hPVE and the α-relaxation of hPId$_3$ are hardly affected by blending.

IV.2. Dielectric Measurements. The investigation of the dielectric relaxation of pure PVE and PI has been previously reported in the literature, but in a narrower frequency range, usually from 10^{-2} to 10^{6} Hz.[7,8] Here we have analyzed our data at 270 K following standard procedures in order to compare our results with those previously reported. In the case of PVE, we have followed a similar analysis procedure of $\epsilon''(\omega)$ to that described in a previous work.[21] The $\epsilon''(\omega)$ data of PVE shown in Figure 4 were analyzed by means of the addition of two contributions: α- and β-relaxations. The α-contribution was described in terms of a Havriliak−Negami (HN) function, which in fact approximately corresponds to a KWW relaxation function in the time domain.[25] The values obtained for the two KWW parameters were $\beta \cong 0.42$ and $\tau_W \cong 6$ s. These values are the same, within the experimental uncertainties, as those reported by Hofmann et al.[21] for a similar sample and temperature range. In the case of the weak β-contribution, following the ideas discussed in the previous section, we have assumed a distribution of simple Debye processes with a log-Gaussian distribution of relaxation times $g_\beta(\log \tau_\beta)$. The imaginary part of the dielectric constant $\epsilon''(\omega)$ corresponding to the β-contribution can therefore be written as

$$\epsilon''(\omega) = \Delta\epsilon^{\beta}_{\mathrm{PVE}} \int_{-\infty}^{+\infty} \frac{\omega\tau_\beta}{1 + (\omega\tau_\beta)^2}\, g_\beta(\log \tau_\beta)\, \mathrm{d}(\log \tau_\beta) \quad (6)$$

The β-contribution to the dielectric constant was fitted in this frame, and the values obtained for the fitting parameters are $\Delta\epsilon^{\beta}_{\mathrm{PVE}} = 0.10$, $\sigma_\beta = 0.187$ eV, and $\tau_\beta(270\ \mathrm{K}) = 7.4 \times 10^{-6}$ s. It can be shown[26] that the description used here in terms of a log-Gaussian distribution of relaxation times is equivalent to the Cole−Cole distribution function previously used by Hofmann et al.[21] to describe the β-process. Taking into account the proper transformation, the σ_β value found corresponds to a Cole−Cole α-parameter value of 0.25, i.e., the same value reported by Hofmann et al.[21] in a similar temperature range. The value of τ_β is also rather similar to that previously reported taking into account the experimental uncertainties.

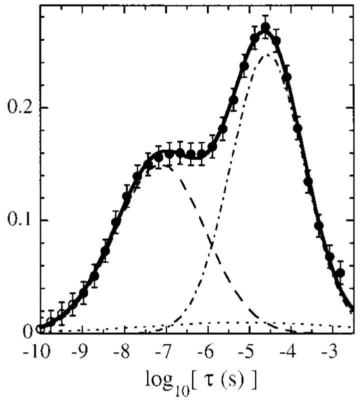

Figure 6. Distribution function of relaxation times obtained from the dielectric loss data of the blend sample hPId$_3$/dPVE at 270 K. Full symbols are used in the time interval corresponding to the frequency region where experimental data exist. Empty symbols are also provided by the CONTIN program though they fall out of this interval. The solid line shows the description with eq 7: the addition of two Gaussian-like distribution functions (eq 8) depicted by the dashed line (fast component) and the dashed−dotted line (slow component) and the contribution of the β-relaxation (dotted line).

In the case of PI data, we have first of all subtracted the "normal mode" contribution following the procedure previously described in the Results section. After that, the resulting α-peak was fitted to a HN function (equivalent to a KWW in the time domain) as in the case of the α-peak of PVE. The values obtained for the KWW parameters were $\beta \cong 0.45$ and $\tau_W \cong 3.8 \times 10^{-8}$ s. These values are similar to those previously reported,[22] although here we have extended the frequency range of measurements. In particular, the β value obtained is within the experimental uncertainties, similar to the average value of 0.4 usually assumed for PI.[18,22,23] Due to this reason, we have also assumed a value of 0.4 for the neutron data analysis previously discussed.

The dielectric $\epsilon''(\omega)$ data from the blend sample hPId$_3$/dPVE were analyzed by the same procedure followed in the previously reported work.[8] This analysis is based on a generalization of the well-known CONTIN algorithm for inverting integral equations.[27] This general method can be applied to obtain the apparent distribution function of Debye processes describing the dielectric data of polymers in general. The imaginary part of the dielectric constant $\epsilon''(\omega)$ can always be written as a superposition of Debye processes (similar to eq 6) with a distribution function of relaxation times $L(\log \tau)$. This function can be obtained directly from the $\epsilon''(\omega)$ data by means of the generalized CONTIN program.

Table 1. Parameters Characterizing the Gaussian Distributions of Relaxation Times Corresponding to the Slow and Fast Components in the Blend Obtained from Dielectric Measurements

	σ	τ_m (s)	A
fast	1.51	7.3×10^{-8}	0.404
slow	1.24	2.7×10^{-5}	0.545

Figure 6 shows the distribution function obtained by this procedure starting from the $\epsilon''(\omega)$ data of the hPId$_3$/dPVE sample shown in Figure 4. As can be seen, this distribution also shows a double-peak structure mirroring the shape of $\epsilon''(\omega)$. As commented above, the peak centered at the slower times should in principle correspond to the dPVE contribution to the $\epsilon''(\omega)$ spectrum while the other one (faster times) should correspond to the hPId$_3$ contribution. At this point we have to remind that the obtained distribution function includes not only the contributions of the segmental dynamics in the blend but also the contribution of the β-relaxation of PVE, which due to the dilution effect is weaker than that in pure PVE. Taking into account the neutron results, the contribution of the β-relaxation of PVE to the dielectric relaxation of the blend was assumed to be the same Gaussian function used for describing the β-relaxation of pure PVE. As can be seen in Figure 6, this contribution appears as a very broad and weak peak and would hardly affect any further analysis of the $L(\log \tau)$ distribution.

To quantitatively check the origin of the two main contributions to $L(\log \tau)$, we have fitted this distribution function by means of the weighted addition of three Gaussian-like distributions:

$$L(\log \tau) = A_f g_f(\log \tau) + A_s g_s(\log \tau) + A_\beta g_\beta(\log \tau) \quad (7)$$

where the subscripts f, s, and β refer to the "fast", the "slow", and the β-relaxation contributions, respectively. As aforementioned the contribution of the β-relaxation is fixed to that expected from pure PVE, whereas both the "fast" and the "slow" contributions are assumed to be Gaussian functions given by

$$g_{f,s}(\log \tau) = \frac{1}{\sigma_{f,s}\sqrt{\pi}} \exp\left\{-\left[\frac{\log\left(\frac{\tau}{\tau_m^{f,s}}\right)}{\sigma_{f,s}}\right]^2\right\} \quad (8)$$

$\sigma_{f,s}$ and $\tau_m^{f,s}$ being respectively the width of the distribution and the main relaxation time of the corresponding ("fast", "slow") contribution.

We emphasize that the main goal of this analysis is to check whether the dielectric results are compatible with those obtained by QENS, and in particular, whether the polyisoprene in the blend behaves similar to pure polyisoprene. As can be seen in Figure 6, the description of $L(\log \tau)$ obtained by using eq 7 is very satisfactory. The values corresponding to the fitting parameters can be found in Table 1. From the values of the amplitude factors A_f and A_s, first of all, we have compared the contribution of the fast process to the observed dielectric relaxation ($\Delta\epsilon_f = A_f\Delta\epsilon_{\text{blend}} = 0.044$) with that expected from the segmental relaxation of PI in the blend. This can be calculated as $0.5\Delta\epsilon_{\text{PI}}$, i.e., $0.5 \times 0.078 = 0.039$. The factor 0.5 is due to the concentration of PI in the blend investigated. Taking into account the abovementioned uncertainties in $\Delta\epsilon$ (10%), the good agreement found shows quantitatively that the fast component of the blend dielectric response is essentially due to the contribution of all the PI units in the blend. As would be expected, also the contribution of the slow component ($\Delta\epsilon_s = A_s\Delta\epsilon_{\text{blend}} = 0.059$) agrees with what is expected from the PVE α-relaxation alone ($0.5\Delta\epsilon^{\alpha}_{\text{PVE}} = 0.5 \times 0.12 = 0.060$). Therefore, it turns out that, in contrast to the previously reported data on the same blend composition but containing homopolymers with different characteristics, now the dielectric response is originated by a superposition of two dielectric peaks, each one associated with each of the two homopolymer components (see Figure 4). We do not need to invoke any bimodal distribution of the hPId$_3$ component to explain the dielectric data. We will return to this point in the Discussion section.

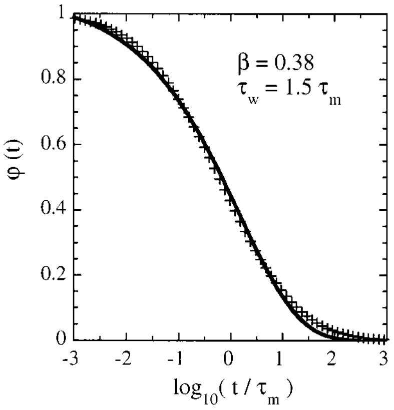

Figure 7. Relaxation function in the time domain obtained by superposition of Debye processes (eq 9), the characteristic times of which are distributed according to the Gaussian function corresponding to the fast component in the blend as observed by dielectric spectroscopy (dashed line in Figure 6). The line shows the fit result with a KWW function. The resulting values for the parameters are indicated.

On the other hand, there is another question that has to be clarified concerning the compatibility of the neutron and dielectric results. In the case of the analysis of the QENS data, we have used for pure hPId$_3$ as well as for hPId$_3$/dPVE a KWW form for the intermediate scattering function. However, in the case of the dielectric data and for simplicity (also for a direct comparison with previously published data), we have used Gaussian distributions of relaxation times. It is well-known that a KWW function can always be represented by means of a distribution of relaxation times, although in this case the distribution is asymmetric. However, we can try to check what is the best KWW approximation to the Gaussian distribution function obtained for the hPId$_3$ dielectric component in the blend. To do this, we have constructed the time domain relaxation function associated with this Gaussian distribution of relaxation times as

$$\varphi(t) = \int_{-\infty}^{+\infty} g_f(\log \tau) \exp\left(-\frac{t}{\tau}\right) d(\log \tau) \quad (9)$$

and fitted it by a KWW function. The result obtained is shown in Figure 7. It is clear that both functions are compatible within the experimental uncertainties. The β value obtained is $\beta \cong 0.38$, which is very close to the $\beta \cong 0.4$ used in the analysis of neutron data.

V. Discussion

The QENS results reported above indicate that the segmental dynamics of PI seems to be hardly affected by blending with PVE, even at the low temperature of 270 K investigated here. We remind that 270 K is the glass transition temperature of pure PVE. Not only the characteristic relaxation time of the α-relaxation in pure $hPId_3$ and in the $hPId_3/dPVE$ sample are rather similar, but also the shape of the relaxation function. This conclusion is in clear contradiction with previously reported 2D-NMR results[10,11] corresponding to similar samples. In that investigation, the characteristic relaxation time of the segmental relaxation of PI in the blend sample was found to be almost 3 orders of magnitude slower than in pure PI. Although the analysis of 2D-NMR results usually involves several assumptions and rather complex manipulations of the data, Chung et al.[10] mentioned that the uncertainty in the evaluation of the characteristic relaxation time was relative small (less than a factor of 2). We emphasize that in our case the results emerge, first of all, directly, i.e., without any data analysis, from the comparison of the experimental scattering function of the $hPId_3$ and $hPId_3/dPVE$ samples. Moreover, a direct inspection of the raw dielectric data of Figure 4 also supports the same interpretation. Furthermore, we remark that the QENS time scales corresponding to pure PI and to PI in the blend match the corresponding scales of the dielectric relaxation at the same value of Q, Q_0 ($Q_0 \approx 0.9$ Å^{-1}) (see Figure 5). A similar result has been recently reported for poly(vinyl methyl ether) in poly(vinyl methyl ether)/polystyrene samples.[2] Though no interpretation of Q_0 is still available, we do not discard its relation to some particular length scale relevant for relaxation techniques. As far as we know, in almost all polymers the Q_0 values found[28] are close to 1 Å^{-1}.

A previous QENS investigation on the segmental dynamics in a copolymer sample of PI and PVE[13] seems also to suggest the same relation between the segmental relaxation of PI in the copolymer and that in the blend. However, we note that in that investigation both components of the copolymer sample were protonated, rendering the analysis of the QENS data very difficult. In a first approach, the authors analyzed the data, which were taken in the same temperature range as investigated here, by assuming that the response of PVE in the experimental window covered by QENS spectroscopy would be completely elastic. By using selectively deuterated samples, our results clearly show that such an assumption was wrong. In the low-temperature range the local dynamics corresponding to the secondary relaxation processes of PVE are active in the blend sample, as in the pure PVE, and have to be properly taken into account in the data analysis.

As was stated in the Introduction, the most controversial point concerning the segmental dynamics in the blend system PI/PVE is the idea of a bimodal distribution for the PI dynamics as was first suggested by the dielectric results reported by Alvarez et al.[8] To analyze those dielectric data, it was found necessary to consider that the PI component in the blend displays a bimodal distribution of the segmental relaxation times. In such a picture, part of the PI (40% for the composition investigated here) moves as in pure PI, and the rest follows the segmental dynamics of PVE in the blend. At this point, it is worthy of remark that the characteristics of the PI sample used at that time were different than those considered here. The samples were lightly cross-linked and did not allow to separate properly the dielectric normal mode contribution. Furthermore, the dielectric measurements were carried out in a rather limited frequency range from 10^{-2} to 10^6 Hz (see Figure 4). On the other hand, the idea of a bimodal distribution of relaxation times for each of the components of a blend was also suggested by the interpretation of the 2D-NMR data of polystyrene/poly(phenylene oxide) blends reported by Chin et al.[29] and the dielectric data of homogeneous diblock copolymer melts of poly(methylphenylsiloxane) and polystyrene.[30]

From a theoretical point of view, the possibility of a bimodal distribution of relaxation times in the PI/PVE system, one close to pure PI and the other close to the average composition, has recently been invoked by the theory of concentration fluctuations proposed by Kumar et al.[16] This theory is in fact a generalization of an approach by Fischer,[14] who only took into account concentration fluctuations. Kumar et al., in addition, consider the concept of a “cooperative volume” over which a fluctuation must take place. Nevertheless, it is worthy of remark that when Kumar et al.[16] try to understand the dielectric data of PI/PVE block copolymers in this framework, they invoke the additional assumption that the sampling of the bimodal distribution of relaxation times is limited by “intramolecular connectivity effects”.

The results presented here clearly exclude the idea of a bimodal distribution of relaxation times for the segmental relaxation of PI in the PI/PVE blend. The combination of a microscopic technique, QENS, with selective isotopic substitutions, and broad-band dielectric measurements carried out at the same temperature and on the same samples reveals that all the PI in the blend sample (50 wt % PVE−50 wt % PI) behaves dynamically very close to pure PI. Though this result has been deduced by the investigation of only one temperature (270 K), we can expect to find the same behavior at any temperature. In fact, 270 K has not any particularity for the blend sample—the reasons for choosing it were detailed in the Introduction. Taking into account the usual temperature dependence of the magnitudes characterizing the dynamics in blend systems,[2] we expect an increasing separation of the time scales corresponding to the fast and slow components from each other with decreasing temperature. However, if a bimodal character for the distribution function of PI in the blend has not been found at 270 K, there is no evident reason for emergence of such a character at other temperatures. Moreover, temperature-dependent dielectric measurements which will be published elsewhere show that the relative strength of the peaks in the blend remains constant below and above 270 K, within the experimental uncertainties.

The behavior found on PI could, in principle, be understood in the framework of the thermodynamic theory of microphase separation in miscible blends proposed by Khokhlov et al.[15] This approach predicts local demixing in overall miscible polymers, which would be very difficult to observe in a static experiment but could have strong effects on the local dynamics. However, the problem is that, in the nanoheterogeneous structure predicted for the blend system, one should expect that also PVE behaves as pure PVE. The dielectric results of Figure 4 clearly show that this is not the case. The α-relaxation of PVE in the blend investigated is “plasticized” by a factor higher than 10^4 in the characteristic frequency/time scale.

On the other hand, the application of the ideas of the so-called coupling model (CM) of Ngai[31] to polymer blends dynamics can, in principle, give a qualitative explanation for the existence of two different segmental relaxations in a given blend, each one related to one of the two components. In fact, these ideas have previously been invoked to rationalize the dielectric, mechanical, and NMR results of the PI/PVE system.[7,32] The CM assumes that the "coupling parameter", n (n is given in terms of the β parameter of, e.g., eq 1 as $n = 1 - \beta$), which accounts for the nonexponential character of the α-relaxation response of a homopolymer, depends on the intermolecular environment. When these ideas are applied to polymer blends dynamics, it is assumed that a distribution of local concentrations should produce a distribution of n or β, which also implies a distribution of relaxation times through the so-called "second universality" of this model. However, it is hard to understand how a distribution of local concentrations can produce a distribution of n or β, if the values of these parameters are the same for the two components of a blend, in particular, if there are no specific interactions between the two homopolymer components. This is the case of the PI/PVE system where the value of β for PI and PVE seems to be close to 0.4. Moreover, although the CM ideas of blend dynamics are usually discussed in terms of the so-called cooperativity plots,[32] an actual quantitative application of the model (e.g., the determination of the distribution of n or β from the experimental data) seems to be rather difficult and involves many additional assumptions.

VI. Conclusions

Combining a microscopic technique, QENS, with molecular isotopic labeling and broad-band dielectric measurements carried out on the same samples and at the same temperature, we have shown that all the PI in the miscible blend sample PI/PVE dynamically behaves very close to pure PI. In contrast, the α-relaxation of PVE component in the blend results to be drastically "plasticized". Moreover, it has been shown for the first time by QENS that the secondary β-like processes seem not to be modified by blending, at least for the blend component displaying the higher T_g. These experimental facts contradict many of the results previously published on the dynamics of the PI/PVE system. As far as we know, they cannot be explained quantitatively in the frame of the models presently available for polymer blends dynamics.

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