Macromolecules **1997,** *30,* 597−604

Study of the Two-Component Segmental Dynamics of Poly(vinylethylene)/Polyisoprene Miscible Blends

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Received July 5, 1996; Revised Manuscript Received November 14, 1996[⊗]

ABSTRACT: The two components of the segmental dynamics of poly(vinylethylene) (PVE) and polyisoprene (PIP) miscible blends, as observed dielectrically, are resolved and analyzed. This analysis is based upon a generalization of the CONTIN algorithm for inverse Laplace transformations presented in a previous publication. By means of this procedure, a distribution of relaxation times, corresponding to Debye-like processes, is directly obtained from the dielectric data in the frequency domain. This method allows a straightforward comparison between our dielectric results and those previously reported from 2D-NMR measurements. The calculated distributions have a bimodal character, i.e., two different dynamical processes contribute to the whole dielectric α-relaxation of the blends. It is found that, although the faster process resembles to the PIP dynamics, the slower contribution involves the dynamics of both the PIP and PVE units. This fact explains the differences between the dielectric and nuclear magnetic resonance results.

Introduction

The α-relaxation of miscible blends shows unique features compared to those of conventional polymers. Thus, it can be said that the shape of the relaxation spectra of a blend (for instance the loss peak as measured by means of frequency domain dielectric or mechanical spectroscopies) is much broader than the one corresponding to its components, especially on the low-frequency side, and it is also strongly temperature dependent.[1−5] This temperature dependence does not follow the time−temperature superposition principle which has been found to be obeyed, at least approximately, by many homopolymers.[6] It has been suggested that the origin of this odd relaxation behavior is related to dynamical heterogeneities due to concentration fluctuations.[1] The basic idea is that these dynamical heterogeneities yield a distribution of those segmental motion processes which are responsible for the dynamical behavior of the component homopolymers. On the basis of these ideas, two different approaches have been recently developed. Fischer's model[3] transforms the distribution of local concentration fluctuations into a distribution of relaxation times through a distribution of glass-transition temperatures. The other method[4] applies the model of Ngai[7] to the particular case of miscible polymer blends. The main question that these models must face is how the segmental dynamics of a polymer is modified when its chains are mixed with those of another polymer.

Among those miscible polymer blend systems which have been investigated, the system poly(vinylethylene) (PVE) and polyisoprene (PIP) is of particular interest because these polymers form nearly athermal blends, i.e. miscibility occurs over the entire composition range despite an absence of specific chemical interactions.[8] Moreover, a combined study of dielectric and mechanical relaxation measurements in the α-relaxation range has suggested that the α-relaxation process involves two different dynamical events in this system.[5] However, it should be noted that, in ref 5, the presence of two different dynamic processes in the blends was observable only in the dielectric measurements at 20 and 25% PVE. Two different dynamical processes have also been detected in this system by means of two-dimensional deuteron exchange nuclear magnetic resonance (2D-NMR).[9] The advantage of this NMR technique is that it allows the observation of the dynamics of each component of the blend separately by using a selective deuteration labeling. In these previous studies, the two different processes observed were associated with the dynamics of the two segmental components, though they seemed to be modified by blending. However, it turns out that the results obtained using both dielectric and 2D-NMR are not completely compatible,[9,10] although the comparison is difficult due to the different methods used for analyzing the data.

In this work we have analyzed the previously reported dielectric relaxation results of the PVE/PIP system[5] using a method developed by us in order to gain insight into the physical origin of the two different dynamics observed in these blends. The method of analysis used allows us to obtain the distribution of simple Debye-like processes directly from the experimental data. This method allows a more straightforward comparison between dielectric and 2D-NMR data because the latter were also analyzed in terms of distributions of Debye-like processes. Thus, the processes contributing to the segmental dynamics of PVE/PIP blends as observed by means of dielectric spectroscopy are characterized throughout the entire range of compositions. The results obtained can rationalize the differences observed in the dynamics of these blends by dielectric and 2D-NMR techniques. These results are also discussed in the framework of the currently available models for polymer blends dynamics.

Experimental Section

The experimental features of the samples, the dielectric setup, and the conditions of the measurements are already described in ref 5. Dielectric measurements were carried out by a BS4000 system from Novocontrol GmbH. The frequency range covered was from 10^{-2} to 10^{6} Hz, and the experimental limit for the loss factor was about 10^{-4}. Blend samples investigated are referred to herein as PVE-25 through PVE-75, where the number denotes the percentage by weight of poly(vinyl ethylene).

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

Analysis

In a previous work[11] we showed how the well-known CONTIN algorithm for inverting integral equations[12] can be generalized according to the following expression:

$$F(x) = \int_{-\infty}^{\infty} f(x,\tau)\, L(\ln \tau)\, \mathrm{d}(\ln \tau) \qquad (1)$$

In the conventional CONTIN algorithm, x stands for the time variable, $F(x)$ is a time decay relaxation function, and $f(x,\tau)$ is a single exponential function, i.e. a simple Debye-like process in the time domain. The generalized CONTIN method can also be applied to the equivalent case in the frequency domain, where x stands for the frequency variable and $f(x,\tau)$ is a Lorentzian-like function. Thus, this method can be applied to obtain the apparent distribution function of Debye-like processes describing the dielectric relaxation of polymers.[13,14] In this case $F(x)$ is the imaginary part of the dielectric permittivity ϵ'' which can be written as:

$$\epsilon''(\omega) = \int_{-\infty}^{\infty} \frac{\omega\tau}{1+\omega^2\tau^2} L(\ln \tau)\, \mathrm{d}(\ln \tau) \qquad (2)$$

Thus, in this way, we were able to obtain directly from the experimental data the distribution of characteristic relaxation times, $L(\ln \tau)$, which is the link which we can use to make a comparative study by taking into account the 2D-NMR results obtained from these same blend systems.[9] In the work reported in ref 9, the 2D-NMR data were also analyzed in terms of a distribution of Debye-like processes. However, let us recall that, in that work, these distributions of characteristic relaxation times were generated by assuming a double Gaussian function shape, whereas in the present work, these distributions of characteristic relaxation times are directly calculated from the experimental data without the need of imposing any assumption on their shapes.

Results

As mentioned above, the PVE/PIP system indicates two different dynamical processes in the α-relaxation range which, in the dielectric spectra, are apparent only for rather low PVE concentrations (see Figure 1). As we can see, while the dynamical response at the 25% concentration in PVE content presents a clear double peak structure, a single peak is displayed at the 50% and 75% concentrations, although a high-frequency shoulder is also hinted at in the 50% concentration. The comparison between dielectric and mechanical measurements[5] seems to indicate that the single peak structure of these samples is a consequence of the higher concentration of PVE, the homopolymer constituent with a higher dielectric strength. This would imply that, for these compositions, there could still be an underlying two-peak structure, which should be, somehow, masked or hindered by the contribution due to the PVE units, which are dielectrically more active. However, the two-peak structure was not detectable by means of mechanical measurements where the PIP contribution dominates.

Thus, in order to gain some insight into these questions, we proceeded to calculate, by means of the analysis procedure aforementioned, the distributions of relaxation times corresponding to eq 2, at different temperatures for blends PVE-25, PVE-50, and PVE-75. In Figure 1 we plot an example of the results obtained for the samples corresponding to PVE-25 (at 238 K), PVE-50 (at 242 K), and PVE-75 (at 259 K). As we can see, a clear double-peak structure of the distribution of relaxation times, which was to be expected from the direct inspection of the experimental data, is found for the PVE-25 sample. However, for the PVE-50 sample, although this double dynamics feature is not clearly detectable by sight in the experimental measurement, we can see from the calculated distribution of relaxation times that this double dynamics is still underlying the dielectric response of the blend at this composition too. Nevertheless, although there are hints that more than a single dynamics can also be present in the PVE-75 sample, the weakness of the faster process at this concentration, together with the broadening of the slower process, makes it difficult to obtain quantitative results of the former process. Thus, we can see that by means of the generalized CONTIN algorithm, we can obtain new qualitative information such as the presence of an underlying two-peak structure at higher PVE-content compositions, when this double-peak structure is not clearly apparent from the dielectric susceptibilities. In addition to this result, the distribution functions allow us to characterize each dynamical process by means of three parameters: a characteristic relaxation time (the one corresponding to the maximum of the distribution), the relaxation strength (the percentage of processes in each component), and the distribution width. These parameters have been estimated by means of log−Gaussian fits of each component of the distribution functions according to the following equation:

$$g(\log \tau) = \frac{1}{\sigma\sqrt{\pi}} \exp\left[-\left(\frac{1}{\sigma} \log \frac{\tau}{\tau_{\mathrm{m}}}\right)^2\right] \qquad (3)$$

σ and τ_{m} being respectively the width and the main relaxation time. Thus, the whole distribution function obtained from the analysis performed was described as

$$L(\log \tau) = A_{\mathrm{f}} g_{\mathrm{f}}(\log \tau) + A_{\mathrm{s}} g_{\mathrm{s}}(\log \tau) \qquad (4)$$

where A is an amplitude factor, and the subscripts f and s refer to the fast and slow processes, respectively. Lines in Figure 1 show an example of such a fit. In parts b, d, and f of Figure 1 the vertical solid lines stand for the limits of the accessible range inside the dynamic window of our frequency technique. These constraints force an uncertainty in the estimation of the fitting parameters (bigger in the case of the σ and A parameters) when the peak maxima are close to these bounds. It is worthy of remark that we have chosen a log−Gaussian shape for the distribution functions, not only for the sake of simplicity but also because the 2D-NMR data reported in ref 9 were also analyzed by imposing this type of distribution, as has been above mentioned. As can be seen in Figure 1, the distributions obtained by us without any restrictions are well-described in the cases of the PVE-25 and PVE-50 samples by the addition of Gaussian-like functions. Nevertheless, for the PVE-75 sample, we should say that, although in principle it is also feasible to fit the distributions of relaxation times by means of a double Gaussian function, the contribution of the fast peak is so small and so close to the high-frequency resolution that this fit must be a strongly biased one and the results of the fitting corresponding to the fast peak are unreliable. That is why for the PVE-75 sample we decided to fit

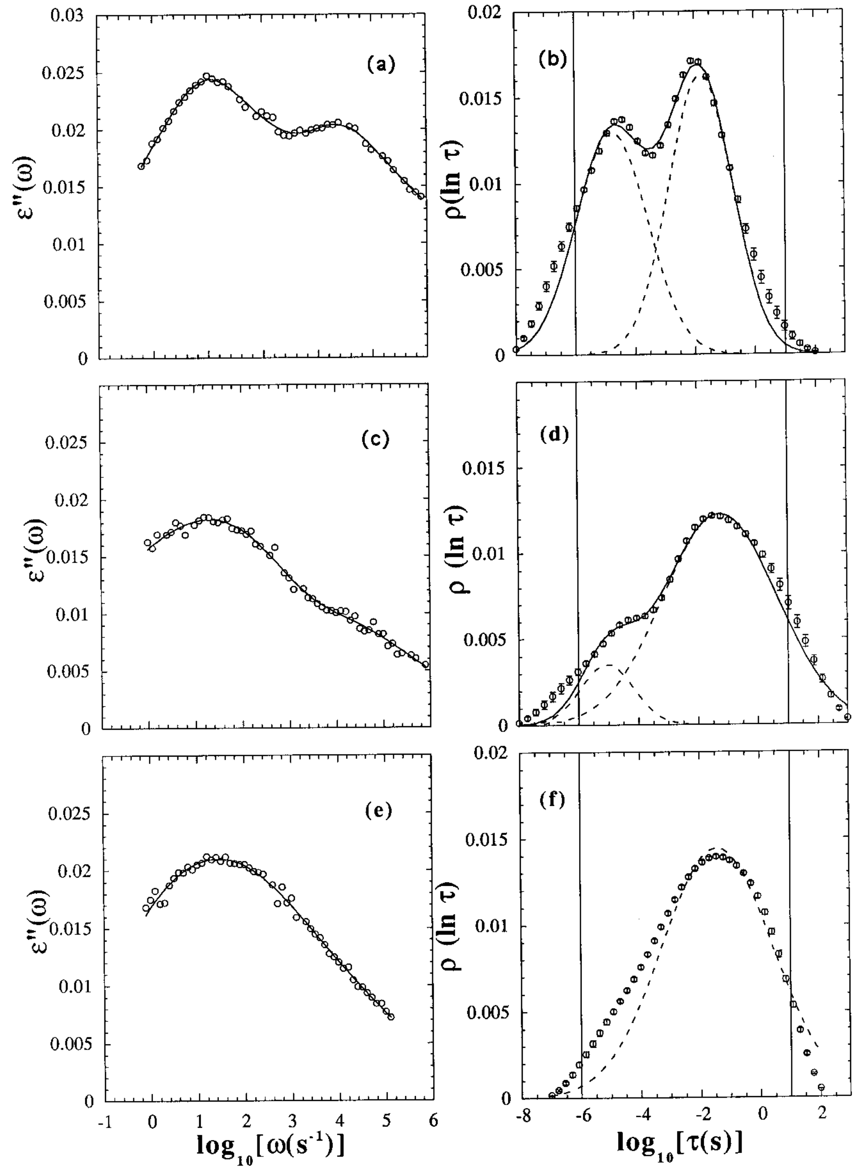

Figure 1. Experimental isothermal dielectric spectra of (a) PVE-25 at T = 238 K, (c) PVE-50 at T = 242 K, and (e) PVE-75 at T = 259 K and their fits (solid lines) by means of the calculated distribution of relaxation times corresponding to eq 2. Distribution of relaxation times and its error bars (b, d, and f) calculated from the data in a, c, and e (respectively). In b, d, and f the solid lines stand for a double-Gaussian fit, the separate contributions of which are shown as dashed lines. Vertical lines stand for the limits of the dynamic window.

only the slow times region by means of a single Gaussian function. The results so obtained for the fitting parameters corresponding to the different compositions investigated are shown in Figure 2.

In parts a, c, and e of Figure 2 we have displayed by means of circles the peak position values corresponding to the log−Gaussian components describing the dielectric relaxation of the PVE-25, PVE-50, and PVE-75 samples, respectively, at different temperatures. The solid circles stand for the maxima of the fast Gaussian and the open ones correspond to the slow Gaussian. In these figures the behavior corresponding to the pure homopolymer constituents have also been included for comparison and are represented by solid lines. In parts b, d, and f of Figure 2 the σ values corresponding to the Gaussian fits have been plotted. As before, the solid circles stand for the fast Gaussian dielectric component and the open ones correspond to the slower one. A comment should be made in the sense that those values under unity are less reliable due to the larger uncertainty in this region.

Comparison with 2D-NMR Results

In Figure 2 the results corresponding to the 2D-NMR study of these blend systems reported in ref 9 have also been included and are represented with square symbols. In the case of this 2D-NMR work, the measurements were performed on the same compositions that we are dealing here with. However, the samples were selectively deuterated in order to monitor separately the dynamics corresponding to each homopolymer constituent, the dynamical response of which was assumed to be described by a single Gaussian distribution of relaxation times. As in the previous case for our dielectric analysis, we have chosen the solid symbols to represent the faster dynamics (when only the PIP chains are deuterated and thus monitored by means of 2D-NMR) and the open ones for the slower dynamics (when the PVE chains are the deuterated ones). Comparison between the 2D-NMR and the dielectric results in this way should be rather straightforward, because in that work, the 2D-NMR data were also analyzed, as above mentioned, by means of distributions of relaxation times

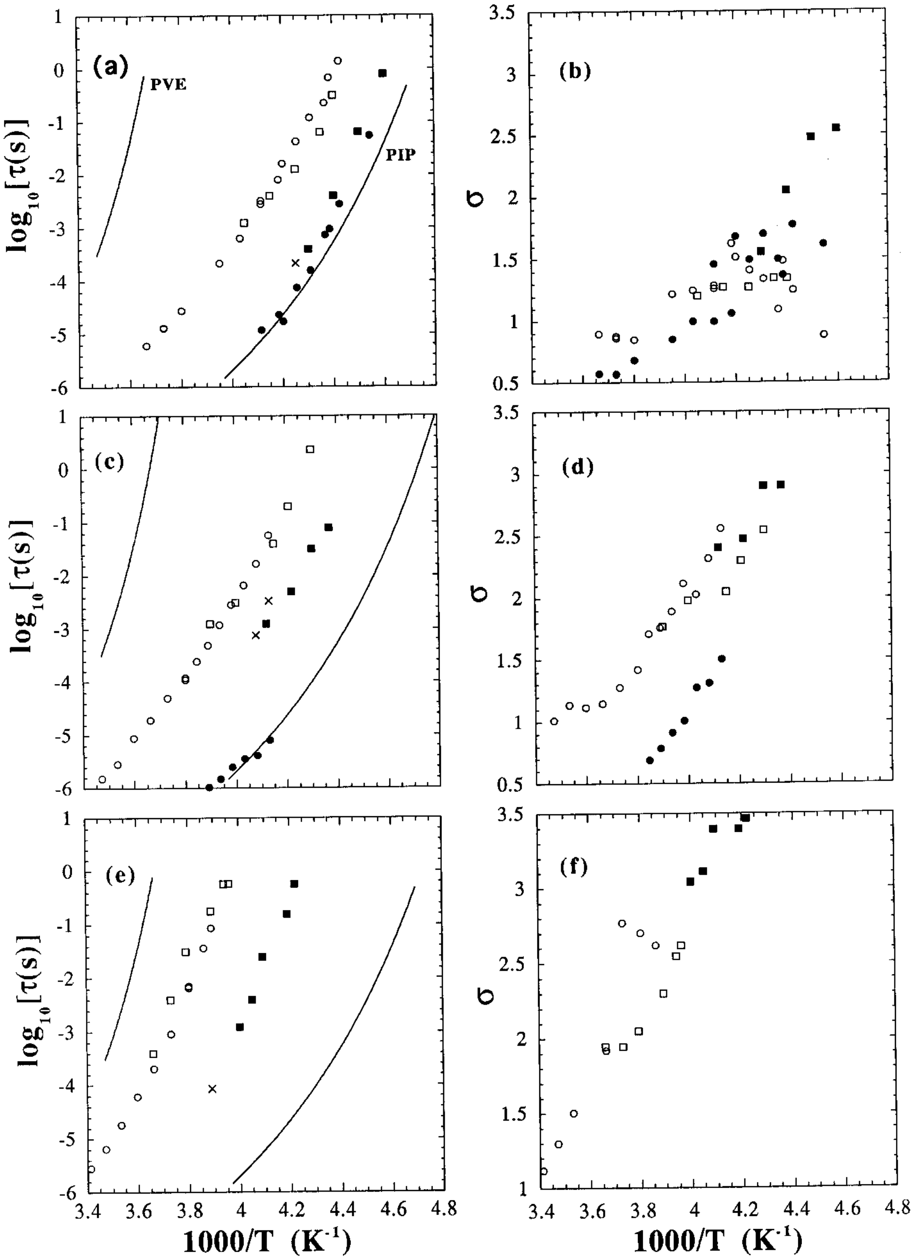

Figure 2. Temperature dependence of the double-Gaussian fitting parameters. In a, c, and e the characteristic relaxation times obtained from the maxima of eq 3 are shown for the PVE-25, PVE-50, and PVE-75 compositions, respectively. ○ and ● stand for the dielectric maxima, and □ and ■ stand for the 2D-NMR values. The solid lines stand for the homopolymer values. In b, d, and f, the σ values are displayed. Again, ○ and ● stand for the dielectric parameters, and □ and ■ stand for the 2D-NMR values.

which were generated by assuming Gaussian functions. However, let us point out that, in our case, the procedure was not exactly the same because we have not generated the distributions but obtained them directly from the experimental measurements.

From parts a, c, and e of Figure 2, it is apparent that, in the three different compositions, both techniques yield practically the same results for the characteristic relaxation times corresponding to the slow dynamics. This slow regime should be mainly attributed to the contribution of PVE-like relaxing units inside the blend, because these were the only deuterated chains in the NMR samples corresponding to these results. Besides, as can be seen, when the PVE content in the blend is increased, this slow regime gets closer to the response of the pure PVE homopolymer. Moreover, from parts b, d, and f of Figure 2, one can see that the σ parameters obtained from both analysis display a broadening when the temperature is decreased. On the other hand, they are of the same order of magnitude, within the experimental uncertainty, although the tendency is that the values of the dielectric σ are slightly higher than the 2D-NMR ones.

Thus, regarding these results, one could conclude that the slow dynamics observed in our dielectric measurements is dominated by the contribution of the PVE chains in the blends.

However, when one inspects the faster dynamical regime, it can be seen that the main dielectric relaxation time for the PVE-25 composition (Figure 2a) is slightly, but systematically, faster than the one obtained from the 2D-NMR results. This tendency is clearer for the middle composition of PVE-50 (Figure 2b), where dielectric times are about 2 decades smaller from the 2D-NMR ones. For the PVE-75 sample, let us recall that this comparison is not possible since the fitting parameters for the fast peak cannot be unambiguously determined, and also because they fall outside our confidence region (i.e. inside the accessible dynamic window). Nevertheless, for the PVE-50 sample, we can unambiguously state that the dielectric results corresponding to the analysis of the fast regime are much faster than the results obtained from the same composition by means of NMR when the PIP chains are the deuterated ones. Moreover, it seems that the characteristic dielectric relaxation times corresponding to this fast regime are quite close to the characteristic dielectric relaxation times of the pure PIP homopolymer. This is also the case for the PVE-25 sample, where the fast dielectric regime in the blend is quite close to the dielectric behavior of the pure PIP homopolymer.

The values of σ corresponding to this fast regime also display a broadening when the temperature decreases, as in the case of the above mentioned slow component. On the other hand, for the PVE-25 sample, the NMR σ values tend to be higher than those obtained from dielectrics, in contrast to the tendency shown for the slow process. This is more evident for the other composition of PVE-50, where the σ parameter values are clearly much higher than those obtained from the dielectric analysis. In the case of the PVE-75 sample, this comparison is not possible for the above mentioned reasons.

Summing up, when one compares the data obtained from dielectric and NMR measurements on the PVE−PIP blends at the compositions of 25%, 50%, and 75% in PVE content, one observes that similar results are obtained at all the compositions for the slow dielectric process and the process measured by 2D-NMR in blends with deuterated PVE chains. On the other hand, a different dynamic behavior is found, especially for the PVE-50 sample, between the fast dielectric process and the NMR results when the deuterated constituent is PIP. In the following we discuss possible causes for this discrepancy.

Discussion

In Figure 3, we show the relative contribution of the fast component (measured as $A_f/(A_f + A_s)$, see eq 4) to the whole dielectric α-relaxation as a function of temperature for the two compositions in which this fast process can be characterized, namely, for the PVE-25 and PVE-50 samples.

It is found that, within the experimental uncertainty, this magnitude is hardly dependent on temperature for the two samples. In previous works[5,10] it was assumed that each dielectric mode represents the dynamics of each of the components modified by blending. Thus, the fast dynamics would correspond to PIP and the slow one to PVE. Although the latter assignment seems to be supported by the aforementioned comparison between 2D-NMR and dielectric results (Figure 2), the former clearly fails, especially for the PVE50 sample. Moreover, as it can be seen in Figure 3, by means of our analysis, it is found that the contribution to the total dielectric response of the faster dynamics is systematically lower than expected, assuming that this fast component corresponds to the whole PIP dynamics. These are represented by the dashed lines in Figure 3, which were calculated by taking into account the relative dielectric strengths and concentrations of PVE and PIP in the samples. The amounts shown in Figure 3 should imply that 65% of the dielectrically active PIP units are contributing to the fast peak in PVE-25, and 42.5% in the PVE-50. The corresponding amount in PVE-75 should be much smaller. Thus, contrary to previous assumptions, the slower dielectric process should involve an important amount of PIP segments in addition to the PVE ones. Moreover, a comment could be made in the sense that, as it can be appreciated in Figure 3, it looks as if the difference between both the actual and calculated contributions remains more or less constant for the PVE-25 and PVE-50 samples, which are the ones in which both processes can be well-resolved or characterized. Again, this would lead to a very small contribution of the PIP units to the fast regime in PVE-75 and would explain why we were not able to resolve it.

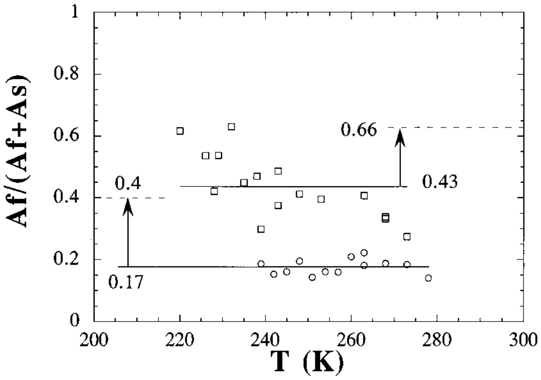

Figure 3. (a) Contribution of the fast processes to the total dielectric response of the blends at the different compositions (□, PVE-25; ○, PVE-50). The dashed lines stand for a calculation of the PIP contribution based on the different respective dielectric strengths and compositions.

These new results confirm the previously obtained ones[5] in the sense that the faster dielectric process resembles the PIP behavior, indicating that this part of the response is mainly associated with PIP segment dynamics. On the other hand, taking into account the above results, the slow process seems to correspond to the dynamics involving segments of PVE and PIP. In this framework, since 2D-NMR (samples with deuterated PIP) measures all PIP dynamic contributions, the PIP time scale determined by this technique would correspond to an average of the fast dielectric mode and some part of the slow mode distribution where PIP should also be involved. This would explain why the time scale of the fast dielectric mode is shorter than the 2D-NMR PIP mean time scale.

Finally, concerning the distribution width of the two modes shown in Figure 2, it seems that this framework also explains the above mentioned differences between the 2D-NMR and the dielectric results. As the faster dielectric mode only involves part of the PIP response, the width of this mode underestimates the total PIP width, whereas the width of the slow mode overestimates the actual PVE width because it includes part of the PIP response. This effect is lower for low PVE contents. However, we have to point out that some uncertainties in this type of calculation could be attributed to a likely contribution of a slower dielectric normal mode of PIP,[15] which might affect in a non-neglectable way the distribution at the slower times.

To clarify the above comments in a more quantitative way, we decided to use the 2D-NMR data in order to subtract the PVE-like contribution from the total dielectric relaxation response, so we could estimate in this way what should be the remaining contribution due to the PIP-like relaxation. This is what it is shown in Figure 4, where we have plotted for the three compositions the total dielectric relaxation response (empty

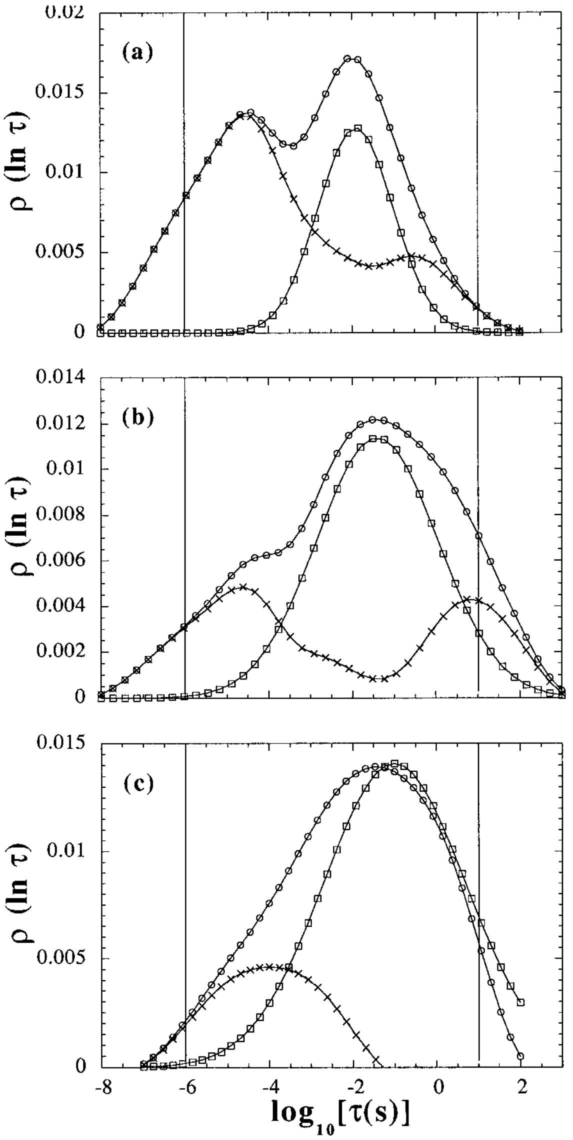

Figure 4. The distributions corresponding to the dielectric spectra of Figure 1 (○) and the contribution to it due to PVE assuming the 2D-NMR parameters and taking into account the respective dipole moments and compositions (□) and the substraction of one another (×).

circles), the contribution to it corresponding to the PVE-like relaxation (empty squares), which has been generated according to the 2D-NMR results and scaled by taking into account the relative dipole moments and the different compositions, and, finally, the result of subtracting the latter from the former (crosses). As mentioned above, this so-deduced contribution should be the one due to PIP-like relaxing units inside the blend. As can be seen in Figure 4 and as discussed above in a rather qualitative way, at least for the PVE-25 and PVE-50 samples, there is an important contribution of PIP-like relaxation in the slower time range. If one directly compares these distributions of relaxation times for PIP with the Gaussian-like distributions proposed in the NMR study, one finds a qualitative disagreement. However, when one calculates the averaged characteristic relaxation time corresponding to these remaining contributions after the subtraction, one obtains the values which are displayed in parts a, c, and f of Figure 2 as crosses and which agree very well with the NMR values for the characteristic relaxation times observed when just the PIP chains are deuterated.

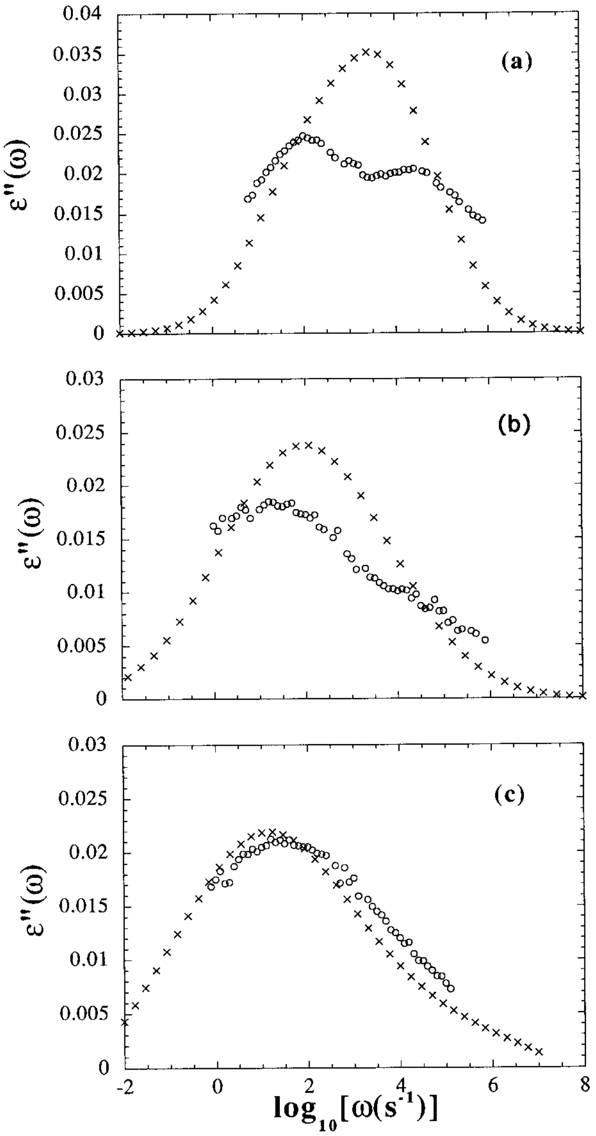

Figure 5. The dielectric spectra of Figure 1 (○). The simulated spectra due to the 2D-NMR weighted Gaussian distributions (×).

Therefore, although the average relaxation time of the PIP contribution obtained from 2D-NMR agrees fairly well with the one deduced from dielectric measurements, the shape of the corresponding distribution functions of relaxation times appears to be rather different.

It is worthy of remark that, although the bimodal shape of the distribution function corresponding to the total PIP contribution (see Figure 4a,b) should be taken only as an estimation, it is clear that it is not possible to reproduce the raw dielectric data starting from a superposition of the distribution functions used to simulate the 2D-NMR data.[9] This is shown in Figure 5, where we have compared the dielectric data of Figure 1 with ones generated by means of a superposition of these distribution functions (properly weighted with the ratio of the dipole moments of PIP and PVE). As can be seen in Figure 5, the two peaks of $\epsilon''(\omega)$ displayed in PVE-25 and the high frequency shoulder in PVE-50 cannot be reproduced.

On the other hand, it is interesting to point out that a bimodal distribution like the one here obtained for PIP has recently been invoked[2] to understand 2D-NMR data in a different miscible blend: polystyrene (PS)/poly-

(phenylene oxide) (PXE). In that work, it was found that the dynamics of either component of the blend can only be simulated by using a bimodal distribution. In our case we only find bimodal character for one of the components, namely, for PIP, which is the component displaying the lower glass transition temperature.

Finally, we discuss our results in light of the theoretical models for blend dynamics mentioned in the introduction.

As far as we know, none of these models can easily explain the main results of this paper, i.e., the bimodal character of the dynamics of PIP in the PVE-25 and PVE-50 samples.

The coupling model (CM) of Ngai[3,7] assumes that the "coupling parameter" accounting for the nonexponential character of the relaxation response of a homopolymer depends on the intermolecular environment. Thus, a distribution of local concentrations becomes a distribution of this parameter, which also implies a distribution of relaxation times through the, so-called, second universality of this model. The CM applied to blend dynamics can predict two different dynamic microenvironments, which, in principle, could explain a double peak in the dielectric response.[10] However, to the best of our knowledge, a bimodal character for the dynamics of one of the components of the blend (in this case PIP) cannot be easily understood in the framework of this model without invoking some kind of microphase segregation of part of PIP.

Fischer's model[4] assumes that the distribution of local concentrations implies a distribution of glass-transition temperatures which finally transforms into a distribution of relaxation times through a Williams—Landel—Ferry-like equation. Recent results[17] appear to confirm the validity of these assumptions. However, the starting point of Fischer's model is a Gaussian distribution of local concentrations. In order to explain our results in terms of this model, a bimodal distribution of local concentrations should be necessary. There is not any clear reason in the framework of this model to explain such a behavior, because the probability of the occurrence of concentration fluctuations should be symmetric around the mean value in a given volume. However, it is worthy of remark that a recently proposed[18] generalization of Fischer's model, which takes into account the concept of "cooperative volume" over which a fluctuation must occur, appears to suggest a bimodal distribution for dynamic concentration fluctuations in, at least qualitative, agreement with our results. On the other hand, very local concentration fluctuations, estimated purely on the basis of random statistics in the framework of simple lattice models, appear to provide a basis to understand the bimodal distributions used to simulate the 2D-NMR patterns in the above mentioned case of PS/PXE blends.[16]

Another explanation of our results which cannot, in principle, be disregarded is the possibility of a microphase segregation of the part of PIP, as has been above mentioned. This behavior should not be expected for a miscible system like PVE-PIP. However, recently Khokhlov et al.[19] have formulated a thermodynamic theory of microphase separation in polymer blends predicting 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.

As a final comment, we think that the complete clarification of this question requires that new kinds of experiments be done. We believe that the most suitable technique is the combination of quasielastic neutron scattering with selective isotopic labeling of the constituent homopolymers. The advantage of this technique with respect to NMR (although NMR can measure dynamic domain size based on proton spin diffusion[20]) is that it leads to information about the spatial scale of the molecular motions through the dependence of the dynamical magnitudes on the momentum transference. Experiments on this line are now being envisaged.

Conclusions

We have shown how an analysis of dielectric data based on a generalized CONTIN algorithm for the frequency domain can extract new dynamic information, both qualitatively and quantitatively, from a polymeric blend which had been previously studied by means of dielectric spectroscopy. A double-peak structure was resolved from the dynamics at some concentrations (for PVE-50, this could not be resolved in previous analysis). Besides, we do not need to impose any assumption on the nature of the distribution of characteristic relaxation times, because we directly calculate them from the experimental measurements instead of generating them by assuming a shape (i.e. Gaussian). This allowed us to obtain estimates of the separate contributions from the constituent homopolymers of the blend. We found that the two different dielectric contributions cannot be directly interpreted to correspond to the dynamics of separate components. Our results suggest that, although the faster dielectric process concerns mainly the dynamics of the PIP segments, the slower one involves both PIP and PVE segments. This implies a bimodal character for the PIP dynamics in these blends which cannot be easily understood in the framework of the available models for blend dynamics, at least in the present form. The comparison between our dielectric results and the previously reported ones for 2D-NMR allows us to estimate the bimodal distribution function of relaxation times corresponding to the PIP dielectric dynamics in the blends.

The results obtained allow to rationalize the main differences between dielectric and 2D-NMR results.

Acknowledgment. The authors acknowledge financial support from the CICyT: project MEC MAT92-0355 and from the Basque Government PI 95/005. We also thank Iberdrola S. A. and Gipuzkoako Foru Aldundia for partial financial support. We thank Dr. K. L. Ngai, Dr. C. M. Roland, Dr. A. Arbe, and Prof. D. Richter for fruitful discussions.

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MA960975X