2030 *Macromolecules* **2002,** *35,* 2030−2035

Temperature−Pressure Equivalence for the Component Segmental Dynamics of a Miscible Polymer Blend

A. Alegría,* D. Gómez, and J. Colmenero

Departamento de Física de Materiales UPV/EHU y Unidad de Fısica de Materiales CSIC-UPV/EHU, Facultad de Química, Apartado 1072, 20080 San Sebastián, Spain

Received March 19, 2001; Revised Manuscript Received December 27, 2001

ABSTRACT: Using broad-band dielectric spectroscopy ($10^{-2}-10^{7}$ Hz), we have investigated the effect of hydrostatic pressure on the segmental dynamics of the poly(vinyl methyl ether) (PVME) chains in a blend with polystyrene. Our results evidence that, for a given value of the relaxation rate, the relaxation process observed is, within the experimental uncertainties, independent of the particular values of pressure and temperature of the sample. This finding, which also applies for the dynamics of pure PVME, indicates that the effects on the component dynamics of hydrostatic pressure and temperature are equivalent. This result is rationalized on the basis of previous results obtained at atmospheric pressure in the same system. The implications of the present results concerning different proposed models for polymer blend dynamics are also discussed.

Introduction

The segmental dynamics, or α-relaxation, of miscible polymer blends depicted unequivocal evidences of dynamic heterogeneity.[1−9] The observed heterogeneity seems to have two different origins. On one hand, the earliest studies associated it with the fluctuations of concentration (FC) present in any polymer blend which would induce a distribution of the segmental mobilities for each component. Moreover, more recent results have shown that even at high temperatures, where the dynamical effects of the FC tend to vanish, the dynamics of the two components remain distinctly different.[9−11] These two features would also be related to the broad glass transition traces observed in miscible polymer blends with components having well-separated glass transition temperatures, T_g. A clear experimental support of such a relationship is the behavior observed in a blend with the two components having essentially the same glass transition temperature.[12] The blends of this particular system display a narrow glass transition process and have no indication of extra broadening in the α-relaxation range. On the contrary, well-studied blends with the pure components having very different glass transition temperatures, like polyisoprene/poly(vinylethylene) (PI/PVE) and poly(vinyl methyl ether)/polystyrene (PVME/PS), show both a very broad feature in the glass transition range and a pronounced broadening of the α-relaxation near T_g.[1−9] In these two systems, moreover, it has been clearly evidenced that the two components of the miscible blend have distinct segmental dynamics.[4−6,9−11,13] In both systems the segments of the polymer having the lowest glass transition temperature move in average considerable faster than those of the other. As a consequence, to obtain detailed information on the segmental dynamics in polymer blends, it is essential to perform experiments allowing a selective investigation of the different polymer components. The experimental techniques more widely used for this purpose are nuclear magnetic resonance (NMR), quasi-elastic neutron scattering (QENS), and dielectric spectroscopy (DR). The latter provides the broadest spectral range and is specially suited for blends with a component having a much stronger dielectric response than the other. This is the case of the system poly(vinyl methyl ether)/polystyrene since the dielectric activity of polystyrene, PS, is negligible as compared with that of poly(vinyl methyl ether), PVME. Taking advantage of this fact, we have recently investigated in detail the dynamics of the PVME segments in blends with PS.[9] The phenomenological analysis performed in that work showed that the dynamics of the PVME segments in the blends, as observed by NMR, QENS, and DR, can be understood as due to a superposition of different segmental relaxation processes similar to those observed in pure PVME. The average relaxation time of the PVME segments in the different blend compositions was found to follow the Vogel−Fulcher equation above the T_g range, being the Vogel−Fulcher temperature the unique parameter in the equation significantly affected by blending. These results showed that the PVME segments in the blends retain their own dynamical individuality, and at high temperatures the relaxation time in the blend would be nearly the same as that in pure PVME. A similar situation can be inferred from the recently reported results (Table 4 of ref 11) on the individual component dynamics of the PI/PVE system as studied by NMR in the high-temperature region.

The above-mentioned particularities of the dynamics of polymer blends have been established from experiments performed at atmospheric pressure, and there is little information about the effect of pressure on the dynamics of these systems. When the effect of pressure on the segmental dynamics of homopolymers is investigated, it is often found that although magnitudes like glass transition temperature and fragility are modified by pressure, pressure and temperature can have an equivalent effect on the shape of the relaxation function when the comparison is made for a given value of the main relaxation time.[14] Thus, the same relaxation spectra are obtained for different couples of pressure and temperature values. However, because of the dynamical heterogeneity of polymer blends, other possible scenarios can be envisaged in such systems. On one hand, the different pressure dependences of the segmental dynamics of the components could modify their mobility in a different way. In addition, the effect of

10.1021/ma010474y CCC: \$22.00

pressure, on the concentration fluctuations and/or on its effect in the segmental mobility, could also modify the dynamics of each component. In the recent literature only the effect of pressure on the dynamic heterogeneity of an athermal diblock copolymer of PI and PVE has been reported.[15] What was observed in this system is that pressure induces homogeneity in the sense that the time scale of the two components seems to become closer. However, both components being dielectrically active, the dielectric investigation of the detailed dynamics of each of them in the system is extremely difficult.

In this work we report on the effect of hydrostatic pressure in the dynamics of the PVME segments within a blend with PS. The blend composition investigated 65PVME/35PS (wt %) was selected due to the following advantages: (i) a pronounced dynamic heterogeneity (being close to the 50:50 composition), (ii) a relatively high dielectric signal (rather high PVME content), and (iii) minimize the nonequilibrium effects that will set up when the dynamics of slow component (the PS segments in this system) is so slow that equilibrium cannot be attained in the usual experimental conditions. This sample allowed us to study in detail the effects of pressure on the dynamics of the PVME segments in the blend over a rather broad pressure range. In this way we will gain new insight into the physical origin of the dynamic heterogeneity in miscible polymer blends.

Experimental Section

Samples. Polystyrene ($M_w = 66\,000$) and poly(vinyl methyl ether) ($M_w = 21\,900$) were obtained from Polymer Laboratories and Aldrich Chemical, respectively. A polymer blend containing 65 wt % PVME and 35 wt % PS (PVME65) was prepared by dissolving the two components in toluene and by casting from the solution. The blend film was maintained at 80° C under vacuum conditions for 72 h to remove the solvent completely. A reference PVME sample was prepared in a similar way. The calorimetric glass transition temperatures T_g of the blend and pure PVME as determined by differential scanning calorimetry (DSC) on a sample of about 10 mg were 265 and 249 K, respectively. The value of T_g for the blend is similar to that usually reported for this blend composition.[16]

Dielectric Measurements under Pressure. Dielectric measurements were carried out in a pressure cell (0−300 MPa) supplied by Novocontrol GmbH. In this system, silicone oil (Dow Corning 210H fluid, $M_n \approx 6600$) acts as the pressure transmitting medium. The range 10^{-2}−10^5 Hz was measured with an EGG5302 lock-in amplifier in combination with a Chelsea dielectric interface whereas for the range 10^3−10^7 Hz a HP4192LF impedance analyzer was used. The whole frequency range was measured by combining two different dielectric analyzers. The sample was kept between two condenser gold-plated electrodes of 20 mm diameter that were maintained at a fixed distance of 0.05 mm by means of Teflon spacers. A grounded guard electrode was used to minimize the contribution to the measured impedance of the silicone oil. This effect has been quantified by comparing the measurements obtained at atmospheric pressure in the pressurizing cell with those obtained with an independent setup (a conventional Novocontrol broad-band spectrometer). The effect of the silicone oil in the dielectric measurements is to produce a power law increasing of the dielectric losses at low frequencies $\propto \omega^{-0.65}$. This is likely due to the interfacial polarization associated with the presence of silicone oil layers in between the sample and the electrodes. The sample measurements were performed by frequency sweeps at constant temperature, with stability better than ±0.1 K, and constant pressure, with stability of ± 2 MPa. The absence of significant pressure gradients in the cell was checked by comparing the measurements at the same conditions but achieved by either increasing or decreasing pressure. Finally, for each pair temperature and pressure the frequency dependence of the complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ was obtained from the measured impedance.

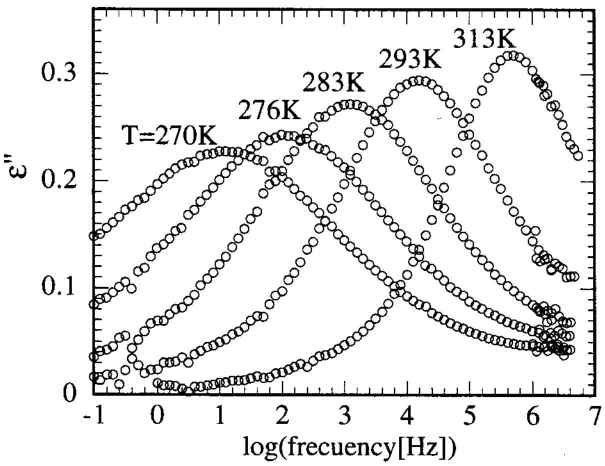

Figure 1. Dielectric relaxation losses of the PVME65 blend measured at atmospheric pressure and at the indicated temperatures.

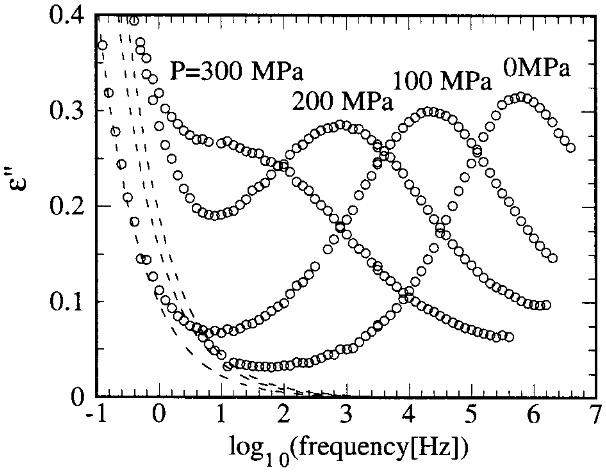

Figure 2. Dielectric relaxation losses of the PVME65 blend measured at a constant temperature of 314 K and at the indicated pressures. The dashed lines are the estimated contributions associated with the pressure transmitting silicone oil to the three measurements under pressure.

Results

Figures 1 and 2 show respectively the effect of temperature and pressure on the dielectric α-relaxation of the blend investigated. As can directly be observed in these figures, the effect of increasing pressure is remarkably similar to that obtained decreasing temperature, except in what concerns the low-frequency behavior. However, as aforementioned, this latter effect is mainly related to the contribution to the measured dielectric losses of the pressure transmitting silicone oil. The dotted lines in Figure 2 show the estimated contribution of the silicone oil in the measured dielectric losses. As expected, this contribution increases at high pressure due to the increasing amount of silicone oil in between the sample and the electrodes. In addition to this effect which masks partially the blend signal at low frequencies, on the high-frequency side of the dielectric losses the signature of the secondary β-relaxation of the PVME component is apparent, mainly at low temperatures. This process was found to be not affected by

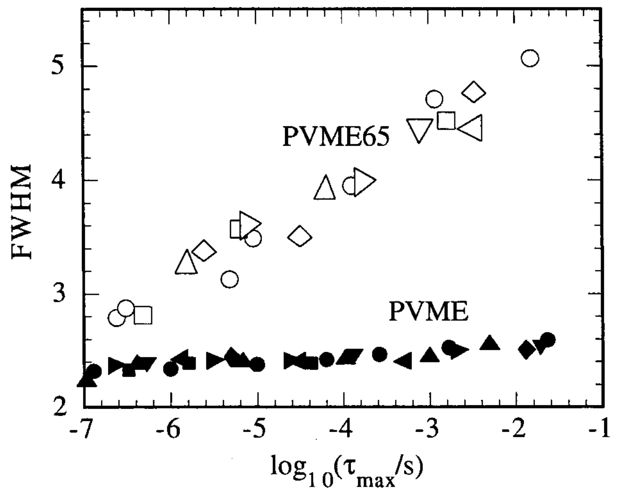

Figure 3. Full width at half-maximum of the α-relaxation peaks as a function of the corresponding characteristic relaxation times obtained at different temperatures and at the indicated pressures: circles, atmospheric pressure data; triangles, 50 MPa; squares, 100 MPa; diamonds, 150 MPa; right-pointing triangles, 200 MPa; inverted triangles, 250 MPa; left-pointing triangles, 300 MPa. Empty symbols correspond to the blend and filled symbols to pure PVME.

blending, except by the corresponding reduction of the relaxation strength (dilution effect).[9] Nevertheless, it is expected to be affected by pressure changes. However, pressure usually affects the secondary relaxations much less than the segmental dynamics,[17] which in combination with its low relaxation strength implies that the changes observed in the dielectric response are mainly those associated with the segmental dynamics. By comparing Figures 1 and 2, it is apparent that by either increasing pressure or decreasing temperature the main relaxation process shifts to lower frequencies and, simultaneously, its width increases. This very dramatic broadening of the relaxation is a clear signature of the presence of a broad distribution in the mobility of the dielectrically active component associated with the existence of FC in the polymer blend.

Trying to make a more detailed comparison of the effect of pressure and temperature on the dynamics of the PVME segments in the blend, after subtracting the low-frequency contribution of the silicone oil, indicated by dashed lines in Figure 2b, we have characterized the resulting relaxation peak by both the characteristic relaxation time and the full width at half-maximum (fwhm), the former evaluated as the reciprocal of the frequency at the maximum, i.e., $\tau_{max} = (\omega_{max})^{-1}$. The values so obtained for all the pressures and temperatures investigated are shown in Figure 3 where we have plotted the fwhm as a function of the logarithm of τ_{max}. It should be noted that for the peaks located near the edges of the experimental frequency window the fwhm were evaluated from the fitting curves obtained by using the well-known Havriliak–Negami equation,[18]

$$\epsilon''(\omega) = -\mathrm{Im}\left[\frac{\Delta\epsilon}{[1 + (i\omega/\omega_c)^{\alpha}]^{\gamma}}\right] \qquad (1)$$

where α and γ account for the relaxation shape and ω_c is a characteristic frequency which is related to τ_{max} by[19]

$$\omega_c\left[\sin\left(\frac{\alpha\pi}{2(\gamma + 1)}\right)\right]^{1/\alpha} = (\tau_{max})^{-1}\left[\sin\left(\frac{\alpha\gamma\pi}{2(\gamma + 1)}\right)\right]^{1/\alpha} \qquad (2)$$

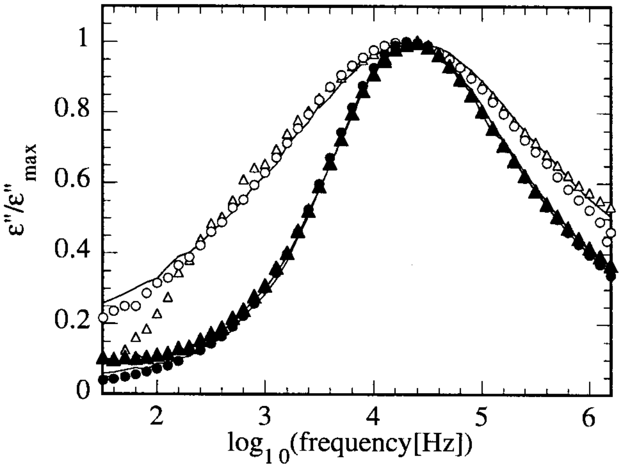

Figure 4. Comparison among the relaxation peaks obtained under isochronic conditions (pressure and temperature yielding a characteristic relaxation time $\tau_{max} \approx 10^{-5}$ s). The circles correspond to data obtained at atmospheric pressure (278 K for pure PVME and 293 K for the blend) and the triangles to data obtained at 200 MPa (313 K for pure PVME and 325 K for the blend), while for the sake of clarity in the presentation, data obtained at other pressures are represented by thin solid lines. Filled symbols are data from pure PVME and empty symbols from the blend.

The corresponding parameters obtained for pure PVME have also been included in the figure for comparison. The higher scattering of the blend data is due to the combination of the effect of both the weaker dielectric signal (dilution effect by blending) and the much broader relaxation peaks of the blend. In addition to the dramatic increase by blending of the fwhm corresponding to the relaxation of the PVME segments, the results depicted in Figure 3 evidence that the effects of pressure and temperature are hardly distinguishable when the comparison is made at the same value of the relaxation time. The temperature–pressure equivalence applies not only for pure PVME[20] (which is in agreement with what is often observed in other polymers[14]) but, more interestingly, also for the dynamics of the PVME segments in the blend. To check this result further, we have performed careful experiments to measure several relaxation curves having nearly identical relaxation times but obtained for different values of pressure and temperature. The so obtained spectra are shown in Figure 4, where similar measurements on pure PVME are also included. These data correspond to isochronic curves with $\tau_{max} \approx 10^{-5}$ s in which the main part of the peak is located in the frequency window of the HP4192LF impedance analyzer. In this way, the main sources of uncertainty, namely the contribution of the pressure transmitting silicone oil and the possible mismatching of data obtained from the two different spectrometers, appear uniquely in the low-frequency tail of the loss peaks. From this comparison it is more evident that, within the experimental uncertainties mentioned above, the temperature–pressure equivalence is observed in both pure PVME and the blend.

Further information about the effect of blending on the dynamics of the PVME segments can be obtained by comparing the isochronic paths, i.e., the couples (T, P) for which the relaxation time is constant, obtained for the blend with those of pure PVME.[20] This comparison is shown in Figure 5, where the isochronic points for the blend has been taken from the measurements in Figure 4. It is apparent that the isochronic data of

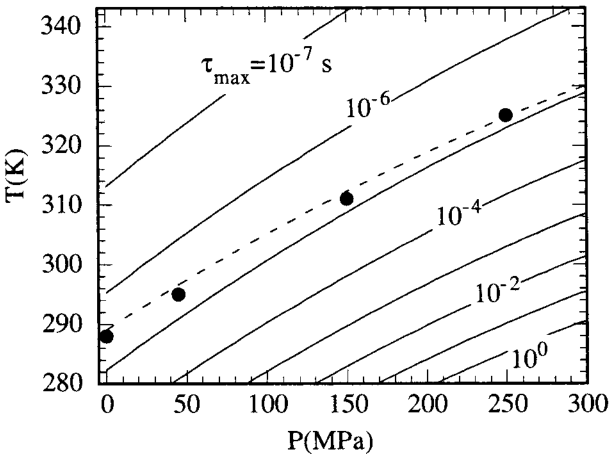

Figure 5. Isochronic points determined from the PVME65 spectra for values of $\tau_{max} = 10^{-5}$ s (squares). The solid lines are the isochronic paths for pure PVME. The dashed line has been calculated according to eq 7 as indicated in the text.

the blend do not follow exactly the isochronic paths of PVME, but the temperature difference between the isochronic points of the blend and the corresponding isochronic path of PVME diminishes at high pressures.

Discussion

The most relevant experimental finding concerning the effect of pressure on the dynamics of PVME segments in the blend is that temperature and pressure have similar effects, once the comparison is made for the same characteristic relaxation time. Taking this result into account, first we will check whether this finding is consistent with the phenomenological description previously obtained[9] for the temperature dependence of the dynamics of the PVME segments in the blends with PS. In this description, we assumed that the dynamics of the PVME segments in the blends results from a superposition of responses with different relaxation times, each of these responses maintaining the characteristic of that of pure PVME, i.e.

$$\epsilon''(\omega) = -\Delta\epsilon \, \mathrm{Im} \int_{-\infty}^{\infty} \frac{g[\log(\tau)]}{[1 + (i\omega/\omega_c(\tau))^{\alpha}]^{\gamma}} \, \mathrm{d}\log(\tau) \quad (3)$$

where the values of α and γ are those found for the relaxation of PVME at the same temperature. Thus, $g[\log(\tau)]$ at each temperature was obtained by fitting the dielectric relaxation data. Following this method, it was found that in the studied compositions the temperature dependence of the average value of $\log(\tau)$ followed, within the uncertainties, an empirical Vogel–Fulcher (VF) equation,[21] i.e.

$$\tau = \tau_{\infty} \exp\left(\frac{B}{T - T_0}\right) \quad (4)$$

with the same values of $\tau_{\infty} = 9 \times 10^{-14}$ s and $B = 1505$ K obtained for pure PVME and a value of T_0 varying linearly with composition. The value found for the PVME65 blend was $T_0 = 213$ K, being the value for pure PVME $T_0 = 200$ K.[9] Since T_0 was the single parameter in eq 4 significantly affected by blending, a distribution function of T_0 corresponding to each distribution of relaxation times at a given temperature was then obtained from the trivial relationship $h(T_0)\,\mathrm{d}T_0 = g[\log(\tau)]\,\mathrm{d}\log(\tau)$, which yields

$$h(T_0) = \log(e) \frac{B}{(T - T_0)^2} g[\log(\tau)] \quad (5)$$

When the distributions $h(T_0)$ obtained at different temperatures were compared, it was found that $h(T_0)$ is hardly dependent on temperature. As a consequence, a temperature-independent distribution $h(T_0)$ was found to be sufficient to characterize the dynamics of the PVME in each blend, the other parameters being those of pure PVME.

Let us check now whether these results are consistent with the pressure–temperature equivalence found above. For this purpose, first the pressure dependence of the relaxation time of the pure polymer has to be taken into account. The VF equation has been generalized to account for the pressure dependence of the α-relaxation time in several ways,[22] which can be summarized as

$$\tau = \tau_{\infty} \exp\left[\frac{B + f_1(P)}{T - f_2(P) - T_0}\right] \quad (6)$$

where the functions of pressure $f_1(P)$ and $f_2(P)$, usually taken as first- or second-order polynomials, should verify $f_1(0) = f_2(0) = 0$. Taking into account the results obtained in the blend at atmospheric pressure, let now assume that T_0 remains the single parameter affected by blending also in eq 6. Under this assumption, the generalization of eq 5 yields

$$h(T_0) = \log(e) \frac{B + f_1(P)}{[T - f_2(P) - T_0]^2} g[\log(\tau)] \quad (7)$$

which connects the distribution function of the component relaxation times in the blend at temperature T and pressure P with $h(T_0)$. In this context, the exact equivalence between the effect of temperature and pressure on the component dynamics in the blend will be satisfied under the following conditions: (i) $h(T_0)$ is independent of pressure and temperature; (ii) $f_1(P) = 0$. If these two conditions are met, all the couples (T, P) producing a given value of $T - f_2(P)$ would yield the same distribution of relaxation times (for a given value of T_0 the same values of τ and $g[\log(\tau)]$ result) and therefore exactly the same relaxation process. Therefore, the experimentally observed temperature–pressure equivalence suggests that this two conditions should be verified, at least approximately, in the blend investigated. Indeed, recent results on the pressure dependence of the relaxation time of pure PVME[20] show that for this polymer $f_1(P) = 1.1P - 7.5 \times 10^{-4}P^2$ and $f_2(P) = 0.132 f_1(P)$, and therefore, in the pressure range investigated $B + f_1(P)$ varies only by ±8%. In the context of a nearly constant distribution $h(T_0)$, this variation would produce changes in $g[\log(\tau)]$ within the experimental uncertainties. Therefore, the pressure–temperature equivalence is consistent with the phenomenological description of the dynamics of PVME segments in the blend with a single distribution $h(T_0)$, essentially independent of pressure and temperature.

Trying to check further this result, we have used eq 7 to evaluate the isochronic paths expected for the blend as compared with those corresponding to PVME. From eq 6 it is straightforward to see that the isochronic paths for pure PVME verify $[T - T_0 - f_2(P)][B + f_1(P)]^{-1} =$ constant. However, the isochronic paths for the PVME segments in the blend would correspond to those couples

(T, P) giving rise to the same $g[\log(\tau)]$, which in the context of a temperature- and pressure-independent $h(T_0)$ and according with eq 7 would verify approximately $[T - T_0 - f_2(P)][B + f_1(P)]^{-1/2}$ = constant. This would be exact only for $f_1(P) = 0$, and in that case the isochronic paths of PVME in the blend would coincide with those of pure PVME. The dashed line in Figure 5 shows the isochronic path of the blend so calculated taking and adequate value for the arbitrary constant. It is apparent that the behavior so obtained is in good agreement with that determined experimentally. Note that in this calculation the specific shape of $h(T_0)$, and subsequently of $g[\log(\tau)]$, does not play a role, being the single assumption that, once the dynamics of pure PVME is fully characterized, a pressure- and temperature-independent distribution of $h(T_0)$ is sufficient to characterize the dynamics of the PVME segments in the blend.

It is important to remark that the previous findings are not the result of a model for the dynamics of polymer blends, but they are the consequence of a rather simple way for describing the experimentally determined dynamics of the low-T_g component of the blend over the whole range investigated, i.e., T ranging from 270 to 400 K and P up to 300 MPa. Therefore, the previous results alone are not able to give information neither on the dynamics of the high-T_g component nor about the dynamical behavior of the blend system as a whole (for example, on the shape and position of the macroscopic glass transition process). Thus, let now look for the implications of the present results concerning the different theoretical approaches proposed so far for describing the dynamics of polymer blends. The earliest theoretical approaches for the dynamics of polymer blends consider the existence of fluctuations of concentration (FC) as the main ingredient. In this framework, the FC which relax more slowly than the α-relaxation induce a distribution of relaxation processes in the blend. This would explain the broadening of the relaxation spectra usually observed in blends. The resulting distribution of relaxation processes would be connected with the distribution of the different magnitudes characterizing the relaxation, namely the main relaxation time and the nonexponential parameters (for example, the β parameter of a stretched exponential function). Since the β values of different polymers are rather close (apart from a few exceptions), a rather good approximation is to consider only a distribution of the relaxation times. This has been the procedure followed in most of the investigations on the component dynamics in a polymer blend, and it was also the starting point of the theoretical approach of Fischer et al.[5] that was afterward developed and extended by Kumar et al.[23] These two approaches consider that the presence of FC is the main ingredient for describing the dynamics of polymer blends. However, more recently a different approach[24] has shown that several of the main characteristics of the polymer blend dynamics are captured simply by taking into account the self-concentrations effects produced by the chain connectivity, without considering the effect of the FC. Particularly, this latter approach predicts that the two components of the blend will have different time scales at any temperature and, subsequently, different glass transition temperatures, if it is defined as the temperature at which a given value of the relaxation time is achieved, ca. $\tau \approx 1$ s. Moreover, within this approach, the different time scales would persist even at high temperatures where the FC would not produce a significant dynamic heterogeneity. As aforementioned this is in agreement with what has been observed experimentally.[10,11]

Our results on the dynamics of the PVME segments in the blends with PS show two main findings:

(i) The dynamics of the PVME segments retains its dynamical individuality. T_0 being the unique parameter of the VF equation significantly affected by blending, the time scale of the PVME segments in the blends at high temperature (and low pressure) will become nearly the same than that in pure PVME. The results recently reported on the high-temperature dynamics of PI/PVE blends (see Table 4 of ref 11) also point out in the same direction. These findings are captured properly in the approach of Lodge et al.[24] by simply taking the chain connectivity effects into account. Furthermore, this model predicts T_g values for the PVME component in the blends in quantitative agreement with those determined experimentally.[24] Contrary, in the framework of the other theoretical approaches aforementioned, at high temperatures, the relaxation times for both components are assumed to take a common value intermediate of those corresponding to the pure polymers.

(ii) A distribution of the VF temperature T_0, essentially independent of temperature and pressure, is sufficient to characterize the dynamics of the PVME segments in the blends, provided the temperature is high enough to avoid nonequilibrium effects. It is worthy of remark that, in the context of the previous phenomenological description of the dynamics of PVME segments in the blends, the distribution of T_0 yields straightforwardly to a corresponding distribution of glass transition temperatures $h(T_g)$ associated with this particular component (note that B and τ_∞ are unaffected by blending). The approach of Lodge et al. cannot account for this latter finding, since in this approach no distribution of relaxation times for each individual component is considered. Capturing this distribution requires necessarily the FC to be taken into account, while they are not included in the approach of Lodge et al. Contrary, the distribution of T_g is an essential aspect in the framework of the theoretical approaches of Fischer et al. and Kumar et al. In both models, approaching the macroscopic T_g, the relaxation processes in the blend become very broad because the FC induce a wide distribution of the relaxation times of each component. However, whereas in the model of Fischer et al. the average time scales of both components remain just the same over the whole temperature range, in the model of Kumar et al. they can differ significantly close to the macroscopic T_g. This arise, mainly, from the assumption that the so-called cooperative volume depends on the local composition, although the effects of the chain connectivity is also taken into account in this approach. When this latter model is applied, at each temperature a self-consistent calculation allows to determine the probability for the concentration fluctuations, from which a distribution of T_g for each component can be derived. For the low-T_g component of blends with high-T_g contrast the distribution so obtained shows a sharp cutoff at the T_g of the pure polymer and eventually a bimodal aspect. Although our results do not show clear evidence of such a bimodal character of the distribution, it cannot be discarded since distributions with rather different shapes can describe, within the uncertainties, the same experimental behavior. On the hand, when the model of Kumar et al. is used,[8,23] the cooperative volume is taken to depend critically on temperature. However, the experimental finding that $h(T_0)$ is essentially independent of temperature (and pressure) is hardly consistent with such a strong temperature dependence. On the contrary, it seems to be better captured by the model of Lodge et al. in which the relevant length scale for the blend dynamics is the monomeric friction factor which is considered essentially constant.[24] This point of view is also supported by models based on entropy or density fluctuations.[25] In these types of models the distance over which a given segment is affected by its environment is considered temperature independent, and the strong temperature dependence of the distribution of relaxation times arises mainly from the different effect on the dynamics that a small fluctuation has at different temperatures. In the case of the PVME/PS system, this effect would be determined by the value of $\mathrm{d}\log\langle\tau\rangle/\mathrm{d}T_0$ at different temperatures (or pressures).

Conclusions

The results discussed above show that, when compared at the same average time scale, pressure and temperature have an indistinguishable effect on the dynamics of the low-T_g component of a miscible blend, at least over the range of temperature and pressures investigated. This experimental finding is found to be consistent with the previous description for the temperature dependence of the dynamics of the same component in the blends at atmospheric pressure. A distribution of the Vogel−Fulcher temperature, essentially independent of both temperature and pressure, is found sufficient to account for the effects of blending on the low-T_g component dynamics, the others parameters characterizing the segmental dynamics of this component remaining the same that those of the pure polymer. However, this distribution does not allow to characterize the whole dynamics of the polymer blend since the connection of such a distribution with the dynamics of the high-T_g component needs the input of an actual model of the polymer blend dynamics.

The present results are only partially captured by some models of the dynamics of polymer blends, namely the models of Kumar et al. and Lodge et al. Particularly, it seems that both the effect of connectivity and the effect of the fluctuation of concentrations are necessary ingredients for any suitable model of the dynamics of polymer blends. Finally, our results favor the idea of a monomeric friction factor depending weakly on temperature as the relevant length scale controlling the blend segmental dynamics.

Acknowledgment. We acknowledge the support given from the following projects: DGICYT: PB97-0638; GV: EX1999-11 and PI1998-20 and UPV/EHU: 206.215-G20/98. The authors also thank Iberdrola S.A. for partial financial support. The support from "Donostia International Physics Center" is also acknowledged. D.G. thanks the grant of the Spanish Ministry of Education.

References and Notes

(1) Wetton, R. E.; MacKnight, W. J.; Fried, J. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 158. Shears, M. S.; Williams, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 608.
(2) Zetsche, A.; Kremer, F.; Jung, W.; Schulze, H. *Polymer* **1990**, *31*, 1883.
(3) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261, 5315.
(4) Alegría, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486.
(5) Zetsche, A.; Fischer, E. W. *Acta Polym.* **1994**, *45*, 168.
(6) Chung, G.-C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 964, 5729.
(7) Katana, G.; Fischer, E. W.; Hack, T.; Abetz, V.; Kremer, F. *Macromolecules* **1995**, *28*, 2714.
(8) Kamath, S.; Colby, R. H.; Kumar, S. K.; Karatasos, K.; Floudas, G.; Fytas, G.; Roovers, J. E. L. *J. Chem. Phys.* **1999**, *111*, 6121.
(9) Cendoya, I.; Alegría, A.; Alberdi, J. M.; Colmenero, J.; Grimm, H.; Richter, D.; Frick, B. *Macromolecules* **1999**, *32*, 4065. Cendoya, I. PhD Thesis, The University of the Basque Country, 1999.
(10) Hoffmann, S.; Willner, L.; Richter, D.; Arbe, A.; Colmenero, J.; Farago, B. *Phys. Rev. Lett.* **2000**, *85*, 772.
(11) Min, B.; Qiu, X.; Ediger, M. D.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 4466.
(12) Alegría, A.; Elizetxea, C.; Cendoya, I.; Colmenero, J. *Macromolecules* **1995**, *28*, 8819.
(13) Arbe, A.; Alegría, A.; Colmenero, J.; Hoffmann, S.; Willner, L.; Richter, D. *Macromolecules* **1999**, *32*, 7572.
(14) Paluch, M.; Hensel-Bielówka, S.; Ziolo, J. *Phys. Rev. E* **2000**, *61*, 526. Floudas, G.; Reisinger, T. *J. Chem. Phys.* **1999**, *111*, 5201.
(15) Floudas, G.; Fytas, G.; Reisinger, T.; Wegner, G. *J. Chem. Phys.* **1999**, *111*, 9129.
(16) Yang, H.; Shibayama, M.; Stein, R. S.; Shimizu, N.; Hasimoto, T. *Macromolecules* **1986**, *19*, 1667.
(17) Sasabe, H.; Saito, S. J. *J. Polym. Sci., Part A-2* **1964**, *6*, 1401. Williams, G.; Edwards, D. A. *Trans. Faraday Soc.* **1966**, *62*, 1329.
(18) Bottcher, C. J. F.; van Belle, O. C.; Bordewijk, J.; Rip, A. *Theory of Electric Polarization*; Elsevier Scientific: Amsterdam, 1973.
(19) Boersma, A.; van Turnhout, J.; Wubbenhorst, M. *Macromolecules* **1998**, *31*, 7453. Diaz-Calleja, R. *Macromolecules* **2000**, *33*, 8924.
(20) Gómez, D.; et al., to be published. Gómez, D. PhD Thesis, The University of the Basque Country, 2000.
(21) Vogel, H. *Phys. Z.* **1961**, *22*, 645. Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(22) Corezzi, S.; Rolla, P. A.; Plauch, M.; Ziolo, J.; Fioretto, D. *Phys. Rev. E* **1999**, *60*, 4444 and references therein.
(23) Kumar, S. K.; Colby, R. H.; Anastasiadis, S. H.; Fytas, G. *J. Chem. Phys.* **1996**, *105*, 3777.
(24) Lodge, T. P.; Mcleish, T. C. B. *Macromolecules* **2000**, *33*, 5278.
(25) Ediger, M. D. *J. Non-Cryst. Solids* **1998**, *235*−*237*, 10.

MA010474Y