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Dielectric Relaxation of the Crystal–Amorphous Interphase in Poly(vinylidene fluoride) and Its Blends with Poly(methyl methacrylate)

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ABSTRACT: The temperature of the dielectric β-transition of poly(vinylidene fluoride) (PVDF), which is generally assigned to the glass temperature of the liquidlike amorphous phase of PVDF, is found to remain invariant in its compatible blends with poly(methyl methacrylate) (PMMA) in which PVDF exhibits crystallinity. This invariance of the β-transition temperature over a large composition range from PVDF homopolymer to 60/40 PVDF/PMMA and its disappearance in the completely amorphous blends are explicable by recognizing the crystal–amorphous interphase associated with lamellar crystallites of PVDF. These experimental results therefore provide a compelling argument that the β-transition is not related to the liquidlike amorphous phase, but rather arises from the crystal–amorphous interphase in lamellar PVDF crystallites, where PMMA is completely excluded despite favorable segmental (mixing) interactions. The latter point derives from recent theoretical considerations which show that the interphase in lamellar semicrystalline polymers is necessitated by the difficulty in abruptly dissipating the high chain flux at the crystal surface to the level commensurate with the isotropy of the amorphous phase; the presence of PMMA in the interphase will therefore be deleterious in resolving the chain flux problem. It follows then that the strong β-transition of PVDF is indicative of a significant fraction of the interphase region in semicrystalline PVDF, which can be attributed to the presence of considerable amounts of head-to-head and tail-to-tail defects in PVDF chains according to the theory. Relevance of this interphase to dielectric constants and electric-field-induced orientation characteristics of PVDF are also discussed.

Introduction

It is now well established that poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) are completely compatible,[1-4] or miscible, over the entire composition range in the melt below the lower critical solution temperature (LCST) at ~330 °C.[5] This has been demonstrated, for example, by the measurements of the Flory–Huggins interaction parameter χ by various methods and the measurements of correlation lengths of concentration fluctuations by the small-angle X-ray scattering (SAXS) method. Upon cooling from the melt, the mixtures containing PVDF fractions less than 50% normally from a completely amorphous phase. In the amorphous blends the complete miscibility of the two polymers is manifested by the continuous change of the "glass temperature" with composition.[3,6]

The mixtures containing PVDF fractions more than 50% tend to exhibit crystallinity of PVDF below ~170 °C. Mechanical relaxation measurements of these semicrystalline PVDF/PMMA blends show two transition temperatures with the upper transition occurring around 60 °C and the other around -40 °C (at 110 Hz).[3,6] The former corresponds to the glass temperature of the amorphous phase comprising approximately 50/50 PVDF/PMMA, whereas the latter occurs at temperatures very close to the β-transition of PVDF homopolymer.[3,6]

According to the conclusions of previous studies on the relaxation mechanisms of PVDF,[7,8] the β-transition is generally believed to arise from the segmental motions in the liquidlike amorphous phase of semicrystalline PVDF and thus is related to its glass temperature. Hence, the fact that this β-transition is changed only slightly upon

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mixing with PMMA, up to ~40% by weight, seems contradictory to the abundance of evidence showing complete miscibility of the two polymers. Indeed, this dichotomy was pointed out early by Paul and Altamilano[3] and later led Hirata and Kotaka[6] to conclude that phase separation must occur in the melt in those mixtures that exhibit crystallinity upon cooling. However, this conclusion is untenable, since the SAXS results of Wendorff[4] show the correlation lengths of concentration fluctuations to be approximately 10 Å or less in the melt over the entire composition range. Furthermore, the small-angle X-ray scattering results from semicrystalline PVDF/PMMA blends show conclusively that all the PMMA chains reside in the interlamellar region between PVDF crystallites without forming any separate PMMA domains.[9,10] Specifically, both the long period and the absolute scattering intensity (or invariant) increase with the PMMA fraction in nearly quantitative agreement with those expected from complete mixing of PVDF and PMMA chains in the interlamellar region.

The upper transition (around 60 °C) of semicrystalline PVDF/PMMA blends in mechanical relaxation measurements is very strong and well-defined.[3,6] It is easily explained as the glass temperature of the amorphous phase of homogeneous PVDF/PMMA mixtures; the temperature reflects the composition of this phase which is different from the average owing to crystallization of certain amounts of PVDF. On the other hand, the lower transition (around −40 °C) of these blends in mechanical relaxation is quite weak and occurs very close to the γ-transition of PVDF, whose temperature and intensity are hardly changed in the blends. Furthermore, sometimes it is difficult to separate the weak lower transition from the more intense and broad peak of the γ-transition of PVDF.[3,6] Hence, one may question the existence of this separate transition as well as the validity of relating it to the β-transition of PVDF.

Here we present the results of dielectric relaxation measurements of PVDF/PMMA blends. PVDF homopolymer exhibits a very strong and well-defined dielectric β-transition, whereas its γ-transition is hardly observable.[7,8] Hence, dielectric relaxation data provide more accurate and unambiguous means of detecting any changes in the β-transition of PVDF in its blends with PMMA. These dielectric results and their comparison with mechanical relaxations are then discussed to clarify the origin of the β-transitions in semicrystalline PVDF and PVDF/PMMA blends.

Experimental Section

Material. The PVDF samples were obtained from Solvay Co. and its M_n and M_w are known to be ~38 000 and ~100 000, respectively. The PMMA samples were obtained from Röhm GmbH, and the M_n and M_w are ~60 000 and ~120 000, respectively. Polymer mixtures were melt-blended in an extruder at 220 °C 3 times in order to ensure homogeneous mixing. Thin films of 40–60 μm in thickness were extruded from the mixtures, and all the films were found to exhibit excellent optical clarity. Aluminum electrodes of 1000 Å in thickness and 2.1 cm in diameter were then evaporated on both sides of the films.

Dielectric Measurements. The dielectric properties were measured with a General Radio bridge (type-1616); the samples were placed in an environmental chamber under a dry helium atmosphere. The temperature was increased linearly at a rate of 2 °C/min from −140 to 150 °C and the bridge was balanced manually.

Results

The results of dielectric constants and tan δ at 1 kHz are shown in Figure 1 for the various PVDF fractions indicated in the figure. The results of tan δ demonstrate very clearly that the temperature of β-transition at ca. −20 °C remains virtually invariant in the blends with PVDF fraction ≥60%, where PVDF crystallinity is detected by X-ray measurements (the total crystallinity determined from X-ray diffraction decreases from ca. 0.45 for the PVDF homopolymer to ca. 0.35 for the 90/10 PVDF/PMMA to ca. 0.20 for the 80/20, and to less than ca. 0.05 for the 60/40 mixtures).[11] The slight shift in the apparent temperature of the tan δ maximum seems to be caused by the presence of the broad γ-transition of PVDF chain around −60 °C.[5–8] Its tan δ maximum decreases rapidly with increasing PMMA fraction and disappears in the completely amorphous blends with PVDF fractions less than 60%. The tan δ peak around 80 °C is very broad, reflecting the contributions from the three transitions occurring in this temperature range: the α-transition[7,8] of PVDF due to the molecular motions within form-II crystallites, the glass transition of the homogeneously mixed amorphous phase of PVDF/PMMA, and the β-transition of PMMA.[12] Hence, locating the glass temperature of the homogeneously mixed amorphous phase of PVDF/PMMA is not possible by dielectric relaxation measurements, whereas its presence is well-defined in mechanical relaxations.[3,6] (Its presence seems to be indicated by the bumps in the dielectric constant changes with temperature, as denoted by the arrows in Figure 1a, however.)

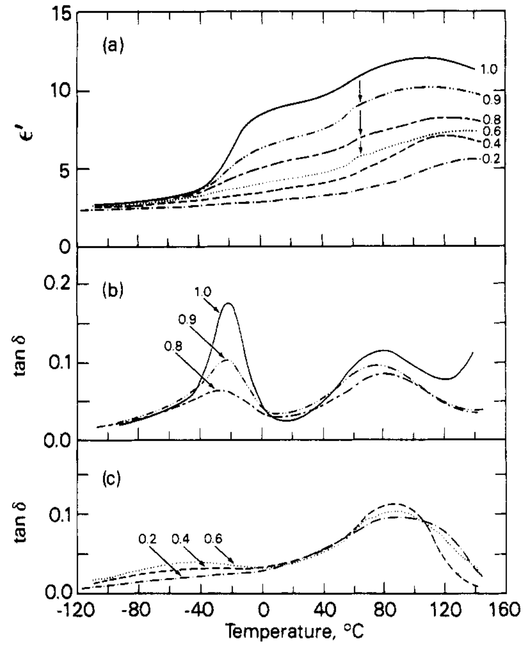

Figure 1. Dielectric constants and tan δ at 1 kHz of PVDF and PVDF/PMMA blends, plotted as a function of temperature for the PVDF weight fractions indicated.

Moreover, annealing the samples of 80/20 and 60/40 PVDF/PMMA compositions at 135 °C for 24 h in order to ensure uniform mixing[13] did not result in any appreciable changes in dielectric characteristics.

Discussion

These rather perplexing characteristics of the β-transition of PVDF in its blends with PMMA exhibit a close similarity to the β-transition results of ethylene copolymers,[14] which show that (i) the β-transition is found only in the composition range for which the copolymers are crystalline and (ii) this transition temperature is invariant over a rather large range in copolymer composition (although this temperature varies strongly with the comonomer type). It is worth noting here that this relationship was inexplicable in terms of general identification of the β-transition of semicrystalline polymers as the glass temperature of the liquidlike amorphous phase. Recently, this seemingly complicated relationship was explained in a rather straightforward manner by Popli and Mandelkern,[14] recognizing the presence of significant amounts of crystal–amorphous interphase region in the lamellar semicrystalline states of these copolymers.[15] They thus showed that the β-transition of polyethylene and ethylene copolymers arises from the motions of chain segments within this interphase region where the transition from the perfect crystalline order to the isotropy of amorphous state occurs.

The results of the β-transition of PVDF in its blends with PMMA can also be explained in terms of the segmental motions in the interphase of lamellar PVDF crystallites, following the theoretical considerations of chain packing at the surface of lamellar crystallites.[16–18] According to these considerations, formation of the interphase in lamellar semicrystalline polymers is necessitated by the difficulty in abruptly dissipating the order at the crystal surface owing to the chain connectivity. Due to the steric packing problem, dissipation of order to achieve the isotropy of the amorphous state requires significant attrition, as much as ca. 70%, of the chain flux emanating from the crystal surface by reentry of chain sequences to the same lamellae. Presence of PMMA segments near the crystal surface will therefore be deleterious in trying to reduce the chain flux. Consequently, the presence of PMMA in the interphase region is highly unlikely despite the favorable (mixing) interactions between PVDF and PMMA segments. The characteristics of the interphase associated with lamellar PVDF crystallites will therefore be hardly changed in semicrystalline PVDF/PMMA blends from those of PVDF homopolymer.

Moreover, this consideration leads to the conclusion that the interphase characteristics of lamellar semicrystalline polymer blends, in general, will be virtually identical with those of the semicrystalline homopolymers. This aspect is at variance with the situation of semicrystalline copolymers: although the β-transition temperature is invariant over a large composition range of copolymers, this temperature is ordinarily different from that of the semicrystalline homopolymer and depends strongly on the comonomer type.

According to recent theoretical considerations of chain packing at the interface of lamellar semicrystalline polymers,[17,18] the interphase thickness depends most critically on the difficulty of quickly dissipating the chain flux by forming reentry loops. In the case of copolymers and branched polymers, the reentry of chains requires the reentering chain sequences to be devoid of comonomer units or branch points (which cannot be incorporated into the crystal lattice) over the length corresponding to the lamellar thickness. Consequently, the ability of chains to reenter the same lamellae from which they emerge is reduced greatly by the presence of even a very small amount of comonomers or branch points distributed randomly along the chain. Therefore, the fraction of chain segments comprising the interphase will increase significantly because of the presence of these chain defects. Moreover, the interphase thickness as well as the lamellar thickness will depend strongly on the fraction of chain defects. The strong dependence of the interphase content, the intensity of the β-transition, and the lamellar thickness of polyethylenes on the comonomer content or chain branching[15] is thus consistent with this deduction from the theory.[17,18]

In this regard, it is important to note that PVDF chains are known to contain considerable amounts of head-to-head and tail-to-tail defects. Although the amount varies with the conditions of polymerization, typical PVDF samples contain ca. 4–5 mol % of head-to-head and tail-to-tail content each[19] and thus can be considered as a random copolymer. The very strong β-transition of PVDF (see Figure 1b), which is indicative of a significant fraction of interphase region in semicrystalline PVDF, can thus be attributed to the presence of these chain defects.

The presence of this interphase, which retains the traits of crystalline molecular order while lacking the rigid lattice constraints, seems to be responsible for a number of properties exhibited by semicrystalline PVDF. First of all, the unusually large dielectric constant normally observed for PVDF (see Figure 1a) seems to be a direct consequence of this interphase. This is demonstrated most strikingly by the results in Figure 1a, which show that as small amounts of PMMA are added and hence the PVDF crystallinity decreases, the dielectric constants above the β-transition temperature decrease rapidly. Therefore, the origin of the large dielectric constant must be associated with the lamellar crystalline features (i.e., the interphase) of PVDF and not with the liquidlike amorphous phase of PVDF. Furthermore, the fact that the increase in dielectric constant through the β-transition follows closely the PVDF crystallinity in its blends with PMMA confirms the conclusion that the β-transition of PVDF is related to the crystal–amorphous interphase. This consideration of dielectric constants of PVDF in terms of the interphase should also be applicable to other semicrystalline polymers in general. Further discussions on other polymers will be presented separately.[20]

Moreover, the molecular orientation characteristics in PVDF films under a high electric field show a fast orienting component that recovers quickly when the field is removed.[21,22] The polarization–electric field hysteresis of PVDF likewise shows a considerable amount of recoverable (nonremnant) polarization in addition to the ferroelectric remnant polarization.[23] These orientation and polarization characteristics of PVDF also seem to be the manifestations of the crystal–amorphous interphase which is associated with the lamellar semicrystalline morphology of PVDF.

The discussions above show clearly the general assignment of glass temperature of PVDF around −40 °C to be incorrect; it should be related solely to the interphase region of lamellar semicrystalline PVDF. This raises the question concerning the glass temperature of the liquidlike amorphous phase of PVDF as well as the fraction of this amorphous phase in semicrystalline PVDF. On the latter point, the dielectric constant results of Figure 1a seem to suggest that the fraction of liquidlike amorphous phase is quite small, since at temperatures below the β-transition the dielectric constant changes little with temperature and its magnitude is very close to what is expected from the optical polarizability or the refractive index.

The importance of recognizing the crystal–amorphous interphase in semicrystalline polymers is demonstrated very clearly in this study. It is now obvious that more attention should be given to the contributions of this interphase in trying to understand the properties of semicrystalline polymers in general.

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Registry No. PVDF (homopolymer), 24937-79-9; PMMA (homopolymer), 9011-14-7.

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Interactions between Smooth Solid Surfaces in Solutions of Adsorbing and Nonadsorbing Polymers in Good Solvent Conditions

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ABSTRACT: Direct measurements of the interaction forces $F(D)$ between two atomically smooth solid (mica) surfaces immersed in toluene have been carried out as a function of surface separation D; interaction profiles were also measured following introduction of (i) poly(ethylene oxide) (PEO) and (ii) polystyrene (PS) into the toluene (at low concentrations) and incubating the surfaces overnight in the solutions. Toluene is a good solvent for both polymers. In the pure toluene the interactions were short-ranged (≤10 nm) and attractive. Following full overnight adsorbance of PEO a quasi-equilibrium force–distance law was indicated on compression/decompression of the surfaces, with repulsion commencing at $D \simeq (8.5 \pm 1)R_g$ (unperturbed radii of gyration for the three molar mass polymers studied) and increasing monotonically at lower D. Rapid compression/decompression resulted in general in lower $F(D)$ values for a given D. This behavior qualitatively resembles that between adsorbed PEO layers in aqueous 0.1 M KNO_3 electrolyte, as reported earlier. In the PS/toluene solution, no adsorbance of polymer was indicated even after overnight incubation of the surfaces: the force–distance profiles were unchanged (within error) relative to those in the polymer-free solvent. A consideration of the magnitude of "depletion layer" forces suggests these (if any) would be undetectable at the polymer concentrations (10^{-4} (w/w)) used in our experiments.

Introduction

The technological exploitation of macromolecules to stabilize colloidal dispersions has a long history,[1] but it is only in the past few years that interactions between polymer-bearing surfaces, which are responsible for steric stabilization, have been studied directly.[2] Earlier measurements involved surface balance[3] and compression-cell techniques;[4] later, more direct determinations were made of the forces between two adsorbed polymer layers.[5,6] Recently, the "mica technique", developed by Tabor and co-workers,[7] and modified by Israelachvili and co-workers to study interactions between two mica surfaces immersed in a fluid,[8] has been extended by us to the case where the mica sheets bear polymer layers adsorbed from solution.[9-15] In addition to its directness and sensitivity, this method has the advantage of measuring attractive forces (if any) as well as repulsion between the adsorbed layers, which was not the case with earlier approaches.

Previous studies have included the case of polystyrene (PS) adsorbed onto the mica from cyclohexane, in poor solvent conditions:[9] the forces $F(D)$ between the two polymer-bearing mica surfaces a distance D apart were measured; the results showed a marked long-range attraction between the adsorbed layers ($F(D) < 0$), which was interpreted in terms of an osmotic attraction between the overlapping polymer layers. Later studies[12,14] in this system probed the effect of raising the temperature T to $T \geq \Theta$, the Flory Θ temperature; the forces between adsorbed layers in cyclopentane at $T \geq \Theta$ were also studied.[15] The interactions between adsorbed polyelectrolyte layers, poly(L-lysine), in aqueous KNO_3 solution were investigated[11] and showed thick, repulsive layers which were irreversibly compressed to yield a final short-range repulsion, following a first approach of the surfaces.

We have also studied the interactions between mica surfaces bearing adsorbed poly(ethylene oxide) (PEO) layers in an aqueous 0.1 M KNO_3 salt solution,[10,13] a moderately good solvent for the polymer. These showed that, once the limiting adsorption of polymer onto the surfaces had occurred, there was a long-ranged monotonically increasing repulsion between the adsorbed layers ($F(D) > 0$) and also that $F(D)$ depended on the *rate* of compression and decompression of the surfaces; in general $F(D)$ for a given D was found to be lower for the more rapid compression/decompression cycles. The repulsion in this system was largely attributed to osmotic interac-

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