Reorientational Dynamics of Dipoles in Poly(vinylidene fluoride)/ Poly(methyl methacrylate) (PVDF/PMMA) Blends by Dielectric Spectroscopy

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ABSTRACT: The reorientational dynamics of dipoles in poly(vinylidene fluoride)/poly(methyl methacrylate) (PVDF/PMMA) blends were investigated by dielectric spectroscopy. Measurements were performed over a wide range of temperature and frequency, and previously unavailable results are reported. Various relaxation processes were identified and their locations assigned to the different morphological regions in PVDF, PMMA, and PVDF/PMMA blends. The development of a relaxation process associated with the imperfections in the crystalline phase was recorded both in pure PVDF and in crystalline blends. An amorphous interphase and a liquid-like amorphous phase are present in pure PVDF, but their relaxation dynamics are dielectrically *indistinguishable*, giving rise to a single non-Arrhenius relaxation mechanism. In the crystalline blends, however, the interphase is devoid of PMMA, and its relaxation dynamics are readily *distinguishable* from those of the PVDF/PMMA miscible phase. Interestingly, the relaxation dynamics in the interphase were found to vary as a function of blend composition. Since the relaxation processes are governed by cooperativity, an explanation of our findings is offered in terms of the interactive nature of the relaxation process.

Introduction

The morphological characteristics of blends of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) have been investigated by a variety of techniques that include dynamic mechanical,[1,2] calorimetric,[3−6] dielectric,[7] X-ray,[8] microscopic,[9,10] NMR,[11] and FTIR[11,12] measurements. It is now generally agreed upon that PVDF and PMMA are completely miscible in the melt and exhibit a lower critical solution temperature (LCST) behavior around 330 °C. Upon cooling from the melt, however, PVDF in the blend can either crystallize or remain amorphous depending on the cooling rate and the blend composition. Crystallization can take place in the blends that contain more than 40% by weight PVDF. Dynamic mechanical, calorimetric, and microscopic studies of crystalline PVDF/PMMA blends reveal the presence of a crystalline PVDF phase and a miscible PVDF/PMMA amorphous phase; a single T_g is usually taken as the proof of miscibility, but only limited information about the nature of various relaxations in the blends can be extracted from such studies.

Our interest focuses on the understanding of the dynamics and the molecular origin of relaxations associated with different morphological regions in PVDF/PMMA blends. Early studies of the relaxation processes in PMMA and PVDF led to the following general observations. An α relaxation due to segmental motions and a β relaxation associated with the localized motions in the side group were found in PMMA.[13] Three relaxations were reported in crystalline PVDF:[14−17] α_a, associated with segmental motions in the amorphous phase; α_c, related to the amorphous portions within the crystalline phase; and β, caused by weak local motions in the glassy state. Efforts to identify the molecular origin of the dielectric response and to associate it with a specific morphology in crystalline polymers and blends have assumed a new dimension with the introduction of the concept of interphase. The term interphase was coined in the seventies, and it is now generally agreed upon that the morphology of crystalline polymers consists of a crystalline lamellar phase, an amorphous phase, and a crystal−amorphous interphase. This view of morphology begs important questions regarding the nature of the molecular motions and relaxations associated with each of these morphological regions. Experimental and theoretical evidence for the existence of a crystal−amorphous interphase in crystalline homopolymers and polymer blends has been claimed by several authors. The initial argument could be traced to the classic studies by Flory,[18,19] who pointed out that the boundary between the ordered crystals and the disordered liquid-like regions in crystalline polymers cannot be as sharp as in monomeric systems. Since then, a number of theoretical calculations (e.g. refs 20−22) and experimental measurements (e.g. refs 23 and 24) have been performed and quantitative descriptions of the interphase have been made. Mandelkern et al.[23] used Raman spectroscopy to calculate the thickness of the interphase in linear polyethylene. NMR studies of melt-crystallized polyethylene by Kitamaru et al.[24] revealed contributions from three distinct morphological components: a crystalline region, a liquid-like “interzonal” region, and an interphase, which was described as an intermediate region in which the rotation of methylene groups in C−C bonds was partially hindered. The formation of an interphase in crystalline PVDF/PMMA blends has also been proposed on the basis of the theoretical considerations of chain packing at the surface of lamellar crystallites.[25,26] It was argued that the transition from the perfect order in the crystal to the isotropy in the amorphous phase cannot occur abruptly and that PMMA must be excluded from the crystal−amorphous interphase. An interesting experimental study of PEO/PMMA blends by small angle neutron (SANS) and X-ray scattering (SAXS) was conducted by Russell et al.[27] These authors reported a 1.5 nm discrepancy between the widths of the diffuse-phase boundary as measured by SAXS and SANS and

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attributed it to the presence of an interphase devoid of PMMA. *Dielectric data* for relaxations in PVDF/PMMA blends are scarce and marred by a narrow frequency range. The experimental evidence from dielectric measurements for the presence of the interphase was claimed by Hahn, Wendorff, and Yoon[7] for PVDF/PMMA blends and by Ando and co-workers[28] for PVDF/PEMA blends. But despite the evidence in support of the existence of the interphase, numerous questions regarding its fundamental character and its relaxation dynamics remain unanswered. Is the interphase completely amorphous, and does it contain one or both components of a miscible blend? What are the relaxation dynamics within the interphase and, in the case of blends, are relaxations affected by the blend composition? These are important considerations because the relaxation processes affect the physical and mechanical response of each morphological region and, hence, the polymer as a whole.

In this paper we present the results of dielectric measurements on PVDF/PMMA blends over a wide range of frequency and temperature. Specifically, this research marks the first time that the high-frequency (up to 1.3 GHz)/high-temperature measurements of the dielectric response of PVDF/PMMA blends have been reported in the literature. The principal objectives of this study are (1) to utilize dielectric measurements in the frequency, time, and temperature domain and elucidate the molecular origin of various relaxations in PVDF/PMMA blends and (2) to establish how the dynamics of various relaxations depend on blend composition and morphology. No similarly comprehensive study has appeared hitherto in the literature.

Experimental Section

Materials. Both polymers used in this study are commercially available. PMMA was Plexiglass VS-100 from Rohm and Haas, a low-T_g injection molding grade. The intrinsic viscosity of this polymer was found to be 0.37 dL/g at 25 °C in chloroform. PVDF was Kynar 721 from Pennwalt. Blends ranging from 0 to 100% PMMA by weight were prepared in a twin-screw extruder.

Techniques. Our experimental facility for dielectric measurements consists of modified commercial and custom-made (in-house) instruments. The three commercial instruments are (1) a Solartron 1260 Impedance/Gain Phase Analyzer (10 μHz to −32 MHz), (2) a Hewlett-Packard 4284A Precision LCR Meter (20 Hz to 1 MHz), and (3) a Hewlett-Packard 8752C Network Analyzer (300 kHz to 1.3 GHz). Each instrument was modified by the addition of a temperature-controlled chamber and interfaced to a computer via a National Instrument's IEEE 488.2 interface bus. Samples were compression molded between the electrodes, and a Teflon spacer was used to control the thickness. Crystalline samples were annealed until an equilibrium degree of crystallinity was attained. Electrode cell configurations for measurements below 10 MHz are described elsewhere.[29,30] Measurements performed in the network analyzer above 10 MHz made use of a specially designed coaxial probe and our own software for the calculation of dielectric constant and loss from the measured reflection coefficient. The Solartron impedance/gain phase analyzer was further modified by the addition of a high-impedance adapter (HIA), assembled in our laboratory, which becomes necessary when the measured impedance exceeds the upper limit of the analyzer (100 MΩ). Further details of our entire setup for dielectric measurements, including the HIA, are available elsewhere.[31] Some additional information was obtained from differential scanning calorimetry (DSC), performed with TA Instrument Co. DSC model 2920 at a heating rate of 10 °C/min.

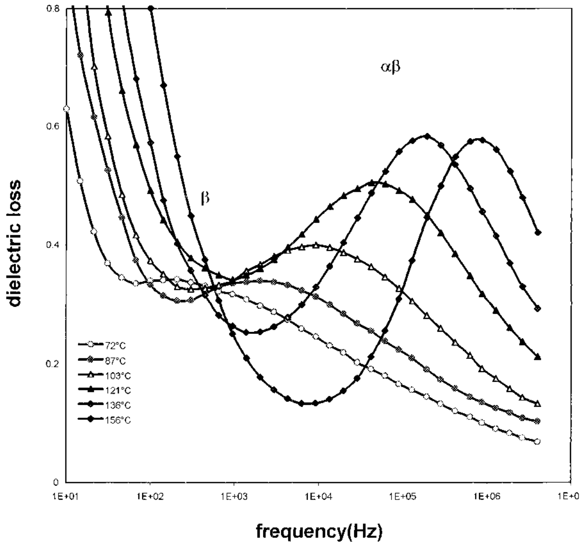

Figure 1. Dielectric loss in the frequency domain with temperature as a parameter for pure PMMA.

Results and Discussion

We begin the discussion of our results by identifying the various types of relaxations associated with different moieties in the blend components and then proceed with the analysis of a series of PMMA/PVDF blends.

Poly(methyl methacrylate) (PMMA). The chemical composition of commercial PMMA varies from one supplier to another, and hence it is difficult to compare directly the dielectric response of samples from different sources. Our goal here was not a comprehensive study of the dielectric response of PMMA but merely the identification of major relaxations in the sample that would help us understand its behavior in the blends. Dielectric loss in the frequency domain with temperature as a parameter is shown in Figure 1. The loss peak maximum shifts to a lower frequency with decreasing temperature, between 156 and 72 °C, while the peak intensity decreases and the distribution broadens. An abrupt increase in the dielectric loss below 100 Hz is the result of a dominant effect of the polarization by migrating charges at low frequency. The loss peaks seen in Figure 1 are comprised of both α and β relaxations. The overlap of these two relaxations and the likelihood of specific interactions between them are also reflected in the apparent absence of thermorheological simplicity.

Figure 2 shows dielectric loss as a function of temperature with frequency as a parameter. Two loss peaks appear in the temperature domain: α relaxation, which occurs at higher temperature and is associated with segmental motions, and β relaxation, which occurs at lower temperature and is associated with the localized motions of side groups in the glassy state. Both peaks shift to higher temperature with increasing frequency. It should be immediately pointed out, however, that the ability to resolve these two peaks is a strong function of the applied frequency. For example, by examining Figure 2 one sees that α and β relaxations can be distinguished clearly at 300 Hz and possibly deconvoluted at 1400 Hz, though the higher temperature peak in the latter case should not be viewed as pure α relaxation because of the partial overlap with β relaxation. Above the frequency of 1400 Hz, the two peaks merge to form an $\alpha\beta$ relaxation.

Poly(vinylidene fluoride) (PVDF). The first series of measurements on PVDF were performed on fully-

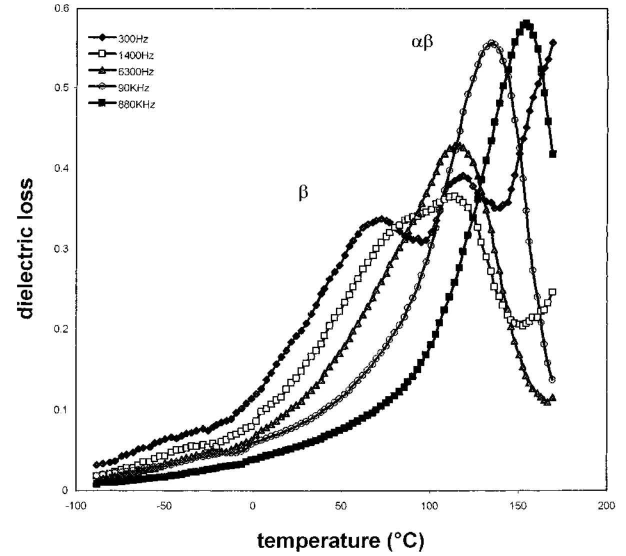

Figure 2. Dielectric loss as a function of temperature with frequency as a parameter for pure PMMA.

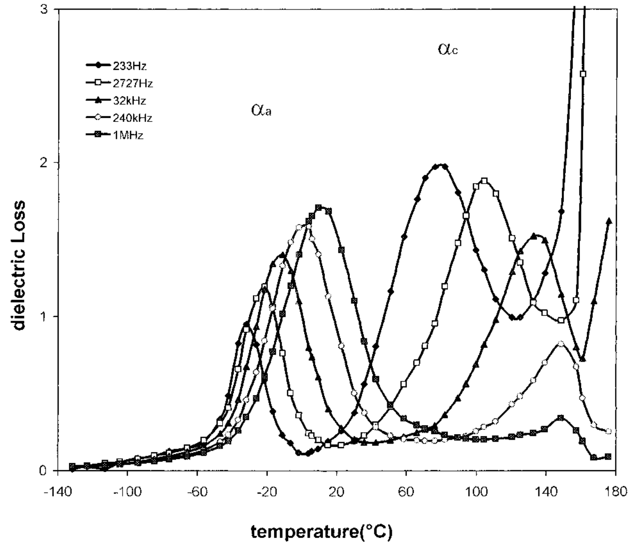

Figure 3. Dielectric loss as a function of temperature with frequency as a parameter for pure PVDF.

crystallized samples (i.e. characterized by an equilibrium degree of crystallinity). Dielectric loss as a function of temperature with frequency as a parameter is shown in Figure 3. Two relaxation peaks are observed; both appear above the "calorimetric glass transition" and shift to higher temperature with increasing frequency. The magnitude of the lower temperature peak, termed α_a, increases with increasing frequency, while the opposite trend is noted for the higher temperature peak, termed α_c. The abrupt increase in dielectric loss observed at high temperature is caused by the onset of melting. The molecular origin of α_a and α_c relaxation is discussed below.

α_a Relaxation. The molecular origin of α_a relaxation lies in the segmental motions within the amorphous phase in PVDF. Dielectric loss due to α_a relaxation in the frequency domain with temperature as a parameter is displayed in Figure 4. The intensity of the α_a peak decreases with decreasing temperature and shifts to lower frequency; this is accompanied by a noticeable broadening of the distribution. The fact that dielectric loss remains finite even at temperatures well below the "calorimetric T_g" (e.g. −94 °C) suggests the presence of a broad and weak β relaxation. The normalized plots of dielectric loss as a function of frequency in the temperature range between −9 and −36 °C (not shown here) reflect thermorheological complexity. In the vicinity of the melting point, α_a relaxation appears at frequencies in the high mega- and low gigahertz range. The results displayed in Figure 5 show dielectric loss near the melting point in the frequency domain with temperature as a parameter. Upon cooling from the melt (200 °C), α_a relaxation shifts to lower frequency with decreasing temperature and the loss peak maximum enters the frequency window of Figure 5 at about 1 GHz at 152 °C. Further cooling causes a slow but gradual shift of the loss peak to lower frequency and a significant drop in the peak intensity as a result of the ongoing crystallization. The high-frequency/high-temperature data of the type shown in Figure 5 have not been reported hitherto in the literature. The mere fact that α_a relaxation exists both below and above the crystalline melting point proves beyond a doubt that its molecular origin does not lie exclusively within the

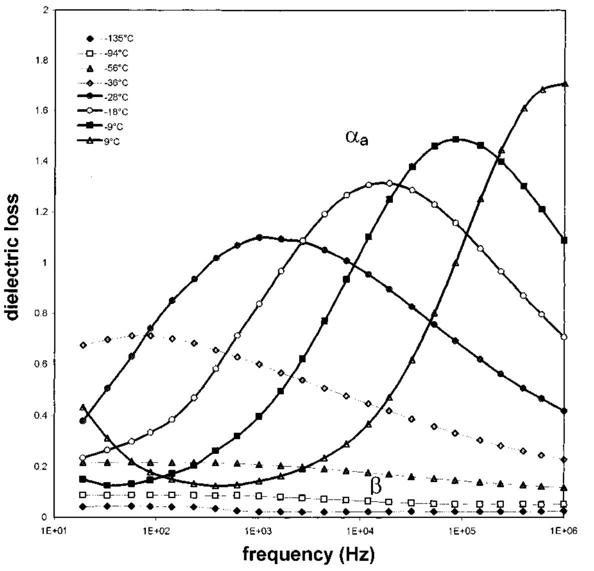

Figure 4. Dielectric loss (α_a relaxation) in the frequency domain (below 10 MHz) with temperature as a parameter for pure PVDF.

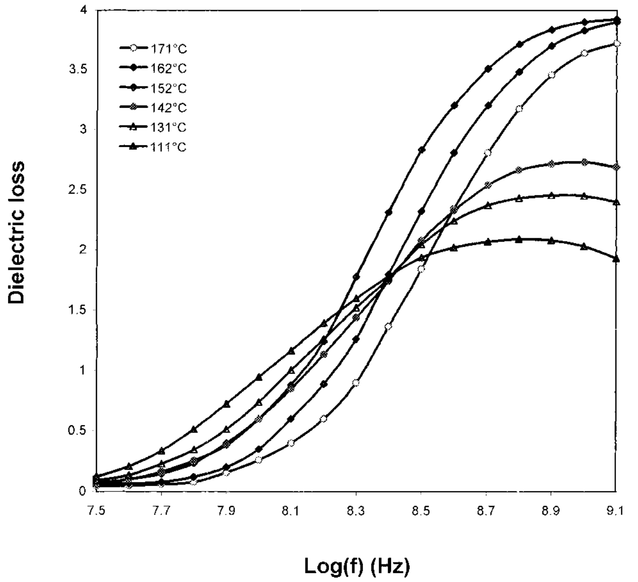

Figure 5. Dielectric loss (α_a relaxation) in the frequency domain (above 10 MHz) with temperature as a parameter for pure PVDF.

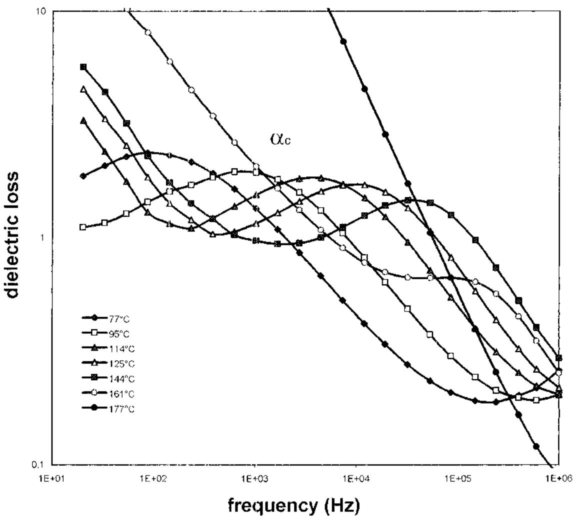

Figure 6. Dielectric loss (α_c relaxation) in the frequency domain with temperature as a parameter for pure PVDF.

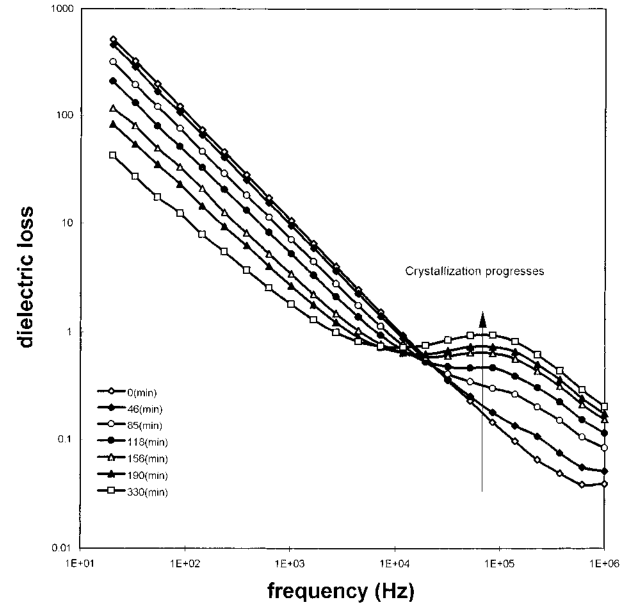

Figure 7. Dielectric loss (α_c relaxation) in the frequency domain at 155 °C with crystallization time as a parameter for pure PVDF.

interphase, as has been suggested,[7] but in the entire amorphous phase in PVDF. The observed dielectric response is affected by the crystalline phase, indicating a gradual transition in morphology from crystalline to amorphous phase, though distinct responses from the interphase and the bulk amorphous phase cannot be detected dielectrically. Further examination of Figure 5 reveals that the most probable relaxation time increases only slightly as the amorphous melt is cooled below the melting point, while the peak intensity decreases significantly. These are strong additional indications that the molecular origin of this relaxation is in the *entire amorphous phase*, which comprises the liquidlike amorphous regions and the interphase. A non-Arrhenius response is observed in the plot of dielectric loss maximum versus reciprocal temperature. The effect of crystallinity on α_a relaxation will be considered together with the effect of blend composition in the section on blends.

α_c Relaxation. The α_c peak is associated with the relaxations within the crystalline phase; its molecular origin must be sought in the various forms of imperfections that include celiae, chain loops at the lamellar surface, chain rotations and twisting within the interior of the crystals, discontinuities, etc.[14-17,32] We have already stated that α_c relaxation is absent in amorphous PVDF; its appearance and growth are a direct consequence of the development of the crystalline phase. Dielectric loss due to α_c relaxation in the frequency domain with temperature as a parameter is displayed in Figure 6. The magnitude of this loss peak decreases with increasing temperature and shifts to higher frequency. A strong effect of the polarization by migrating charges at lower frequencies is reflected in a rapidly increasing loss. Activation energy plots were constructed by plotting the frequency of the loss maximum as a function of reciprocal temperature, and a non-Arrhenius behavior was observed, as will be shown later in the text. In comparison with the α_a relaxation, the α_c peak appears at a higher temperature (at constant frequency), as seen in Figure 3, or lower frequency (at constant temperature), as shown in Figure 6. In the temperature domain, the α_c peak shifts to higher temperature with increasing frequency (Figure 3) but the relaxation process gets interrupted by the onset of melting and the peak disappears completely at around 177 °C. That the molecular origin of α_c relaxation is related to the crystalline phase is readily confirmed by the results displayed in Figure 7, which depicts a gradual growth of the α_c peak during isothermal crystallization at 155 °C. The loss peak is initially absent in the sample brought from the melt to 155 °C, and the dielectric loss decreases with increasing frequency with a slope of −1, indicating that the response is governed solely by the polarization by charge migration (e.g. refs 29 and 30). The loss peak first appears after about 5 min at 100 kHz and grows gradually in intensity as crystallization progresses. It is therefore clear that α_c relaxation is related to the crystalline phase. Relaxations in the amorphous phase are governed by a different molecular mechanism; the α_a peak at 155 °C is located at much higher frequency (around 1 GHz) than the α_c peak. The reader can easily verify this by comparing Figures 5 and 7.

Poly(vinylidene fluoride)/Poly(methyl methacrylate) Blends. We were able to distinguish five relaxation mechanisms in PVDF/PMMA blends: α_a relaxation, which is associated with local segmental motions in the crystal−amorphous interphase only (*unlike* in pure PVDF); α_c relaxation, which is related to the various imperfections in the crystalline PVDF phase (*like* in pure PVDF); α_m relaxation, which is attributed to the molecular motions in the miscible amorphous PVDF/PMMA phase; and a β relaxation in each component.

α_a Relaxation. We shall start our discussion of blends by examining how α_a relaxation, which has already been described for pure PVDF, is affected by the addition of PMMA. Because of the absence of crystallinity and interphase in the 20/80 PVDF/PMMA blend and pure PMMA, no peak was found in the temperature range of α_a relaxation in these systems. We therefore begin by focusing on samples that contain 50% or more of PVDF and hence are crystallizable. The formation of an interphase is contingent upon the presence of the crystalline phase in the blend, although, morphologically, the interphase contains almost exclusively amorphous chains. On the basis of dielectric measurements in the temperature domain, Hahn et al.[7] suggested that the molecular origin of the α_a relaxation

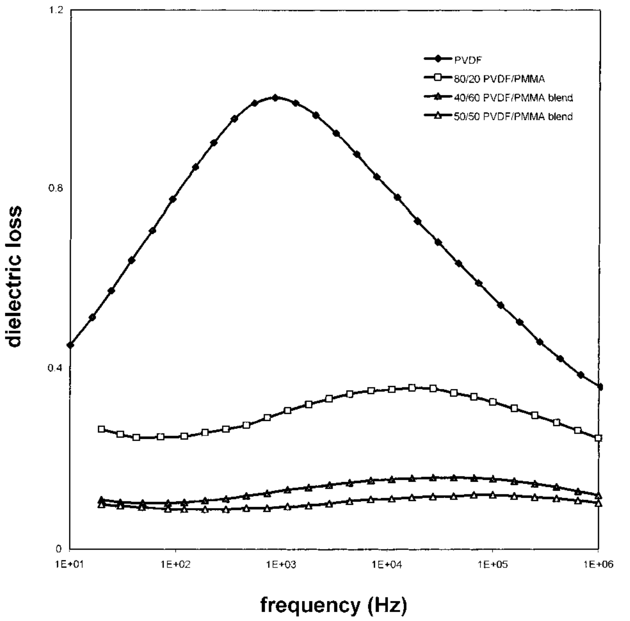

Figure 8. Dielectric loss in the frequency domain at −29 °C for blends of different composition.

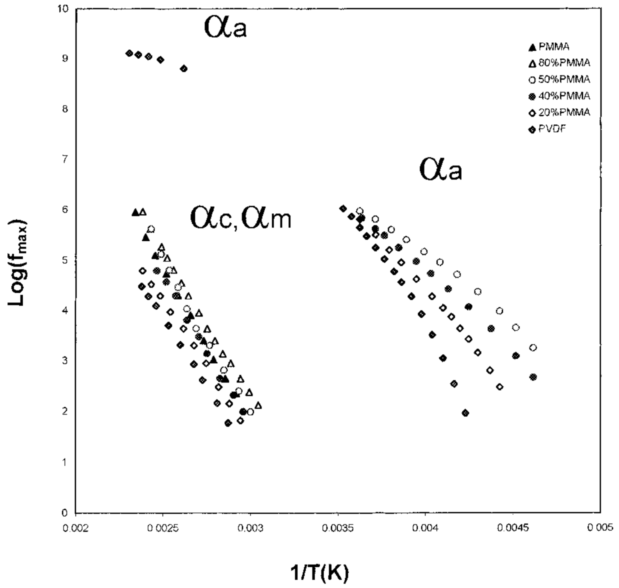

Figure 9. Frequency at maximum loss as a function of reciprocal temperature for PVDF/PMMA blends of different composition.

was within the interphase. The essence of their argument is based on the experimental finding that, at a given frequency, the temperature of the α_a relaxation peak maximum remains unchanged as a function of blend composition. They further assumed that the exclusion of PMMA from the interphase leaves an almost pure PVDF phase whose composition does not depend on either the degree of crystallinity or the composition of the miscible phase. That, however, was not borne out by our experimental results in the frequency domain. The conclusions drawn by these authors could be rationalized under the experimental conditions of their study but cannot be generalized because of (1) the narrow frequency range used and (2) the lack of reliable data in the frequency domain. In the fundamental studies of relaxation mechanisms there exists a clear preference for dielectric measurements in the frequency domain. This is best understood by examining our results for dielectric loss in the frequency domain with composition as a parameter at −29 °C, shown in Figure 8. It is obvious that the loss peaks for different blend compositions in the frequency domain do not appear at the same frequency; instead they are shifted to higher frequency with increasing PMMA content and hence must have different relaxation characteristics. The loss peak frequencies in Figure 8 are 630 Hz for PVDF; 20 kHz for 80/20 PVDF/PMMA blend; 56 kHz for 60/40 PVDF/PMMA blend; and 100 kHz for 50/50 PVDF/PMMA. Interestingly, however, the loss peak frequencies for different compositions come closer together with increasing temperature. An even clearer picture emerges from a very informative composite plot of log frequency at loss peak versus reciprocal temperature for a series of blends, shown in Figure 9. All crystalline blends with over 50% PVDF displayed a non-Arrhenius response. The observed convergence of the four curves in Figure 9 at about 15 °C and a frequency of approximately 3 MHz is astonishing! It is also readily observed that the frequency of the loss peak drops faster with temperature as the content of PMMA (high-T_g component) in the blend is decreased, and that is most interesting too. These observations confirm that the temperature dependence of α_a relaxation varies with blend composition, but they raise intriguing questions about the origin of this relaxation process. Before offering an interpretation of our results, we would like to point out that similar findings have been reported (but not explained) in a series of dynamic mechanical studies on blends of PVDF and various acrylic polymers, by Paul and co-workers.[1,33−35] For example, in an excellent early work on PVDF/PMMA blends, Paul and Altamirano[1] observed a shift in dynamic mechanical tan δ (Figure 13 in ref 1) to lower temperature (higher frequency) in going from pure PVDF to a 60/40 PVDF/PMMA blend.

On the basis of the evidence offered thus far, we submit that the origin of α_a relaxation in crystalline PVDF/PMMA blends is in segmental motions within the interphase from which PMMA was excluded. This is in agreement with the conclusions of Hahn, Wendorff, and Yoon,[7] though we differ with these authors on three major points. First, their classification of α_a as a β relaxation, which is commonly characterized by a temperature independent Arrhenius-type activation energy, has caused some confusion in terminology. Although the Arrhenius-type behavior could be approximated within their narrow frequency interval, it is clearly incorrect over a wide frequency range, as seen in Figure 9. Second, it is also clear from Figure 9 that α_a relaxation is a function of blend composition. And third, α_a relaxation in pure PVDF is associated with segmental motions in the entire amorphous phase, and not only the interphase, as described earlier in the text.

The interplay of various relaxation processes and blend morphology in the blends of different composition was considered next. Depending on the factors that include crystallization conditions, the interaction between blend components, and the cooperative diffusion coefficient, the amorphous component in the blend can be (1) located in the interlamellar zone between the crystalline lamellae, (2) excluded from the interlamellar zone but contained within the spherulite, and/or (3) rejected either partially or completely from the spherulite, resulting in the formation of a matrix in which the spherulites are embedded (e.g. ref 41). The published evidence and the results of our study indicate that the interlamellar location of the amorphous component best represents the morphology of PVDF/PMMA blends.

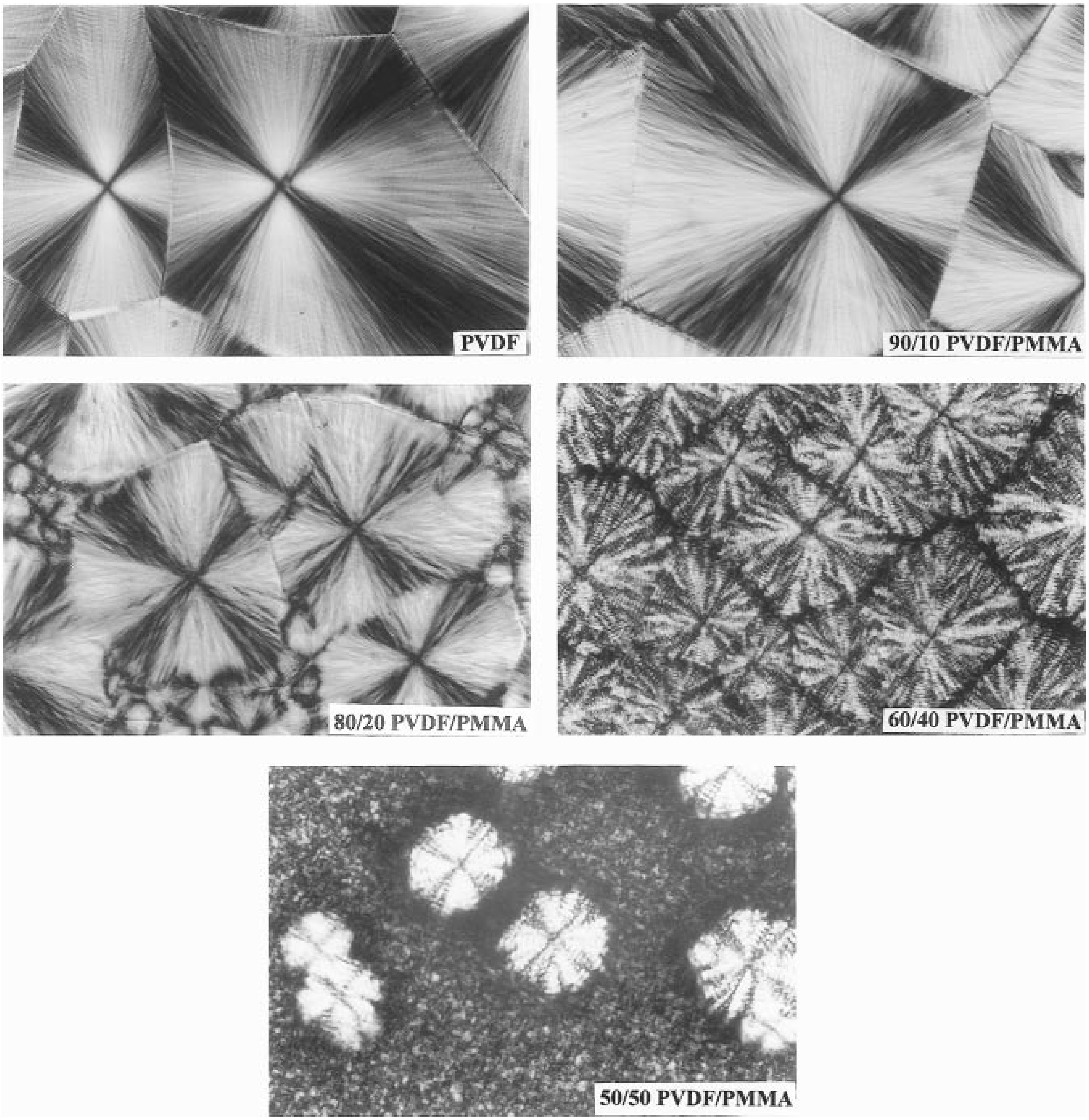

Figure 10. Optical micrographs showing the spherulitic morphology in a series of semicrystalline PVDF/PMMA blends.

Strong supporting evidence comes from the SAXS results of Morra and Stein,[8] who showed that the thickness of the amorphous region between the crystalline lamellae increases with increasing amount of PMMA. Their findings are corroborated by the optical micrographs of a series of PVDF/PMMA blends, taken in our lab and shown in Figure 10. An increase in the amount of PMMA in the blend results in smaller and coarser spherulites, but the volume-filling crystallization pattern is common to all blends. Our concept of the morphology of PVDF and PVDF/PMMA blends is shown schematically in Figure 11. In pure PVDF (Figure 11A), the noncrystalline region comprises the liquid-like region (C) and the interphase (B). The latter is a transition region, and its relaxation characteristics cannot be distinguished dielectrically from those of the liquid-like region. In PVDF/PMMA blends (Figure 11B), however, PMMA is excluded from the interphase and the relaxations in the interphase (B) can now be distinguished from those in the miscible phase (C) by dielectric measurements. In sum, the addition of PMMA to PVDF leads to (1) a gradual replacement of the liquid-like interlamellar PVDF region by the miscible PVDF/PMMA phase and (2) the formation of an interphase with relaxation characteristics that are different from those of the miscible amorphous phase.

Relaxations in the amorphous portions of crystalline polymers differ from those in the entirely amorphous polymers, and no rigorous model has been advanced to describe them. However, it is invariably informative to conduct a qualitative analysis of relaxation processes in crystalline polymers based upon the models for amorphous polymers that are adjusted for the presence of a crystalline phase. The fundamental argument should begin with the proposition that the relaxation processes are governed by cooperativity. In general, cooperativity dictates that a number of molecular segments or moieties respond in unison to an applied signal

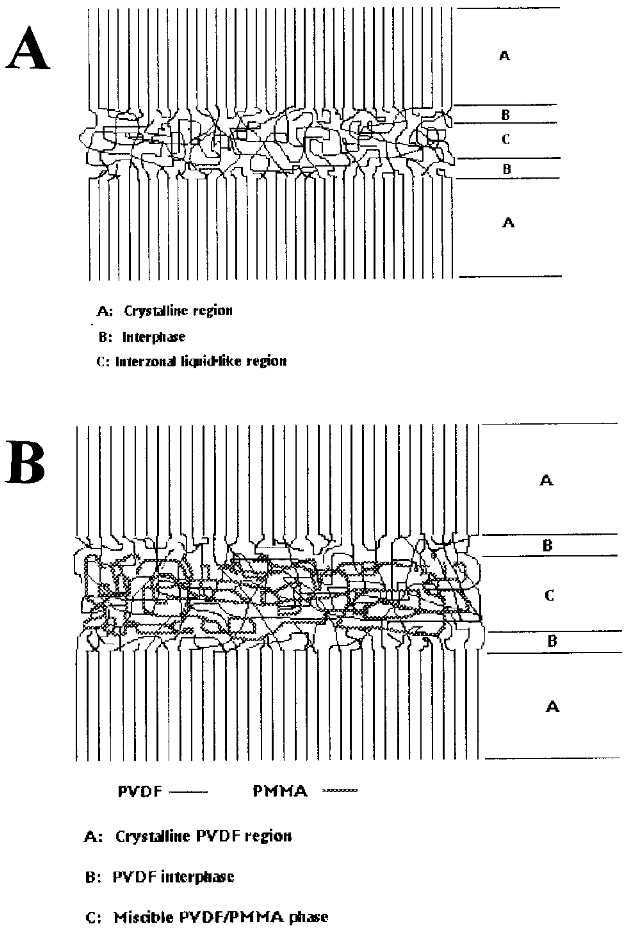

Figure 11. Schematic of morphology of PVDF and crystalline PVDF/PMMA blends.

(electric field in this study) in order for a relaxation to take place. According to the well-known Adam–Gibbs theory, the size of a cooperatively rearranging region increases with decreasing temperature and becomes infinite as temperature approaches the second-order transition where the conformational entropy vanishes. Although the Adam–Gibbs theory predicts a WLF response above T_g, it assumes a single relaxation time and excludes transitions in domains smaller than the critical domain size. Matsuoka[37] has worked out a theory that also begins with the fundamental premise that the relaxation of polymeric segments in the condensed state requires intermolecular cooperativity. According to his model, intermolecular cooperativity is governed by domains within which molecular segments, or conformers, can only relax together. Matsuoka argues for the existence of a dynamic distribution of domain sizes at any temperature; the characteristic domain size is simply the dominant one, and that is where most rearrangements in amorphous polymers occur. Although this concept is not directly applicable to crystalline polymers, where amorphous regions are separated by the crystalline phase, the fact is that intermolecular cooperativity remains the basis for the relaxation process, and hence we proceed with an argument within the general framework of Matsuoka's model. The presence of the crystalline phase causes a reduction in the global size of amorphous domains and the emergence of local environment as a key to the relaxation dynamics. How does that affect the relaxation dynamics within the interphase? The cooperative rearrangements within the interphase are restricted by the crystalline lamellae on the one end and the miscible amorphous phase on the other. An increase in the amount of PMMA in the blend will increase the T_g of the miscible amorphous phase, and that will augment the restriction to relaxations in the interphase imposed by the miscible amorphous phase. In principle, that is tantamount to a reduction in the domain size and such interpretation is intuitively appealing. How is this reflected in the dielectric response? With an increasing amount of PMMA in the blend and a simultaneous increase in the restrictions to the relaxation in the interphase imposed by the miscible phase, the dielectric response will probe an increasingly more local region (analogous to a smaller domain size). If this were true, one would expect the relaxation time to shift to higher frequency with increasing amount of PMMA in the blend, signifying that blend composition does affect the relaxation dynamics in the interphase. The key point to remember is that this occurs not as a result of a decrease in the most probable relaxation time but because of an increasingly local nature of the measured response! In other words, we do not measure a shift in the distribution of relaxation times (a shift may or may not exist); instead, we simply detect an increasingly higher frequency portion of the spectrum. We believe that the proposed mechanism is actually corroborated by the experimental evidence shown in Figure 9. The observed upward shift in the curves (Figure 9) with increasing amount of PMMA is interpreted as a consequence of the decrease in the cooperative domain size. The same conclusion is drawn from the normalized plot (not shown here) of dielectric loss as a function of frequency, where one sees an increase in the distribution breadth with increasing amount of PMMA in the blend. Since the characteristic domain size decreases with increasing temperature, the effect of the crystalline phase and the miscible phase on the relaxation in the interphase should gradually diminish and vanish when the characteristic domain size becomes sufficiently small in comparison with the overall dimensions of the amorphous phase. In Figure 9, we observe that point at 15 °C and 3 MHz. Above that point, blend composition has no effect on the dynamics of α_a relaxation in the interphase and the relaxation dynamics of the PVDF in the interphase match those of the entire amorphous phase in pure PVDF. This is interpreted as another proof that *the interphase and the bulk amorphous phase are dielectrically indistinguishable in pure PVDF.* An alternative way of displaying the temperature dependence of segmental motions consists in constructing the fragility or cooperativity plots, exploited first by Angell[38] and later redefined by Ngai.[39] Cooperativity plots contain the most probable relaxation time as a function of normalized reciprocal temperature, expressed as T/T_g or $(T - T_g)/T_g$, where T_g is taken to represent the temperature at which the relaxation time attains an arbitrary value between, say, 0.01 and 100 s. An examination of the cooperativity plot in Figure 12 affords a unique insight into the effect of blend composition on dipole dynamics. The observed decrease in cooperativity with increasing amount of PMMA, marked by a decrease in steepness, can be viewed as a consequence of the reduced distance over which cooperativity is required.

α_c and α_m Relaxations. α_c and α_m relaxations in the frequency domain with blend composition as a parameter are depicted in Figure 13 obtained at 118 °C. We first examine the response of blends that contain less than 50% PVDF, where crystallinity does not develop

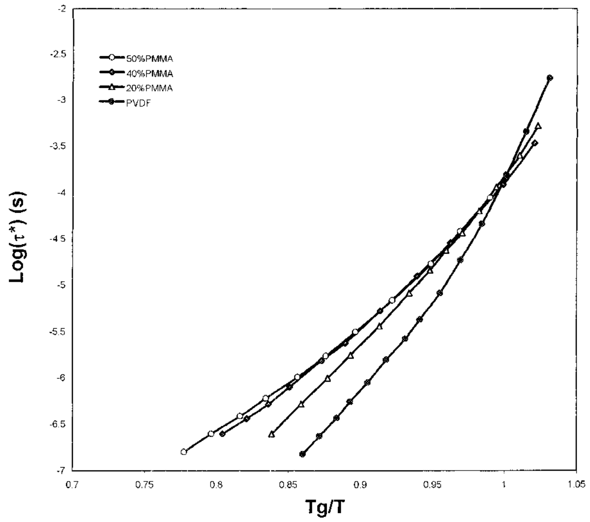

Figure 12. Cooperativity plot of relaxation time as a function of reduced temperature for crystalline PVDF/PMMA blends with blend composition as a parameter.

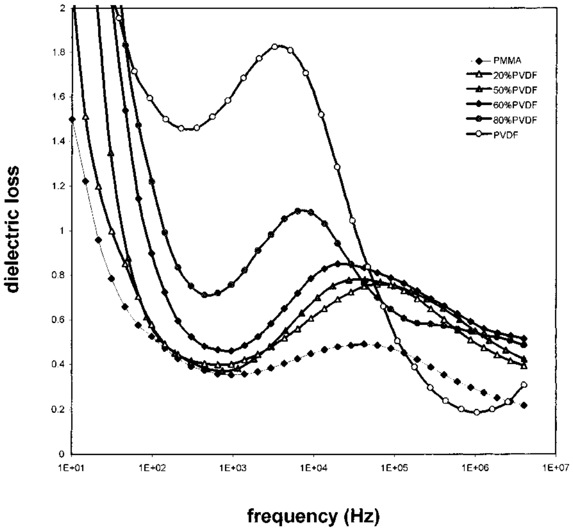

Figure 13. Dielectric loss in the frequency domain with blend composition as a parameter. Temperature = 118 °C.

and hence only α_m relaxation is present. As intuitively expected, by decreasing the amount of the higher T_g component (PMMA) from 100% to 80%, the α_m peak maximum shifts to a higher frequency (at constant temperature). The relaxation mechanism becomes considerably more complex in the crystalline blends with 50% or more PVDF, where both α_c and α_m relaxations are present. The two relaxations appear at similar frequency and/or temperature, and hence it is usually difficult, though not impossible, to resolve the two peaks. Naturally, only α_c relaxation is present in pure PVDF, as seen in Figure 13. In the 80/20 PVDF/PMMA blend the α_c peak shifts to a slightly higher frequency and the presence of α_m relaxation is clearly discernible at the high-frequency side of the spectrum. At lower temperature the two relaxations overlap and give rise to an $\alpha_c\alpha_m$ peak. The two relaxations should move further apart at higher temperature, but α_c relaxation cannot be easily separated due to the onset of melting, as discussed in the section on pure PVDF. α_c and α_m relaxations in the 80/20 PVDF/PMMA blend are also seen in Figure 14, which shows dielectric loss as a function of temperature (at 90 kHz) with blend composition as a parameter. Turning our attention back to the frequency domain, we find that the α_c peak continues to shift to higher frequency with decreasing amount of PVDF in the blend. A broad relaxation in the 60/40 and 50/50 PVDF/PMMA blends (Figure 13) is a result of the overlap between α_c and α_m relaxations in the frequency domain; deconvolution is mathematically feasible but would be too arbitrary for a physically meaningful quantitative evaluation. We stress, however, that the presence of two separate relaxations with different molecular origins is beyond doubt and has been confirmed by the experimentally observed growth of the α_c peak and the gradual reduction of the α_a peak during crystallization. It can be generally stated that α_c and α_m relaxations become progressively more difficult to separate, as the content of PMMA in the blend increases above 20%. There are two fundamental reasons for that. First, the addition of PMMA decreases the perfection of lamellar crystals and thus shifts the loss peak due to the crystalline phase (α_c) to higher frequency. And second, an increase in the amount of PMMA (high-T_g component) will shift the loss peak due to the miscible amorphous phase (α_m) to lower frequency as a result of an increase in the T_g of the miscible phase. We therefore conclude that α_c and α_m relaxations in the crystalline blends with more than 20% PMMA are bound to overlap, and that explains the difficulties in resolving these processes in the 60/40 and 50/50 PVDF/PMMA blends in Figure 13.

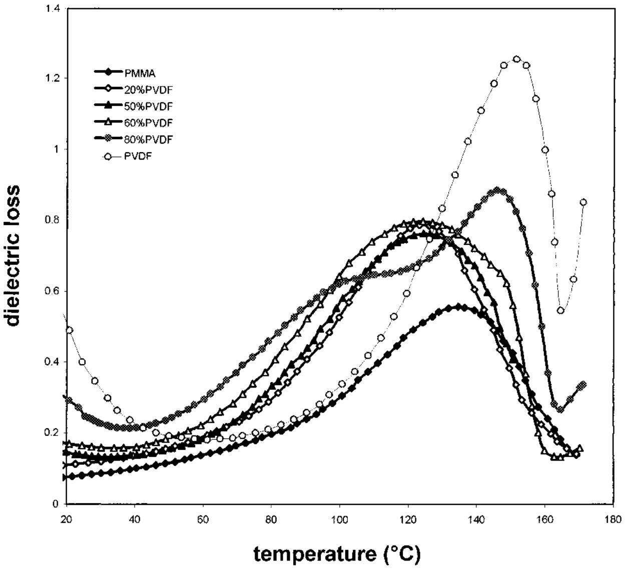

Figure 14. Dielectric loss as a function of temperature with blend composition as a parameter. Frequency = 90 kHz.

Effect of Crystallization on Reorientational Dynamics of Dipoles. As a final comment, we would like to stress that an examination of the dielectric response *during* crystallization is most informative because (1) it can reveal unique information about the nature of molecular motion or relaxation and (2) it can be potentially used to develop a methodology for in-situ real time monitoring of crystallization kinetics by dielectric measurements. The first aspect has been exploited in this study. For instance, we were able to define the origin of α_c relaxation by observing the appearance and growth of that peak during crystallization, as exemplified in Figure 7, and to confirm the origin of the α_a relaxation by observing its disappearance at high frequency during crystallization, as exemplified in Figure 5. The second aspect has not been explored here but carries a strong appeal. It is clear, for example, that data in Figures 5 and 7 follow a systematic trend during crystallization, are representative of changes on the molecular level, and are potentially attractive as a source of information for the development of fundamental correlations with crystallization kinetics.

Conclusions

We have investigated the relaxation processes in poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA), and a series of PVDF/PMMA blends by dielectric spectroscopy. In pure PVDF, α_a relaxation was attributed to the entire amorphous phase and not solely the crystal−amorphous interphase, while α_c relaxation was associated with the imperfections within the crystalline phase. Both of these assignments were corroborated by the experimental evidence that includes results obtained at frequencies and temperatures not reported hitherto in the literature. In PVDF/PMMA blends, we were able to distinguish five relaxation mechanisms: α_a relaxation, which is associated with local segmental motions in the crystal−amorphous interphase; α_c relaxation, which is related to the various imperfections in the crystalline PVDF phase; α_m relaxation, which is attributed to the molecular motions in the miscible amorphous PVDF/PMMA phase; and a β relaxation in each component. In crystalline blends, PMMA is excluded from the interphase. The relaxation dynamics within the interphase in the blends are sufficiently different from those of the miscible amorphous phase, and the two can be distinguished dielectrically. Two important characteristics of α_a relaxation in PVDF/PMMA blends are (1) non-Arrhenius behavior and (2) dependence on blend composition over a range of temperature. These characteristics are rooted in the interactive or cooperative nature of the relaxation process.

References and Notes

(1) Paul, D. R.; Altamirano, J. O. *Adv. Chem. Ser.* **1975**, *142*, 371.
(2) Mijovic, J.; Han, C. D.; Luo, H. *Polym. Eng. Sci.* **1982**, *22*, 234.
(3) Wang, T. T.; Nishi, T. *Macromolecules* **1977**, *10*, 421.
(4) Wendorff, J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 439.
(5) Noland, J. S.; Hsu, N. N.-C.; Saxon, R.; Schmitt. J. M. *Adv. Chem. Ser.* **1971**, *99*, 15.
(6) Hourston, D. J.; Hughes, I. D. *Polymer* **1977**, *18*, 1175.
(7) Hahn, B.; Wendorff, J.; Yoon, D. Y. *Macromolecules* **1985**, *18*, 718.
(8) Morra, B. S.; Stein, R. S. *Polym. Eng. Sci.* **1984**, *24*, 311.
(9) Saito, H.; Fujita, Y.; Inoue, T. *Polym. J.* **1987**, *19*, 405.
(10) Douglass, D. C.; McBrierty, V. J. *Macromolecules* **1978**, *11*, 766.
(11) Coleman, M. M.; Zarian, J.; Varnell, D. F.; Painter, P. C. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 745.
(12) Roerdink, E.; Challa, G. *Polymer* **1980**, *21*, 509.
(13) McCrum, N. G.; Read, B.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.
(14) Ishida, Y.; Watanabe, M.; Yamafuji, K. *Kolloid-Z.* **1964**, *200*, 48.
(15) Peterlin, A.; Holbrook, J. D. *Kolloid-Z.* **1965**, *203*, 68.
(16) Sasabe, H.; Saito, S.; Asahina, M.; Kakutani, H. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1405.
(17) Nakagawa, K.; Ishida, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1503.
(18) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(19) Flory, P. J. *J. Am. Chem. Soc.* **1962**, *84*, 2857.
(20) Mansfield, M. L. *Macromolecules* **1983**, *16*, 914.
(21) Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules* **1984**, *17*, 862.
(22) Marqusee, J. A. *Macromolecules* **1989**, *22*, 472.
(23) Mandelkern, L.; Alamo, R. G.; Kennedy, M. A. *Macromolecules* **1990**, *23*, 4721.
(24) Kitamaru, R.; Horil, F.; Hyon, S.-H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 821.
(25) Yoon, D. Y.; Flory, P. J. *Macromolecules* **1984**, *17*, 968.
(26) Kumar, S. K.; Yoon, D. Y. *Macromolecules* **1989**, *22*, 4098.
(27) Russell, T. P.; Ito, H.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1703.
(28) Ando, Y.; Hanada, T.; Saitoh, K. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 179.
(29) Mijovic, J.; Bellucci, F.; Nicolais, L. *J. Electrochem. Soc.* **1995**, *142*, 1176.
(30) Mijovic, J.; Yee, C. F. W. *Macromolecules* **1994**, *27*, 7287.
(31) Fitz, B. MS Thesis in Polymer Science and Engineering. Polytechnic University, 1995.
(32) Karasawa, N.; Goddard, W. A., III. *Macromolecules* **1995**, *28*, 6765.
(33) Imken, R. L.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1976**, *16*, 593.
(34) Bernstein, R. E.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1978**, *18*, 683.
(35) Wahrmund, D. C.; Bernstein, R. E.; Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1978**, *18*, 677.
(36) Hudson, S. D.; Davis, D. D.; Lovinger, A. J. *Macromolecules* **1992**, *25*, 1759.
(37) Matsuoka, S. *Relaxation Phenomena in Polymers*; Hanser Publications: Munich, 1992.
(38) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131−3*, 13.
(39) For a recent review, see: Ngai, K. L. In *Disorder Effects on Relaxation Processes*, Richert, R., Blumen, A., Eds.; Springer-Verlag: Berlin, 1994; pp 89−150.

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