Study of Reorientational Dynamics during Real-Time Crystallization of Absorbable Poly(p-dioxanone) by Dielectric Relaxation Spectroscopy

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ABSTRACT: The real-time crystallization of absorbable poly(p-dioxanone) (PDS) was studied by dielectric relaxation spectroscopy. The dipole dynamic changes in the diminishing amorphous phase were investigated over a wide range of crystallization conditions. The location, shape, and magnitude of the α relaxation and the apparent activation energy were monitored and compared before and after the onset of crystallization. We observed no correlation between the degree of crystallinity and the location (hence, the most probable relaxation time, τ) of the α relaxation from just after the initiation up to the latest stages of the isothermal crystallization. However, an abrupt change in the intensity of the α process and the apparent activation energy allowed for the precise detection of the onset of crystallization. This was probably caused by a reorganization of dipole units occurring a few moments before the crystallization began. As crystallization proceeded, an asymmetric broadening of the α peak was observed that was directly influenced by the appearance of a new lower frequency process that originated in the highly confined amorphous portion located inside the spherulites. Finally, PDS crystallization kinetics determined from the changes of the relaxed permittivity with time are discussed and compared with calorimetric and optical microscopy data. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 2436–2448, 2000

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INTRODUCTION

Polymers and copolymers based on p-dioxanone have become increasingly important in a variety of biomedical applications because of their in vivo degradability, low toxicity, softness, and flexibility. Because of the low glass-transition temperature (−10 °C) of the homopolymer, these crystallizable materials, besides being well suited for surgical monofilaments, can be injection-molded into a number of nonfilamentous surgical devices such as clips and fasteners. To obtain optimum mechanical and biological properties for future polymer devices will require a firm understanding of morphological development and, in particular, a knowledge of the crystallization process.

As a first step toward reaching these goals, we recently conducted comprehensive studies on crystal morphology, nucleation, and spherulitic growth rates of poly(p-dioxanone) (PDS) homopolymer and an 89/11 PDS/glycolide segmented block copolymer with differential scanning calorimetry (DSC) and hot-stage optical microscopy (HSOM). An unusually wide range of
crystallization conditions was experimentally accessible, allowing the inspection of various morphological features and accurate estimations of characteristic growth parameters, including radial growth and nucleation rates. Crystallization kinetics determined by bulk calorimetric measurements appear to be consistent with the morphological observations (via HSOM). Crystallization curves followed an Avrami dependence, with a calculated Avrami exponent, \( n \), of 2.5, which is consistent with simultaneous nucleation and spherulitic growth processes.\(^8\) In this article, we expand our previous study of PDS crystallization to include, among other features, dipole dynamic changes in the amorphous phase, using real-time dielectric relaxation spectroscopy (DRS).

The structure and molecular mobility of the amorphous phase in the presence of crystals in semicrystalline polymers have been the focus of an increasing number of studies in the last few decades.\(^9\)–\(^13\) Most of the data have been collected on materials with prefixed morphology, whereas only a few measurements have been performed during real-time crystallization.\(^14\)–\(^17\) This is because the time of crystallization often interferes with the time required for measurement. Some of the work relevant to this study is recapped below. Coburn and Boyd\(^18\) investigated the influence of crystallinity on \( \alpha \) and \( \beta \) processes, dipole relaxations that occur exclusively in the amorphous phase, in poly(ethylene terephthalate) (PET) by DRS. Polymer films were made in advance under different conditions, ranging from 0 to 62% crystallinity. The results indicated high sensitivity of both relaxations toward crystallinity, with a larger overall degree of crystallinity obtained for samples prepared under pressure. In another effort, the real-time monitoring of isothermal PET crystallization through the measurement of the complex dielectric permittivity was reported by Ezquerra et al.\(^15\) They described changes of the relaxation function with time during the crystallization process by the empirical Havriliak–Negami equation. Observed discrepancies between experimental values and values obtained from the traditional two-phase model were explained by the changes in the nature of the amorphous regions as crystallization proceeded. The same group studied the molecular dynamics of the \( \alpha \) relaxation by DRS during isothermal crystallization of poly(aryl ether ketone ketone). The dielectric strength was correlated with the degree of crystallinity derived from real-time wide-angle X-ray patterns via synchrotron radiation.\(^19\) As a continuation of this work, Nogales et al.\(^20\) used dielectric methods to characterize changes occurring in a series of flexible copolymers of hydroxybutyrate (HB) and hydroxyvalerate (HV) during isothermal crystallization in real time. With respect to different microstructure caused by varying HV molar contents, the data suggested that the progressive immobilization of copolymer segments as crystallization proceeds cannot be exclusively associated with the amount of crystalline material. The two terms compact spherulites and loose spherulites are also introduced to explain different degrees of restriction in molecular mobility that are dependent on the amorphous material being located in the interlamellar space or in the gaps between lamellar stacks, respectively.

In this study, we examine dipole dynamics of absorbable PDS during real-time crystallization. The influence of the evolving crystalline structure on the reorientational ability of dipole units in the diminishing amorphous phase was closely monitored and discussed.

**EXPERIMENTAL**

**Materials and Methods**

The material studied was dyed PDS:

\[
\overset{\text{O}}{\big/} -\text{(CH}_2\text{CH}_2\text{OCH}_2\text{C-O)}- 
\]

The dye used was D&C Violet No. 2 at approximately 0.2 wt %. Surgical sutures are frequently dyed to aid in their visualization in the surgical site. The resin had a weight-average molecular weight of approximately 80,000 g/mol as determined by gel permeation chromatography. The inherent viscosity, as determined in hexafluorisopropanol at 25 °C at a concentration of 0.1 g/dL, was 1.85 dL/g. The polymer was made at Ethicon, Inc. by ring-opening bulk polymerization. Because of the high sensitivity of the polymer to hydrolytic degradation, samples were stored under high vacuum; during testing, exposure to ambient atmosphere was limited.

Two types of measurements were performed by DRS. In one, the polymeric samples were melted at 140 °C (equilibrium melting temperature) for 5 min in a separate oil bath apparatus; samples were then quickly brought to a second, already preheated oil bath to perform isothermal mea-
measurements. In another set of experiments, the samples were quenched initially to −20 °C from the melting state (140 °C) and then subsequently heated at the constant heating rate of 0.75 °C/min.

Techniques

**DRS**

Dielectric measurements were performed on a Hewlett-Packard 4284A precision LCR meter (20 Hz to 1 MHz). The instrument was modified by the addition of a temperature-controlled chamber and interfaced to a computer via a National Instruments IEEE 488.2 interface bus. A disposable homemade three-electrode cell was utilized for these measurements as described elsewhere. The cell consists of two glass slides separated by a Teflon spacer, with thin aluminum electrodes placed on the inside surface of each glass slide. A high-temperature adhesive (Specialty Tapes, Inc.) was used to bond Teflon to glass. A guarded electrode was introduced to minimize the fringe fields and eliminate the possibility of surface conduction.

**DSC**

Calorimetric results were generated on a TA Instruments differential scanning calorimeter, model 2910 MDSC, with dry N\textsubscript{2} as a purge gas. The instrument was calibrated with an indium standard for temperature and heat change. The experiments on the isothermal melt crystallization of PDS homopolymers were carried out as follows: A 5-mg sample was first melted and maintained for 5 min at 140 °C to remove any nucleation sites present in the sample. Subsequently, polymers were rapidly cooled down (ca. 30 °C/min) to the constant test (crystallization) temperature. This isothermal method assumes that no crystallization occurs before the sample reaches the test temperature; experimental results indicated that this assumption is reasonable. Crystallization behavior was characterized over a wide range of temperatures, from 15 to 80 °C. The isothermal heat-flow curve was integrated to determine the crystallinity as a function of time. Further experimental consideration of our DSC facility has been described in detail elsewhere.

Wide-Angle X-Ray Diffraction (WAXD)

Some supporting data on the crystallization behavior of PDS homopolymer were obtained from WAXD. The X-ray measurements of the isothermally grown films were carried out on a Siemens Hi-Star™ unit with Cu Kα radiation at a wavelength of 1.542 Å. The instrument was operated at 40 kV and 40 mA with a collimator size of 0.5 mm. Samples were mounted on the goniometer in such a way that the surface of a polymer film was positioned normal to the X-ray beam. The convolution of the X-ray images and the calculation of crystallinity content were conducted with DIF-FRAC PLUS™ software developed by Siemens.

Polymer films suitable for X-ray examination were made with a Mettler FP82HT hot-stage apparatus with a Mettler FP90 central processor to control sample conditions. A small amount of ground polymer was placed on the microscope glass slide, and a thin cover glass was positioned on top of it. The resulting sandwich was then inserted into a hot-stage block regulated at 140 °C. The sample was held at this temperature for 2 min under a constant nitrogen purge. A thin film was obtained by the application of a slight pressure on the top of the cover glass. Monitoring with a digital micrometer, we adjusted the polymer thickness to 0.135 mm for each sample run. Polymers were then quickly brought to a second, already preheated measuring device to conduct isothermal measurements.

RESULTS AND DISCUSSION

Effect of the Crystal Formulation on the Reorientational Dynamics of the α Relaxation

This section introduces dielectric data obtained during real-time crystallization of PDS over a wide range of isothermal and nonisothermal conditions. Dielectric measurements were performed almost exclusively in the frequency domain with temperature or crystallization time as a parameter. Several approaches describing the dipole dynamics of this absorbable polymer have been explored and are discussed next.
We start our analysis in the frequency domain by plotting dielectric loss and dielectric constant as a function of crystallization time at room temperature (22.2 °C), as shown in Figure 1(a,b), respectively. Frequency sweeps were taken from 100 Hz to 1 MHz. For each time run, the frequency sweep was completed in less than 35 s, which allowed real-time measurements during crystallization. The initial curve at \( t = 0 \) corresponds to the fully amorphous polymer that was quenched prior to crystallization. As crystallization proceeded, several important features were observed. As shown in Figure 1(a), the frequency of the maximum loss, \( f_{\text{max}} \), for a fully amorphous \( \alpha \)-relaxation was initially located in the high megahertz region. To locate precisely this peak, measurements at frequencies higher than 1 MHz are needed. The value of \( f_{\text{max}} \) is inversely proportional to the most probable relaxation time, \( \tau \). Soon after the first crystals developed, the maximum of this peak [the change in the slope in Fig. 1(a)] shifted to about 1 MHz. With further crystal growth, a gradual reduction of the intensity of the \( \alpha \)-relaxation was observed denoting the loss of the amorphous portion in the polymer, but the location of this peak remained unchanged until the very late stages of the process. Similar observations during isothermal crystallization have been reported earlier on other polymers, including PET, poly(vinylidene fluoride), and copolymers of HB and HV. Furthermore, systematic changes in the relaxed part of the dielectric constant [marked by the arrow in Fig. 1(b)] allows one to compute crystallization kinetics at a constant single frequency. This analysis is presented and discussed later in the text.

The observed insensitivity of the relaxation time, \( \tau \), throughout most of the process suggests that the domain size of this segmental motion is sufficiently small that the growing crystal units do not perturb dipole relaxation. However, after 60 min at 22.2 °C, when crystallization was apparently near completion, a shift of the frequency of the maximum loss, \( f_{\text{max}} \) toward a lower frequency was detected, as shown in Figure 1(a). The \( f_{\text{max}} \) downward shift occurs after the crystalline phase achieves a significant volume fraction. This indicates a slowing down of the chain mobility as the molecule starts to feel the presence of growing crystal structures. Ezquerra et al. explained this frequency shift by the prompt transition between looser spherulites, where restrictions of the amorphous portion are expected to be weaker, and compact spherulites, where these restrictions become stronger.

In addition to these phenomena, during the crystallization of PDS we observed a new process located at a slightly lower frequency range that emerged and systematically increased with time, as indicated by the upward arrow in Figure 1(a). Two isosbestic points on both sides of the peak accompanied this relaxation. The existence of isosbestic frequencies at which \( \varepsilon'' \) is independent of crystallization time is an important feature and
may suggest the following: (1) the origin of the two relaxations in Figure 1(a) is the same, but their relaxing units exist in different environments; (2) there is a gradual volume transformation from higher to lower frequency relaxation with time; and (3) the location of this new process is not affected by the frequency shift of the main peak observed after 60 min of crystallization [see Fig. 1(a)]. Considering all of these points, we believe that the origin of the new relaxation comes from a highly restricted amorphous portion located between crystalline lamellae within the spherulites in the polymer: the intraspherulitic amorphous phase. The other type of amorphous phase fills the interspherulitic space, and its relaxation remains unaffected by the presence of spherulites. With further crystal growth, this dominant part of the relaxation, interspherulitic in nature, is gradually transformed into an intraspherulitic form, but it is not causing the increase in \( \tau \) (the most probable relaxation time). However, there is a point when the highly restricted form starts to become a predominant factor in the relaxation spectrum. This evidently occurs at crystallization times greater than 60 min, when the frequency shift of the main \( \alpha \) relaxation is observed. As an example of the temperature effect, a plot of dielectric loss in the frequency domain during isothermal crystallization of PDS at 35 °C is shown in Figure 2. Because both relaxations are thermally activated processes, their peak maxima are now shifted to higher frequencies. Two isosbestic points for the new process are still present at this temperature. A large conductivity contribution is seen at a lower frequency, but its presence does not affect the isosbestic phenomenon. The initial frequency shift of the \( \alpha \) relaxation observed between 0 and 2 min in Figure 2 may reflect a sudden drop of the apparent activation energy, accompanied by the onset of crystallization. We discuss these data further in the following section.

**Activation Energy**

A common experimental strategy was used to study the temperature dependence of the \( \alpha \) relaxation in fully amorphous and partially crystallized PDS samples. The polymer was initially quenched from the liquid state to below its glass-transition temperature; this was followed by a constant heating step of 0.75 °C/min. The frequency sweeps were performed at a series of temperatures, ranging from −8 to 20 °C. Because of the sufficiently slow crystallization of PDS at these temperatures, it is safe to assume that no additional crystal growth took place during the frequency sweep. In Figure 3, we plotted dielectric loss in the frequency domain for PDS, with temperature as a parameter. With an increase in temperature, the dipole peak was systematically shifted to a higher frequency accompanied by a slight increase in intensity. It has been suggested\(^\text{19}\) that the onset of crystal growth coin-

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**Figure 2.** Dielectric loss in the frequency domain with time as a parameter during isothermal crystallization at 35 °C.

**Figure 3.** Dielectric loss in the frequency domain with temperature as a parameter. The arrow indicates the temperature scan (8 °C) in which crystallinity is first detected.
cides with the first drop in the loss peak intensity. This phenomenon was detected at 8 °C, as indicated by an arrow in Figure 3. At still higher temperatures, the intensity of the loss continued to decrease because of further crystal growth.

The fine sensitivity of the intensity of the dielectric loss peak to crystallization allows for the collection of the temperature dependence of the process at various stages of crystallization, from low, sub-glass-transition temperatures (quenched, purely amorphous material) to temperatures above the glass-transition temperature (when the amorphous material is heated), at which point crystallization occurs. The results shown in Figure 3 were used to construct an Arrhenius plot (frequency at maximum loss as a function of reciprocal temperature) shown in Figure 4. To analyze the temperature dependence of the α process by this method, we assumed that crystallinity does not affect the most probable relaxation time, τ; that is, the location of the α process in the frequency domain remains intact. As presented in the previous section, this was supported by experimental evidence during the major part of the process. The two lines intersecting at 7.5 °C in Figure 4 appear to indicate two distinct Arrhenius regimes (two activation energies and two prefactors) for PDS dipolar relaxation in this frequency range. Interestingly, the intersection of the two lines is located at the onset temperature of crystal growth indicated by the sudden decrease in dipolar loss peak intensity in Figure 3. Before crystallization, the apparent activation energy of the α relaxation is 44.8 kcal/mol, but as soon as the crystals begin to form, this value decreases to 27.7 kcal/mol and remains constant thereafter, unaffected by the continuing crystal growth. This 40% decrease in the apparent activation energy is significant, and its sharp occurrence at the onset of crystallization suggests a possible change of the relaxation mechanism. Although this aspect of dipolar dynamics in crystallizable polymers has not been previously reported in the literature, the dielectric behavior of PDS is not entirely unique, as we have encountered it in other polymer and nonpolymeric systems. Dielectric data generated by us on various crystallizable nonreactive (i.e., phenyl glycidyl ether, 15-crown-5) and reactive non-polymer-forming systems, including partially reacted diglycidyl ether of bisphenol A and N-methyl-P-nitroaniline formulations, revealed a trend similar to what has been found in this PDS study. The common findings for these systems can be briefly summarized as follows: (1) there is a substantial decrease (15–45%) in the apparent activation energy of the α relaxation with the formation of the first crystal structure in the system; (2) from this point on, the temperature dependence of the α process assumes an Arrhenius form, even in the systems characterized initially by a strong non-Arrhenius response, (3) for materials that are highly crystallized (90–95% crystallinity), the activation energy is considerably higher than the energy of the same material with a low-to-moderate crystal content; and (4) the shape parameter n, which is, according to the model of Schölßler and Schönhals,23 responsible for short-range interaction, is not affected by crystallinity.

This discovery that the growing crystal structures have no influence on the ability of the majority of dipole units to relax is intriguing. The interpretation of this and other findings requires an understanding of the molecular mechanism that governs the α relaxation during monitoring of these events. As a possible path to explain the process, a sudden reorganization of dipole units that occurs a few moments before the crystallization begins is presently offered. This one-time contemporary rearrangement of the molecules in the amorphous phase may cause a reduction of the apparent activation energy of the α process by lowering the overall cooperativity of dipole units. An additional support for this idea comes from several independent studies conducted on the isothermal crystallization of PET,24 isotactic polypropylene,25 and poly(butylene terephthalate)26 by simultaneous time-resolved small-angle
X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) using conventional source or synchrotron radiation. Scattering data, which were all generated with conditions similar to our conditions, showed that the SAXS peak occurred before the WAXS crystal reflection peak. This suggests that some type of density fluctuations, probably a kind of phase separation of spinodal decomposition, caused by the long-range ordering of polymer chains were present prior to the crystal growth. However, to further link dipole relaxation response to the prenucleation density fluctuation observed during the induction period, an additional detailed examination of this possibly profound phenomenon is needed.

**Breadth and Shape of the Relaxation Spectrum**

To gain further insight into the crystallization mechanism of PDS, we examined the shape and breadth of the relaxation spectrum before and after crystallization. The comparison is made in Figure 5, where the normalized (master) plot of dielectric loss as a function of frequency has been constructed with data from Figure 3. Before the onset of crystallization (at less than 8 °C), dipole loss curves superpose quite well, suggesting thermodielectric simplicity \(^{27}\) in the applied frequency interval between 100 Hz and 1 MHz. As crystallization proceeded at higher temperatures, we observed significant but rather gradual broadening of the relaxation spectrum. This is in general agreement with previous reports on a great variety of semicrystalline polymers. \(^{9,11,13,17,19}\) The effect has been explained \(^{19,20}\) as due to restrictions of the available possible conformations of the macromolecules introduced by crystallinity, which, in turn, increases the interchain coupling or cooperativity \(^{28}\) in the system. This argument seems to contrast with our data because this study clearly indicates that a new process emerges with the onset of crystallinity [see Figs. 1(a) and 2] that strongly affects the lower frequency side of the \(\alpha\) peak. We believe that the new process cannot be solely attributed to an increase of cooperativity because the apparent activation energy of the \(\alpha\) relaxation does not follow this trend.

Another issue regarding the shape of the \(\alpha\) process is raised during the consideration of the Schlösser and Schönals model (SS), \(^{23}\) which interprets broadening and symmetrization of the \(\alpha\) relaxation during crystallization as due to the restrictions in the long-range motions of the polymeric chains. According to the theory, this would affect primarily the low-frequency side of the peak, with the high-frequency side remaining unchanged by crystallization. Although there is a great deal of experimental evidence in the literature \(^{13,15,17,19,23}\) to support the SS model, the high-frequency side of the normalized peak shown in Figure 5 seems to broaden continuously with the progress of crystallization. In terms of symmetrization of the \(\alpha\) process, these PDS data, supported by the computational analysis of the relaxation spectrum introduced next, are also in conflict with the SS model.

We now proceed to describe the dynamics of the \(\alpha\) process by fitting the normalized dielectric loss data shown in Figure 5 to the Kohlrausch–Williams–Watts (KWW), or stretched exponential, expression: \(^{29}\)

\[
\Phi(t) = \exp\left[-\left(t/\tau\right)^{\beta}\right]
\]

where \(\Phi(t)\) is the normalized relaxation function, \(\tau\) is the characteristic relaxation time, and \(\beta\) is the stretched exponential parameter (0 < \(\beta\) < 1). For the sake of clarity, we describe briefly our fitting process. It was first necessary to establish if the normalized dielectric loss data were dielectrically simple; that is, the shape of the relaxation spectrum did not depend on temperature. This condition was fulfilled, at least for the initial amorphous polymer, as indicated in Figure 5. Data

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**Figure 5.** Normalized plot of \(\varepsilon/\varepsilon_{\text{max}}\) versus \(\log f_{\text{max}}/\log f\) with temperature as a parameter. Solid lines are fits to the KWW equation.
were then converted to the complex general form and expressed as follows:

$$
\varepsilon^*(\omega) - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)
\times \left[ 1 - i\omega \int_0^\infty \Phi(t) \exp(-i\omega t) \, dt \right]
$$

where \( \omega \) is the angular frequency; \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the low-frequency and high-frequency permittivities, respectively; and \( \Phi(t) \) is the normalized relaxation function. The KWW expression (eq 1) then replaces the normalized relaxation function in this integral, and a computer routine solves for the best fit \( \beta \) parameter. Our goal in this part of the study is to examine how the empirical parameter \( \beta \) varies with crystallization.

As indicated in Figure 5, a reasonably good fit was obtained on amorphous samples (at less than 8 °C), with the exception of the low-frequency and high-frequency tails. These deviations were most likely caused by the presence of the conductivity term and secondary high-frequency relaxations, respectively. The calculated \( \beta \) parameter of fully amorphous PDS sample is 0.40, which is close to the value of 0.41 available in the literature for amorphous poly(aryl ether ketone ketone).19 The value of parameter \( \beta \) in the KWW function remained constant prior to PDS crystallization but systematically decreased as crystallization proceeded. A strongly asymmetric distribution of the peak is preserved up to the 16 °C run, at which point the lack of data at the higher frequency side prevented an accurate fitting procedure.

There are several reasons for the broadening of the \( \alpha \) relaxation during PDS crystallization. We may distinguish them: (1) the new low-frequency process (which we propose is due to intraspherulitic and, therefore, confined amorphous chains); (2) the low-frequency side of the \( \alpha \) process (the main \( \alpha \) relaxation, originating from interspherulitic, bulk amorphous material), which may be disturbed (broadened) by the presence of various imperfections in the crystal structure; and (3) the high-frequency side of the \( \alpha \) process, which may be broadened by a distribution of short-range processes due to interspherulitic constraints at higher crystallinity.

**Crystallization Kinetics Based on Relaxed Permittivity Measurements**

It has been shown that PDS can be easily quenched into a completely amorphous state and that the homopolymer can be isothermally crystallized with a relatively slow crystallization rate within a wide temperature range.6,7 This feature makes PDS a suitable polymer for the study of dipolar relaxations in the presence of crystallinity because dielectric measurements can provide real-time monitoring of the crystallization process. Likewise, the rationale of using DRS for kinetic purposes is its ability to examine a wide range of crystallization rates in a variety of materials, including some biologically important groups of slow-crystallizable polymers and copolymers. At temperatures higher than the glass-transition temperature, the limiting low-frequency dielectric permittivity can be used to follow different structural changes in polymers observed in real time.14 The decrease of relaxed (low-frequency) permittivity, \( \varepsilon_0' \), with crystallization time can be, in principle, associated with the progressive reduction of the amorphous phase as segments of the polymeric chains (and, therefore, dipoles on the chains) become immobilized in crystals. In an earlier study on isothermal crystallization of poly(aryl ether ketone ketone), Ezquerra et al.19 showed a very strong correlation between the strength of the dielectric relaxation, \( \Delta \varepsilon = \varepsilon_0' - \varepsilon_\infty' \) (where \( \varepsilon_\infty' \) is the unrelaxed, high-frequency permittivity) and the crystallinity, as calculated from X-ray images. This and other studies9,13,16,31,32 have shown that the extrapolation of crystallinity to \( \Delta \varepsilon = 0 \) yields in some polymers a predicted crystallinity somewhat lower than 100%. However, we felt justified in using dielectric measurements to determine relative crystallization kinetics for our isothermally grown PDS films because this material typically crystallizes under good conditions to only about 40%.

The crystallization kinetics of PDS were computed with the type of data displayed in Figure 1(b). Because unrelaxed high-frequency permittivity, \( \varepsilon_0' \), was unchanged (within experimental error) during crystallization, relative kinetic data could be determined with only the parameter \( \varepsilon_0' \) being monitored at a constant frequency as a function of time. In Figure 6, we have plotted \( \varepsilon_0' \), against time for a series of selected temperatures at a frequency of 25 kHz. Before crystallization, all of the samples were in a fully amorphous state.
Initial values of $\varepsilon'_0$ (at $t = 0$) were systematically lower for higher temperature runs because of lower dipole strength at elevated temperatures. At the onset of crystallization, $\varepsilon'_0$ began to progressively decrease with time, with the rate being a strong function of temperature. Isothermal crystallization kinetics were obtained by the normalization of data from Figure 6 with the following formula:

$$\text{crystallinity}(t) = \frac{\varepsilon'_0(0) - \varepsilon'_0(t)}{\varepsilon'_0(0) - \varepsilon'_0(\infty)}$$

(3)

where $\varepsilon'_0(t)$ denotes the value of relaxed permittivity at time $t$, whereas $\varepsilon'_0(0)$ and $\varepsilon'_0(\infty)$ are its initial and final values, respectively.

In Figure 7, the extent of crystallization is plotted versus time for several selected isothermal runs ranging from room temperature to 50 °C. For comparison, our earlier results on the PDS homopolymer obtained with DSC under the same experimental conditions are included. The two techniques are in excellent agreement for all isothermal runs at 50 °C and below. However, above 50 °C DRS-determined and DSC-determined crystallization kinetics diverge, as shown in Figure 8. The DRS data show a much faster crystallization process than those generated by DSC. Dielectric data at 55 °C (not shown here) showed only slight disagreement with DSC kinetics, indicating a transition zone behavior. A question is raised on the nature of these discrepancies. We offer evidence suggesting that the isothermal crystallization processes of PDS conducted at 50 °C and lower are fundamentally different from those performed at the higher crystallization temperatures.

Let us consider first the relative size of developed PDS spherulites at the end of a crystallization prior to impingement for various crystallization temperatures measured by HSOM. In Figure 9, the maximum radius of the spherulite is plotted against crystallization temperatures for

Figure 6. Relaxed dielectric constant (permittivity), $\varepsilon'_0$, as a function of crystallization time at 25 kHz with temperature as a parameter.

Figure 7. Extent of crystallization as a function of time from 25 to 50 °C, as calculated from DSC and DRS techniques.

Figure 8. Extent of crystallization as a function of time at 60 and 75 °C, as calculated from DSC and DRS techniques.
the PDS homopolymer. At temperatures below 55 °C, there is only a slight gradual increase of the final spherulitic radius with a rise in temperature. That is, \( dR_{\text{max}}/dT \) is a low positive value. However, at temperatures of 55 °C and greater, an abrupt jump in \( dR_{\text{max}}/dT \) is observed. This substantial change in the morphology of PDS films can be explained, at least partially, by the higher nucleation rates characterizing the lower temperature zone.\(^7\)

In addition to the HSOM findings, we present in Figure 10 the heat of crystallization against crystallization time at various temperatures. These curves are generated from an integration of the DSC exotherms.\(^6\) An important feature is that the same final plateau level of the heat of crystallization is achieved in runs carried out up to 50 °C, suggesting that an equal amount of crystallinity is developed in this temperature range. However, samples crystallized at 55 °C and higher show a systematic increase in the heat of crystallization with an increase in crystallization temperatures. These calorimetric data are supported by WAXD data. The extent of crystallization calculated from WAXD measurements as a function of temperature is plotted in Figure 11. There appears to be a discontinuity between a plateau region of constant crystallinity for samples crystallized at 50 °C and below and a region above 50 °C where these final values gradually increase with temperature. In addition to this observation, a good agreement was found between WAXD-measured and DSC-measured (heats of fusion) degrees of crystallinity. Using a linear extrapolation, we determined the heat of fusion for 100% crystalline PDS homopolymer to be 124 J/g. This is the same value reported earlier for PET.\(^18\)

Although previous results confirm a good agreement between WAXD and DSC data regarding the overall final degree of crystallinity, it does not prove that the DSC-based kinetic calculations are valid. In Figure 12(a), we compare DSC crystallization kinetics with data generated with our hot-stage microscopy apparatus\(^7\) as a function of...
temperature. A convenient DSC kinetic parameter is the reciprocal of the crystallization half-time, \( 1/t_{1/2} \), whereas changes in spherulitic radii with time, \( dR/dt \), represent spherulitic growth rates. We have observed that for PDS, \( dR/dt \) values are extraordinarily constant at a constant temperature, in some cases even after 9 h.\(^7\) It has been postulated\(^5,33\) that \( t_{1/2} \) reflects the overall rate of crystallization because it incorporates a convolution of both nucleation and spherulitic growth components. Optical measurements, however, can be effectively used to study these crystallization components individually and thus allow a more precise characterization of the development of spherulite morphology. Because the maximum nucleation rate is observed at a temperature slightly below 40 °C, the DSC crystallization rate peak, which reflects the properties of both crystallization mechanisms, appears to be shifted to lower temperatures. A similar trend was detected for absorbable poly(l-lactide).\(^7\) The solid line in Figure 12(a) connecting the spherulitic growth data is the Lauritzen–Hoffman equation,\(^33\) which uses no adjustable parameters. An almost perfect fit through the data indicates the validity of both the experimental results and this theory.

Now we would like to take the reader’s attention back to the shape of the DSC-generated curve shown in Figure 12(a). A comparison with the spherulitic growth rate curves reveals a narrower distribution of rates determined by DSC measurements. A simple illustration is given by the two solid horizontal lines in Figure 12(a), which are not the same length, indicating unequal breadths of the distribution. The DSC crystallization rates located along the higher temperature half of the peak seem to be largely underestimated. As shown earlier, the data in the DSC peak at temperatures below 55 °C agree very well with DRS-measured kinetics. In Figure 12(b), DRS data generated at temperatures above 55 °C are included in the kinetic composite plot for comparison. The dielectric parameter \( t_{1/2} \) is the crystallization time needed to achieve 50% crystallinity, as determined from the changes in relaxed permittivity at the selected constant frequency. It is evident from Figure 12(b) (as marked by the two equal lines) that the addition of DRS results to the chart considerably improves the breadth of the DSC distribution curve. This finding suggests that the dielectric technique can compensate for the discrepancy observed at higher temperatures between calorimetric and optical measurements.

The origin of these kinetic deviations is not yet known; however, we offer an explanation next. In one of our previous studies,\(^6\) we reported that DSC is not a suitable technique in cases where isothermal crystallization kinetics are very slow. For that reason, our isothermal crystallization study on an 89/11 PDS/glycolide copolymer could not be performed with the DSC technique. This was the direct result of the crystallization rate being so low that the rate of heat gain in the

Figure 12. (a) Composite plot of the reciprocal half-time of crystallization, \( 1/t_{1/2} \), from DSC measurements and the spherulitic growth rate, \( dR/dt \), as a function of crystallization temperature. (b) Composite plot of the reciprocal half-time of crystallization, \( 1/t_{1/2} \), from DSC and DRS measurements and the spherulitic growth rate, \( dR/dt \), as a function of crystallization temperature.
calorimeter was less than the heat-loss rate, resulting in no net change in the enthalpy signal. In addition, an inability of the instrument to account for a continuing incremental crystallization was also observed during calorimetric measurements of dyed PDS at 75 °C. The value of the Avrami constant $n$, determined at that temperature, deviated considerably from the value of 2.5, which was found for all other isothermal runs. Consequently, the 75 °C heat of crystallization curve (not shown here) indicated a much lower final crystallinity content than what had been expected from WAXD measurements. All of these factors greatly affect the reliability of DSC-determined kinetics in this temperature zone but do not provide enough evidence to explain apparently slower PDS crystallization at still lower temperatures. Experiments using some alternative approaches to this problem are under way.

**CONCLUSION**

The crystallization of absorbable PDS has been studied by DRS under a wide range of experimental conditions. The location, shape, and magnitude of the $\alpha$ relaxation, as well as the apparent activation energy, were monitored and compared both before the onset of crystallization and during its growth. The location of the maximum dielectric loss peak (and, hence, the most probable relaxation time, $\tau$) was independent of the isothermal crystal growth from a point immediately following the onset of crystallization to a very late stage of the process. This allowed us to develop a method that uses the apparent activation energy of the $\alpha$ relaxation to monitor cooperativity trends before and during the progress of crystallization. Interestingly, we have observed two perfect Arrhenius temperature dependencies with a transition located precisely at the onset of crystallization. From that moment on, the apparent activation energy and, hence, cooperativity remained unaffected by the continuing crystal growth. An explanation of this phenomenon has been offered by a sudden, one-time reorganization of dipole units that sets in probably just before crystallization begins.

During the isothermal crystallization of PDS, a rather asymmetric broadening of the normalized $\alpha$ process has been observed. The value of the parameter $\beta$ in the KWW function remained constant at 0.40 prior to PDS crystallization but systematically decreased as crystallization proceeded, maintaining a relatively good fit through the rest of the data. We have postulated that the main reason for the broadening of the relaxation spectrum during PDS crystallization is the increase of chain confinement of the amorphous phase manifested by the new process located at a lower frequency. Two isosbestic points are found on sides of this new relaxation, suggesting that this process is not independent (the same underlying motions) of the $\alpha$ relaxation but has dipole units affected by different restricted environments. The origin of the new relaxation most likely comes from a highly confined amorphous portion located between crystalline lamellae within the spherulites in the polymer: the intra-spherulitic phase. The other type of amorphous phase fills the interspherulitic space, and its relaxation remains unaffected by the presence of spherulites.

Finally, the changes of the relaxed dielectric permittivity, $\varepsilon'_0$, with crystallization time at a constant frequency were used to determine crystallization kinetics for this polymer. An excellent agreement between the isothermal kinetic data obtained from DRS and DSC methods is observed up to 50 °C. However, at higher temperatures, crystallization rates measured by DRS kinetics were considerably faster. To explore this phenomenon, a comparative analysis with optical measurements was made. It has been suggested that DSC data are inappropriate for describing the overall kinetics at higher crystallization temperatures.

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**REFERENCES AND NOTES**