Phase Transformations in Polyphosphazenes by the Depolarized Light Intensity Method. 1. General Features and Examples

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ABSTRACT: The depolarized light intensity (DLI) technique has been shown to be a very useful method for following birefringent (polarized light intensity) changes in thermotropic polyphosphazenes. Transformation readily occurs upon heating or cooling specimens through the two first-order transitions $T(1)$ and T_m, respectively. At $T(1)$ a 3D birefringent phase passes into a 2D pseudohexagonal phase upon heating; upon cooling the 2D state reverts to a more organized 3D phase of higher anisotropy and crystallinity. This phase is usually 3D orthorhombic and often differs from the initial phase present before it passed through T(1). Upon heating and cooling through T_m, the phase change is thermodynamically reversible but not morphologically so until after the initial fusion. In addition to these nonisothermal heating/cooling experiments, crystallization rates may be measured isothermally at sub $T(1)$ temperatures. Crystallization at sub T_m temperatures from the isotropic state for PBFP occurs too fast sometimes even for measurement by the DLI technique. Heat treatment conditions influence nucleation and crystallization rates.

Introduction

More than 2 decades have elapsed since it was demonstrated that the depolarization light intensity technique (DLI)[26] was suitable as a method for following first-order transitions[1,2] (including kinetics of crystallization[3]) in polymers. Since the 1960s it has been widely used to monitor phase changes, associated with birefringence, for (1) amorphous to crystalline, (2) crystalline to crystalline, and (3) crystalline to amorphous transformations in homopolymers, copolymers, and polymer blends. The technique has been used widely and provides a relatively simple and quick way of comparing polymeric materials from many points of view.[4-8] Measurements have also been made in order to study the influence of nucleants and/or other additives upon transformation rates.[7,8] There has been some theoretical work[9,12] dealing with the technique itself and with the effect of sample thickness in respect of the dimensions of the morphological moieties formed whenever a phase change takes place. Experimentally it has been demonstrated that the intensity of the light transmitted reflects the extent of the phase changes under quiescent conditions, even though there is an inconsistency with theory.[9]

Now, with the growing interest in liquid crystal forming polymers, it is demonstrated in this paper that the DLI procedure again conveniently fulfills a need for following rapid transformations not readily met by most existing techniques, however sophisticated. We have shown here that the DLI equipment (with in situ cooling/heating facilities) coupled with a video camera, VCR and TV assembly, provides a powerful approach for on-line monitoring of morphological transformations occurring in thermotropic polymers. An analysis of the recorded data allows one to determine overall rate constants, mechanisms of nucleation besides spherulitic and other growth rates that happen under widely different circumstances. This modified method is now shown to be very useful especially for the study of the kinetics and morphological changes in polyphosphazenes. In these systems nucleation and growth often proceeds rapidly, being completed sometimes in seconds and therefore lying well outside the capability of most standard techniques that are normally used for following phase changes in birefringent polymers.

A commercially available DLI apparatus,[13] with a gravity drop sample holder, lends itself well for making measurements quickly, using thin polymer films housed between microscope cover glasses. Samples can be moved quickly (in 1 s approximately) from the isothermal heat treatment oven into the stirred isothermal crystallization bath, normally filled with silicone oil and located just below it, where the hot sample adjusts quickly to the isothermal bath temperature. (The Chino controller for this air oven indicated temperatures lower than measured in the sample area and required calibration. Temperature equilibration between the heat treated gravity dropped sample and the silicone oil bath fluid was facilitated by improved stirring so that rapid transformation (~5 s) could be monitored. The manufacturer's design does not permit this fast equilibration.) The programmed thermocontrolling system includes heating and/or cooling capabilities that are well documented in commercial brochures.

The main purpose of this paper is to demonstrate the feasibility and facility with which the DLI technique may be used for investigating complex changes that often occur in polyphosphazenes, for example, undergoing different heat treatments, with special emphasis on the thermotropic state.

Morphological and structural changes in polyphosphazenes have been fairly well documented recently by stepwise heating/cooling experiments.[14,15] On-line X-ray monitoring of phase transformations using SAXS and WAXS modes with the aid of a synchrotron high intensity radiation source have been monitored during ramp heating/cooling as well as isothermally.[16,17] The limitations of the DSC technique, for example, for following rapidly occurring phase changes (particularly those involving short induction times) have been mentioned briefly.[18] Recently, a modified DSC procedure has been developed to obtain rate measurements at relatively short times.[19]

Intensity changes were simultaneously recorded with a versatile millivolt recorder which operated in parallel with the viewing equipment. recorder signal vs temperature/time provided a record of the relative changes in transmitted light intensity and/or birefringence scarring in the polyphosphazene films. Many of these data are presented in later figures in this paper.

Phosphazene films, located between glass cover slips and carefully clamped in the sample holder, were immersed in the silicone oil bath and ramped up and down at a fixed heating/cooling rate by using the Chino temperature programmer in the DLI apparatus.[13] Cooling was provided by circulating water through a coil immersed in the oil bath. Otherwise, rapid isothermal temperature changes

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Table I
Characterization Data for Polyphosphazenes[a]

material	$10^{-6}M_n$	$10^{-6}M_w$	T_m, °C $T(1)$, °C		ΔH, J/G[b]
PBPP	0.16	1.18	138 157[c]		39.4
PB(4F)PP	0.04[1]	0.23	166		46.7
PB(4Cl)PP	0.03	0.14[6]	155		33.4
PBFP	0.18	0.34	78	219	31.3

[a] Previous reports on all of these materials have appeared in the literature. Polymers show good elemental analysis. Thermogravimetric and IR analysis has also been employed in materials characterization. [b] Integrated value, all $T(1)$ peaks if more than one is present. [c] After annealing (second scan).

were induced by dropping the sample in its holder from the heat treatment oven situated above, into the thermostatted silicone oil bath, maintained at the preselected isothermal crystallization temperature. Whenever the sample was transferred from the oven to the bath, a preset video camera and/or millivolt recorder was activated to monitor the morphological changes and transmitted light intensity associated with the birefringence changes in the polyphosphazene film.

Results and Discussion

This aspect of the paper is divided into two main areas, namely, (1) kinetics of isothermal crystallization and (2) DLI intensity–temperature–time transformations, to demonstrate the utility of the technique for investigating polyphosphazenes.

A complete analysis of the data for PBPP in Figure 3 is not presented at this time since the main purpose of this paper is to emphasize the versatility of the DLI technique for studying a wide range of isothermal transformations rates, taking place mainly from the disordered thermotropic (2D) to the 3D chain extended states. The amorphous to 2D change that is anticipated to occur just below T_m is often limited by the stability of the polymer itself and by the silicone fluid stability. (Besides, there are thermal stability problems with some poly(aryloxyphosphazenes) that in the thermal decomposition temperature, T_d, of many of these same polymers lies below the melting temperature, T_m.)

It discolors with time not far above 300 °C. The disordered 2D phase is comprised of highly anisotropic hexagonally arrayed domains of molecular chains staggered and extended to an unknown degree in the thermotropic state. Complete structural details are lacking at this time since well-defined narrow molecular weight fractions of polyphosphazenes are not yet available. Even so, important basic aspects of crystallization in these polymers can be established anyhow, and the feasibility of the DLI technique demonstrated.

(1) Kinetics of Transformations. In principle, the overall transformation rate of the polymer film may be obtained from the measured change in transmitted light intensity, I, versus time, t, in isothermal plots obtained at different crystallization temperatures. The equations relate the untransformed polymer fraction, Θ, as

$$\Theta = (I_t - I_\Theta)/(I - I_\Theta)$$

$$\Theta = \exp(-kt^n) \qquad (1)$$

which depicts the Avrami form of the kinetic expression[3,19,20] that is often used for the rate analysis notwithstanding its limitations.

Additionally, other important parameters such as spherulitic growth rate, G, (where appropriate), the concomitant nucleation rate, $\dot{N}$, and overall transformation rate, k, may be all measured simultaneously with our DLI aparatus and accessories. This interrelatable information may be written simply as

$$\Theta = F(G^3\dot{N}) \qquad (2)$$

as proposed and demonstrated[21] a long time ago, ignoring molecular weight effects on transformation rates.

It is well established that the intensity of polarized transmitted light, I_t, through a relatively thin film of crystalline or crystallizing material is given by the expression

$$I_t = A \sin^2 (\pi t\Delta/\lambda)$$

where Δ is the birefringence, t the sample thickness, and λ the wavelength of light. Under quiescent growth conditions (absence of imposed stresses) the birefringence in a linear function of the optical retardation, R, divided by sample thickness in the limit $0 < \lambda < \pi/4$. There is no large scale order that may cause the dependence of the DLI signal on sample orientation. The area sampled is large enough so that the overall orientation birefringent moieties is random and representative. By analogy then with the Avrami equation then

$$I_t = I_\infty \, [1 - \exp^{(-kt^n)}]$$

where I_∞ is the value of transmitted light intensity at the end of the transformation. In polyphosphazenes that may pass from one birefringent state to another, this equation is still valid,[19] whenever Θ is expressed as eq 1.

The induction time, τ, and half-time, $t_{1/2}$, of any transformation may be obtained directly for the intensity–time plots as illustrated for example in Figures 3–5 elsewhere. These curves clearly highlight the rapid nature of the change that occurs isothermally from the 2D to the 3D state for several aryloxyphosphazenes. After PBPP polymer is heated at 215 °C (5 min) prior to crystallization at selected temperatures (undercoolings) not far below the $T(1)$ transition temperature, a considerable spread in rates is noted. Whenever the heat treatment time is still maintained at 5 min, but the heat treatment temperature is raised from 215 °C to 340 °C, a measurable increase in τ and $t_{1/2}$ occurs, respectively. These changes are indicative of heat treatment effects on nucleation and domain formation and require further study. From other X-ray work[14,15] and the present information, it seems that transformation from the thermotropic (2D) to the 3D state depends primarily upon the temperature and to a lesser degree upon the duration of the heat treatment which the sample experiences between T(1) and T_m. (Of course, considerable care must be exercised to avoid polymer degradation; that is one reason why heat treatment temperatures have been kept below 300 °C.) However the dependence of rate of transformation upon sample treatment conditions in the $T(1)$ to T_m interval means that the polymer history is very important and should be reported always for polyphosphazenes, if not for thermotropic polymers in general. In the thermotropic state between $T(1)$ and T_m the values of τ and $t_{1/2}$ must be related to the ^{31}P and ^{13}C NMR solid-state[21] chemical shifts and relaxation times, under investigation presently. Likewise, DLI rate data have been obtained for PB(4Cl)PP and PB(4F)PP that have higher melting and glass transition temperatures than PBPP (unpublished work). Again, the versatile nature of the DLI measurement is demonstrated for the study of fast as well as slow rates of transformation through monitoring light intensity changes that illustrate ordering and the birefringent state of polyphosphazenes. Besides, it can be used in an affirmative manner to es-

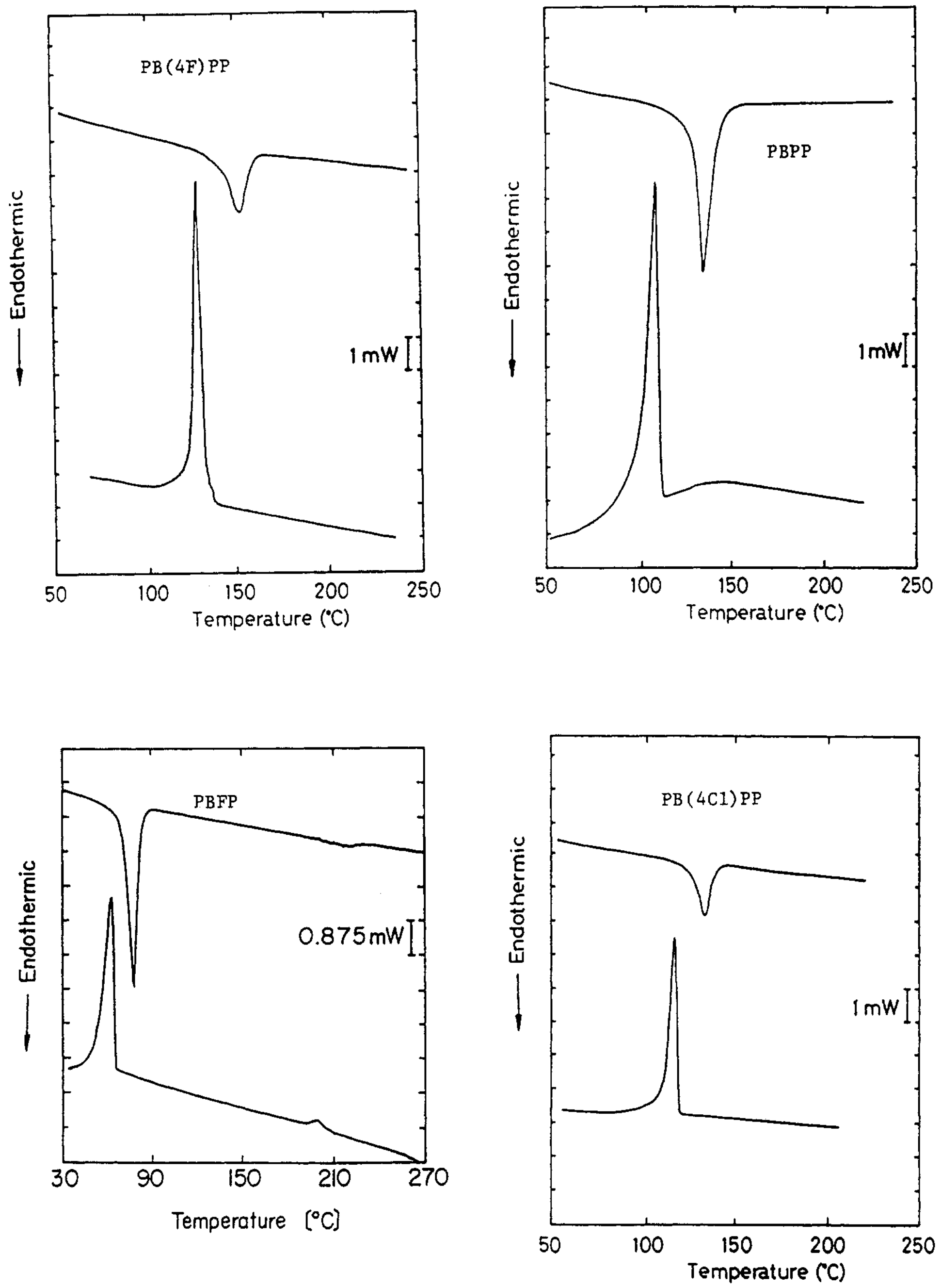


Figure 1. DSC traces for the polyphosphazene samples investigated (programmed heating/cooling rates = 10°/min). For samples (a) PBPP, (b) PB(4F)PP, and (c) PB(4Cl)PP only the thermotropic T(1) transition is shown. For PBFP, $T(1)$ and T_m are recorded.

tablish that the Avrami analysis may be applied the isothermal transformations in Figure 3 in the sub $T(1)$ region in accord with an $n = 2$, i.e. two dimensional phase change (see eq 1 and also ref 19).

The transformation from the 2D to the 3D state involves a considerable change in polymer mobility as witnessed by creep,[22] volume (dilatometry[22]), and ^{31}P NMR measurements.[23] A low birefringent spherulitic phase is also observed to nucleate in the birefringent 2D phase and grow to fill the TV monitor screen, which is a fraction of the area sampled by the polarized light beam passing through the specimen. This type of transformation is apparent in both PBPP and PB(4F)PP. The in situ transformation is illustrated in the micrographs in Figure 6 for PB(4Cl)PP after heat treatment at 215 °C (5 min) followed by crystallization isothermally at 120 °C.

The present DLI–video monitoring assembly has the added advantage that kinetic and accompanying morphological changes can be followed simultaneously during the phase change. In a sense then, the modified DLI provides versatility that is not encountered in most many techniques used at this time.

(2) Intensity–Temperature–Time Curves. For PBFP cast film, the intensity increases at first gradually and then more steeply as $T(1)$ itself is traversed (see Figure 7). Initially, the transformation is broader than that found on the second heating, when it sharpens and moves upward about 10 °C on the temperature scale, in line with trends reported in detailed DSC runs[18] for the same heating rate and temperature range. Similar trends[24] have been reported whenever the birefringence–temperature changes are followed within a given PBFP spherulite by using a hot-stage and Berek compensator. Closely related behavior is found from direct birefringence–temperature for another spherulitic PBFP film comprised of relatively large spherulites (≤200 μm), cast from THF solution. It is important to emphasize that the spherulites retain their original shape and size as the intensity (or Δn) changes so

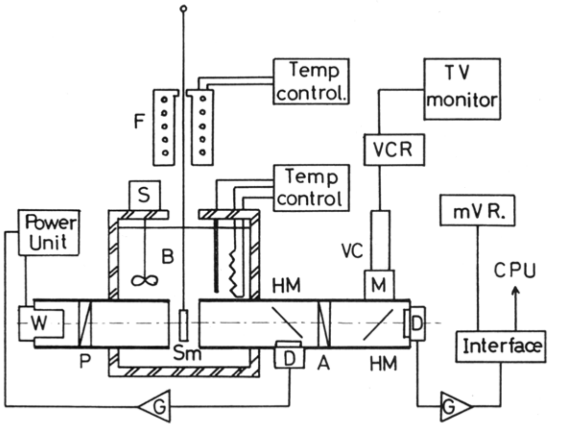


Figure 2. Schematic illustration of commercial DLI apparatus with main components and accessories: F, high-temperature air furnace; S, stirrer; W, tungsten lamp; B, silicon oil bath; Sm, thin polymer sample between microscope cover glasses; D, photosensor; HM, half mirror; M, microscope (X10); VC, video camera; P, polarizer; A, analyzer; G, amplifier.

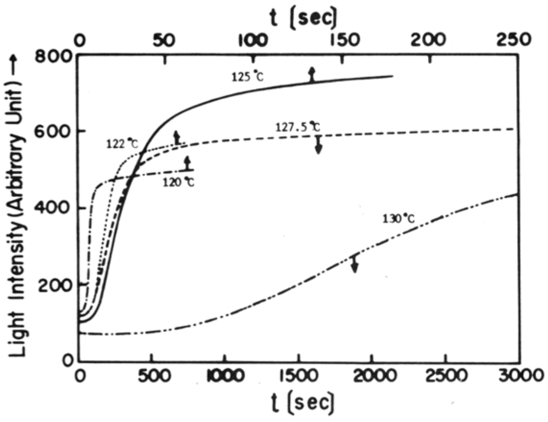


Figure 3. Transmitted light intensity in arbitrary units (between cross polars) vs time (min) for thin PBPP film crystallized isothermally at temperatures indicated below the thermotropic transition following heat treatment at 215 °C (5 min). All curves reach a common asymptotic level of light intensity at the end of the transformation.

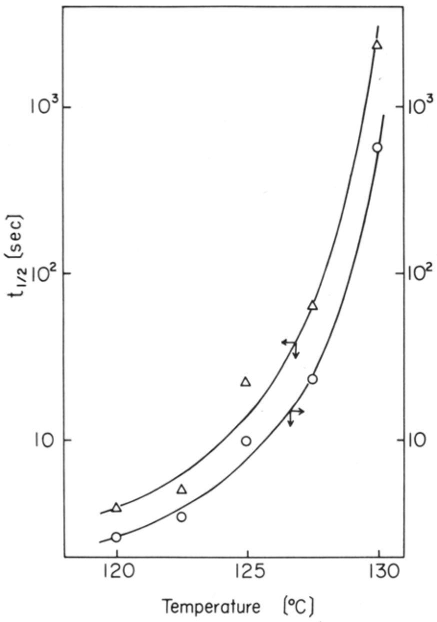


Figure 4. Half-time, $t_{1/2}$ (s) (△), and induction time, τ (s) (○), of isothermal crystallization for PB(4F)PP at several temperatures after heat treatment at 215 °C.

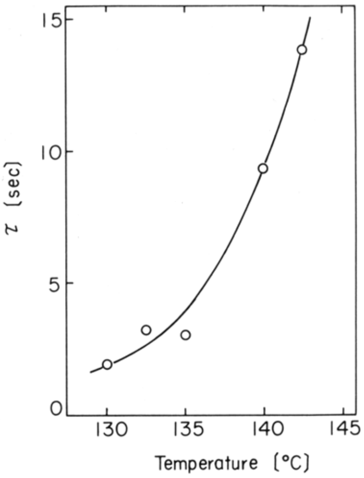
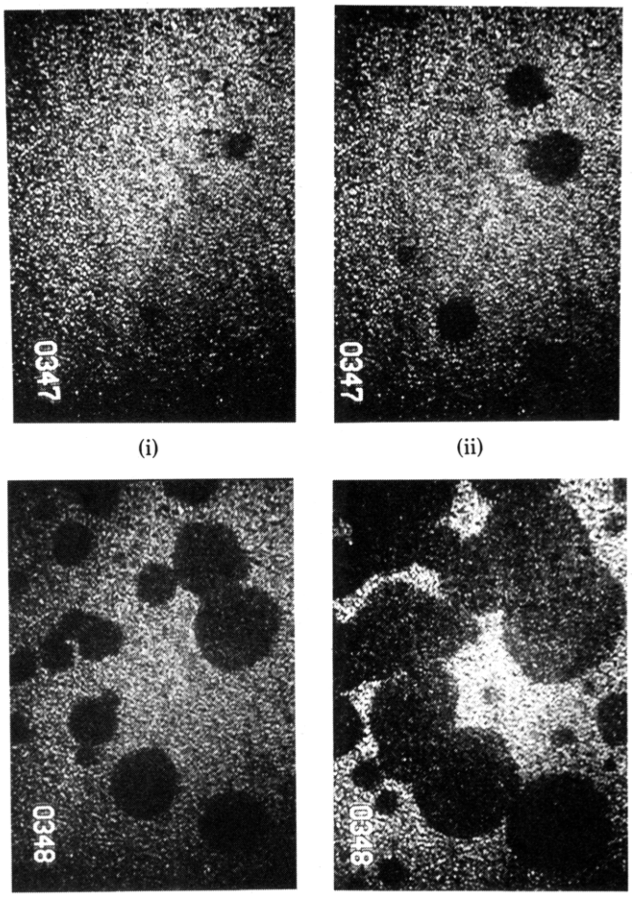


Figure 5. Induction time, τ (s) (○), for PB(4Cl)PP at several temperatures after heat treatment at 215 °C (5 min).



(i) (ii)

(iii) (iv)

Figure 6. Morphological spherulitic transformation (in PB(Cl)PP) occurring isothermally at 120 °C after the sample was heated for 5 min at 215 °C (crossed polars). A sporadic change is apparent starting from time zero to almost the end of the change.

that internal reorganization at the molecular level is responsible, implying that mobility within spherulites presumably obtains from side groups and backbone motions. This is not the case when the sample has been melted ($>T_m$) and a new structure and morphology results. The light intensity–cooling curves (shown in Figure 7) are also in accord with property–temperature trends noted by DSC[18] and Δn measurements,[23] but at variance with published results.[24] For instance, PBFP spherulites grown from solution are negatively birefringent and remain so,

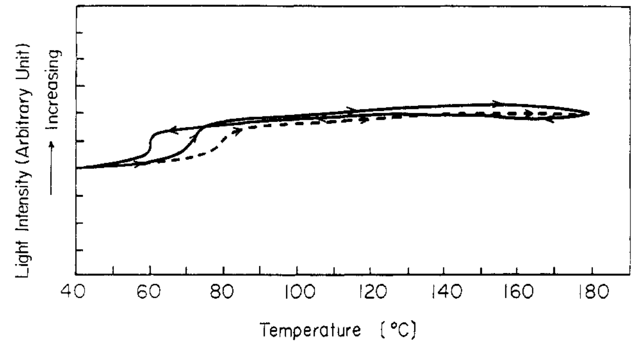


Figure 7. Transmitted light intensity measurements for heating/cooling PBFP film (27 μm thickness). Arrows indicate the heating/cooling directions of change. The second heating is denoted by a dotted line.

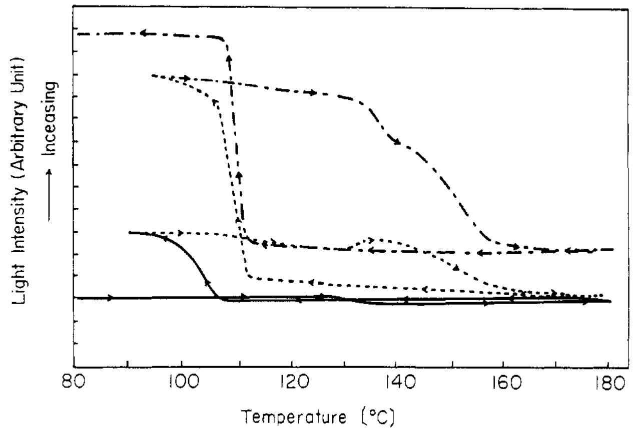


Figure 8. Changes in transmitted light intensity with temperature for PBPP: heated through $T(1)$ (solid line); second heating/cooling (dotted lined); third heating cooling (dotted–dashed line) (film thickness 80 μm approximately).

below the melting point of the material. Unlike the halogenated aryloxyphosphazenes examined here, the polarizability of the chain backbone, not the side groups, dominates the anisotropy of the sample during heating and cooling through $T(1)$ as seen in Figure 7.

A THF solution-cast film of PBPP, comprised only of microspherulites, when heated at about 6.5°/min from 50 °C to 80 °C shows a small increase in intensity about 130–135 °C, which is close to the $T(1)$ region of PBPP. On cooling the sample from 180 °C the transmitted light intensity remains almost constant until 105 °C is reached. At this temperature a substantial decrease in intensity occurs (see Figure 8) over a 10-deg interval. Spherulites (ca. 10–20 μm in diameter) nucleate rapidly throughout the sample (over this range), and there is a corresponding monotonic increase in intensity which reaches a minimum level about 130 °C and then peaks at 136 °C before undergoing a gradual drop followed by a levelling off again as 180 °C is approached. Subsequent cooling depicts a constant but gradual rise in intensity as it increases very rapidly from 110 °C approximately, levelling off just below 100 °C. When the temperature is raised once more, the intensity was found to decrease slowly, showing a relatively sharp fall (at 134–138 °C) followed by a second and more extensive drop, before levelling asymptotically as 180 °C is again approached. There is a small shift in intensity compaed to the starting level. Subsequent cooling indicates a rapid rise in intensity around 113 °C, reaching a maximum value about 5° lower and thereafter remaining almost constant until 180 °C. These trends in intensity parallel closely the behavior monitored by other techniques such as DSC and Δn used for the characterization of PBPP polyphosphazene. There is a progressive increase in the location of the onset temperature for the 2D to 3D transition. There is a progressive increase in intensity as this $T(1)$ region as traversed. This is to be associated with enhanced anisotropy and ordering of the molecular chains into the 3D orthorhombic form, from the 2D pseudohexagonal phase.

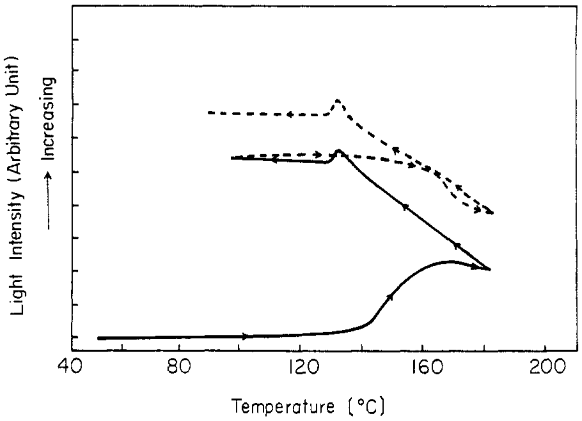


Figure 9. Transmitted light intensity vs temperature for PB(4F)PP film for first heating/cooling (solid line) and second heating/cooling (dotted lined) through the $T(1)$ transition.

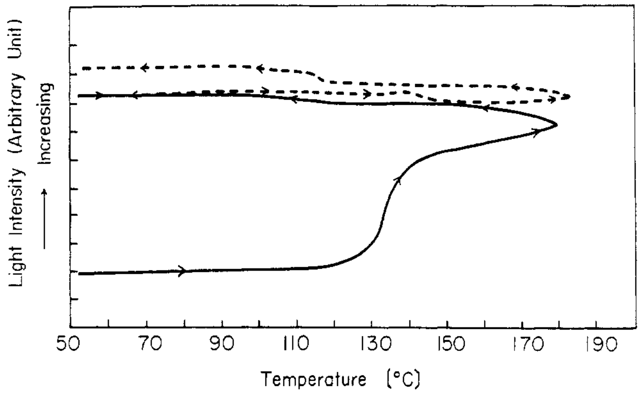


Figure 10. Transmitted light intensity vs temperature for PB(4Cl)PP film (thickness 80 μm) exhibiting transitional behavior through $T(1)$; solid line first heating/cooling. Second heating/cooling is less pronounced through $T(1)$.

In the case of PB(4F)PP the transmitted light intensity through an 83-μm film (see Figure 9) increases significantly around 140 °C, peaking about 165 °C (i.e. as the $T(1)$ region is traversed). After a short holding period at 180 °C the first cooling shows a substantial but gradual rise of intensity, commensurate with a change in birefringence, passing through a maximum at about 134 °C where a spherulitic texture develops and can be followed on the TV monitor. During subsequent reheating of this sample the transmitted light intensity remains invariant until 160 °C approximately where it decreases abruptly before 180 °C is reached. This change in intensity corresponds to a decrease in birefringence for the transformational change from the 3D to the 2D state as the $T(1)$ region is traversed. Further cooling leads once again to the intensity peaking again in the vicinity of 134 °C where spherulitic nucleation and growth occurs as the sample again passes into the 3D state. Growth and nucleation rates have been recorded but are not completely understood nor analyzed here, since the primary purpose of this paper is to illustrate the overall utility of the DLI technique for the investigation of thermotropic polymers.

In Figure 10, changes in depolarized light intensity upon heating a PB(4Cl)PP finely textured thin film are illustrated. Clearly a large increase in intensity occurs on the first heating as the $T(1)$ transition is tranversed, but there is no change in spherulitic texture (only enhanced brightness occurs). On cooling down the sample from 180 °C to 50 °C, a weak transition is just perceptible about 120 °C, but during the second heating the light intensity decreases noticeably about 140 °C. Upon cooling from 180 °C approximately a slight increase in intensity occurs. After the sample was cooled again, a noticeable transition occurs about 114 °C with a concomitant rise in intensity to a level that remains essentially constant back to 50 °C. The transitional behavior depicted in this figure is consistent with enhanced molecular chains ordering that the finely textured occurs upon cycling the PB(4Cl)PP material through $T(1)$ starting with solution cast material which was of relatively low birefringence. The molecular subtleties of these transition under heating/cooling can only be settled by using other complementary techniques like ^{31}P and ^{13}C solid-state NMR under identical heat treatment conditions.

Conclusion

This preliminary work using thermotropic polyphosphazenes has illustrated the validity of the modified DLI technique for studying (1) kinetics of phase transformation and (2) morphology–temperature–time changes encountered in relatively thin films of solution cast polymers. The technique seems to be suitable for following both fast and slow transformation rates and appears to be a valuable procedure that merits detailed investigations.

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(26) Note that the temperature scale on all the DLI heating/cooling curves presented is not equally divided everywhere because of the nonlinear heating rates that lie in the range 5–10 °/min.

Notes

Synthesis and Electrochemical Characterization of Siloxane Polymers Containing Hydroquinone and 1,4-Naphthohydroquinone

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Introduction

Recent work in our laboratory has demonstrated the utility of several siloxane-based redox polymers in mediating electron transfer between an oxidoreductase enzyme and a conventional electrode surface.[1] The unique flexibility of the polysiloxane backbone allows a sufficiently close contact to occur between the redox couples of the polymeric system and the enzyme's redox centers so that efficient charge transfer can be achieved. For example, siloxane polymers containing ferrocene or 1,1′-dimethylferrocene[2] have been shown to facilitate electron transfer from reduced glucose oxidase to an electrode.[1] These redox polymers provide an important advantage in the design of enzyme-based sensors: because the redox species are covalently bound to the polymer backbone, they are not free to diffuse away from the electrode surface into the bulk solution. Thus, unlike systems based on freely diffusing electron-transfer mediators, such as ferrocene and its derivatives[3-5] or tetracyanoquinodimethane (TCNQ),[6-10] sensors incorporating these polymeric redox systems may be of potential clinical value in implantable measuring devices. With this in mind, we have extended our studies of siloxane-based redox polymers to include systems that contain quinone moieties as the electroactive species. Quinones have previously been employed as freely diffusing electron-transfer mediators in enzyme-based bioanalytical sensors.[11-15] In this paper, we describe the synthesis and electrochemical characterization of siloxane polymers that contain hydroquinone and 1,4-naphthohydroquinone and discuss the potential use of these materials in sensor applications.

Experimental Section

A. Polymer Synthesis. The synthetic route for the siloxane polymer containing hydroquinone is described in Scheme I. The