

UV-induced changes to the structure of polycarbonate

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Experiments reveal that acetone absorption induces crystallinity in polycarbonate and that the irradiated samples exhibit enhanced solvent crystallization.

Many polymers exhibit structural changes when they are exposed to UV radiation. Such changes include minute alterations in the packing of polymer molecules, which in turn leads to drastic changes in the strength, color, and resistance to solvents. In this way, some of the changes can limit the service life of objects that are exposed to UV light during their daily use. Radiation-induced photodegradation of polymers has thus been studied extensively for several decades, for example, to reliably predict the mechanisms of degradation and to quantify the effect of radiation intensity on degradation products.^{1,2}

As part of this body of research, many groups have previously characterized the absorption of solvents in polymers. From this work, it has been shown that absorption rates are controlled by temperature, solvent strength, and the thermal treatment of the polymer matrices. Indeed, absorption rates may be controlled by the concentration of the solvent molecules through the polymer matrix. This is known as ‘Case I’ transport, and is characterized by the diffusion coefficient (D). In some instances, the motion of polymer molecules can also influence the sorption rates. This so-called Case II transport is characterized by the velocity (v) of the molecules.³ Another ‘anomalous’ transport type—encountered when solvent mobility and polymer motion rates are comparable—has also been proposed.⁴ A model was developed to determine v and D in this case,⁵ and we later refined this model for use in a finite medium during the entire sorption process (Harmon’s model).⁶ In later work, it was also determined that during anomalous absorption of solvents (i.e., methanol, acetone, and carbon tetrachloride) in polycarbonate (PC), the microstructure of the PC changes from the amorphous state to the crystalline state.⁷ Furthermore, the mechanism of acetone transport in gamma-irradiated PC has been observed as different at low and high temperatures,⁸ yet the reason for this shift in behavior has previously been unclear.

In this work,⁹ we were therefore prompted to investigate the transport of acetone in UV-irradiated PC. This study is part of our ongoing interest in the characterization of radiation effects on polymer matrices,

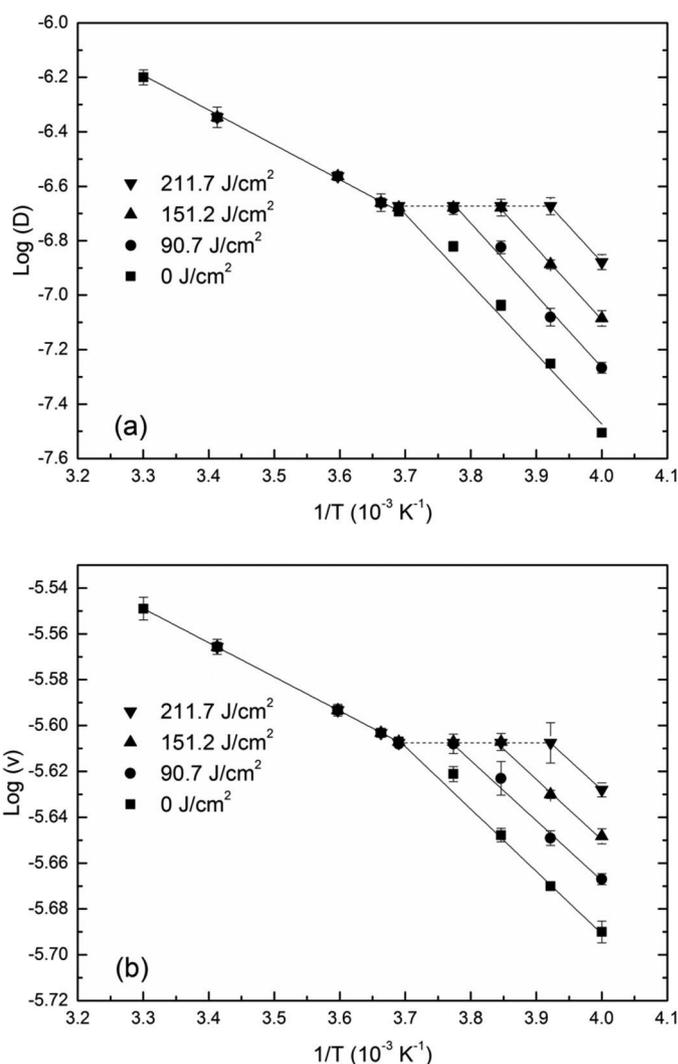


Figure 1. Arrhenius plots for the calculated (a) diffusion coefficient (D) and (b) molecule velocity (v), as a function of temperature (T), for the differently irradiated polycarbonate (PC) samples.

in probing events that induce volume changes in polymer changes, and in developing methods to detect these changes. Specifically, we

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measured acetone absorption in UV-irradiated PC (subjected to UV doses of 0, 90.7, 151.2, and 211.7J/cm²) at temperatures between -23 and 25°C.

To analyze the anomalous transport data we obtained from our measurements, we used the Harmon model (i.e., that includes contributions from Case I and Case II transport).⁶ We were thus able to determine *D* and *v* by mass uptake. We also monitored the glass transition temperature and molecular weight of the PC samples before and after sorption. In addition, we used x-ray diffraction (XRD) measurements to assess the crystallinity of the PC samples.

Our results indicate that the glass transition temperatures and molecular weight of the PC samples decreased with increased radiation dose. We also find that the percentage crystallinity of the sample, prior to solvent sorption, increased from 0 (in the control, i.e., non-irradiated, sample) to 7.6% for the sample irradiated with the highest dose. We believe that these results make logical sense, i.e., the reduced molecular weights gave rise to increased mobility and thus facilitated crystallization.

We also see similar trends in the results we determined for both *D* and *v*, as a function of temperature (see Figure 1). In general, we find that *D* and *v* increase with increasing UV dose. Furthermore, we clearly observe linear and superimposable doses at higher temperatures, a transition temperature, and another linear region that varies with dose. The results indicate, however, that the direction of Case II transport was opposite to that of Case I diffusion. This is because the solvent

was expelled from the samples upon solvent-induced additional crystallization.

From our XRD results (see Figure 2) we observe two peaks from the PC at 30°C, at 2θ (measured diffraction) angles of 17.3 and 25.7° (corresponding to the orthorhombic structure). In contrast, the -10°C spectrum exhibits peaks at 2θ angles of 17.0, 25.5, and 33.6° (corresponding to the orthorhombic structure), as well as at 8.4, 29.8, and 32.2° (arising from a monoclinic structure). The transition temperatures we observe (see Figure 1) are therefore likely caused by a phase change in the PC, i.e., crystallization changing from purely rhombohedral to rhombohedral and partial monoclinic lattices (polymorphism).

In summary, we have conducted experiments to investigate the absorption of acetone within UV-irradiated polycarbonate (at temperatures between -23 and 25°C). We used Harmon's model to analyze the anomalous transport data, and thus obtained diffusion coefficient and velocity measurements. From our results, we find that the PC samples exhibit a transition temperature, i.e., the diffusion and velocity characteristics are different at high and low temperatures. Moreover, from our analysis of the PC crystalline forms, we observe that only orthorhombic crystals occur above this critical temperature, whereas the crystals that form below this temperature are polymorphic (a mixture of orthorhombic and monoclinic phases). The XRD results are therefore key to understanding the shift in PC sorption behavior at different temperatures. Overall, this work broadens our knowledge of the effects of radiation on PC, but it also paves the way for future experiments to elucidate the effects of solvents and swelling stresses on polymer morphology. We are now planning to study the crystallinity of fibers that are spun from solution, and to thus design materials with controlled polymorphs.

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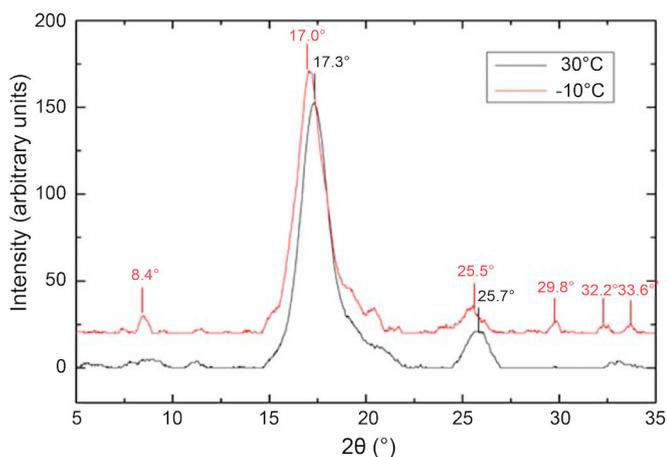


Figure 2. X-ray diffraction patterns for PC immersed in acetone at a temperature of -10°C (red) and 30°C (black). The spectrum obtained at the hotter temperature exhibits two peaks (17.3 and 25.7°) that arise from the sample's orthorhombic structure. In contrast, the -10°C spectrum exhibits peaks from both its orthorhombic (at 17.0, 25.5, and 33.6°) and monoclinic (at 8.4, 29.8, and 32.2°) phases. 2θ : Measured angle of diffraction.



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