

The Effect of Orientation on the Morphology and Kinetics of Solvent Crazeing in Polystyrene

C. H. M. JACQUES, H. B. HOPFENBERG, and V. STANNETT,
*Department of Chemical Engineering, North Carolina State University,
Raleigh, North Carolina 27607*

Synopsis

Unoriented, uniaxially oriented, and biaxially oriented polystyrene films were crazed by immersing samples in liquid *n*-hexane at 45°C. The craze morphology and crazing kinetics were studied as a function of the preorientation and thermal histories of the polymer films. The shape of the micropores was related to the degree of orientation of the film. Ellipsoidal microvoids were formed on the surfaces of uniaxially oriented films containing a residual glassy core. Unoriented samples displayed spherical microvoids 0.1 to 3 μ in diameter. The major-to-minor axis ratio of the micropores increased monotonically from 1/1 to 10/1 as the sample orientation was increased from 0% to 200%. The kinetics of the crazing process similarly increased with uniaxial orientation. Surfaces of unannealed films which crazed mainly during the sorption of liquid *n*-hexane displayed numerous micropores when examined by the SEM. Conversely, films which were extensively annealed crazed mainly during desorption regardless of subsequent orientation. These extensively annealed films exhibited surfaces with many fine cracks and few, if any, micropores.

INTRODUCTION

The sorption of normal hydrocarbon liquids in glassy biaxially oriented and cast-annealed polystyrene often causes crazing of the film.¹⁻⁴ In the absence of an externally applied stress, this solvent-initiated crazing is conveniently viewed as an extreme example of case II transport. Case II transport occurs when the sorption is entirely controlled by a stress-induced relaxation process occurring at the boundary between the outer swollen gel and the unpenetrated glassy core of the polymer. Ideally, during an unsteady-state sorption experiment, this boundary moves at a constant velocity toward the film midplane.⁵ Crazing will occur at this boundary when the combined orientation and swelling stresses are sufficiently large to cause localized fracture of the polymer.

Michaels, Bixler, and Hopfenberg¹ described the appearance of *n*-heptane-crazed biaxially oriented and cast-annealed polystyrene films as white, opaque membranes. Examination of the membrane cross sections with a light microscope revealed that the crazed regions of treated, biaxially oriented films were morphologically quite different from the crazed regions of treated, cast-annealed films. The light microscopy data of Michaels

et al.¹ were supplemented by gas permeability data which suggest that the crazed regions in the biaxially oriented material consisted of a network of interconnected channels, while the crazed portions of the cast-annealed polystyrene were composed of nonintercommunicating spherical microvoids (ca. $3\ \mu$ in diameter) dispersed in a continuous polymer matrix.

Crazing kinetics, as well as craze morphology, are affected by changes in polymer orientation. Hopfenberg, Holley, and Stannett^{2,3} have found that the rate of *n*-pentane crazing is three to four times greater for biaxially oriented polystyrene films than for cast-annealed films of the same material. Bray et al.⁶ and Baird et al.⁴ have shown that subtle differences in polymer orientation can result in significant changes in the rate of solvent crazing. The effect of orientation on the craze morphology *per se* as well as the concomitant crazing kinetics have not, however, been studied systematically.

The purpose of the present investigation, therefore, was to study in more detail specific changes in the morphology of individual surface crazes and crazing rates as a function of film orientation. Scanning electron microscopy has been used to observe *n*-hexane-induced surface crazes in a series of uniaxially oriented polystyrene films. The nature of those crazes which appear during penetrant sorption are compared and contrasted with crazes which appear during desorption.

EXPERIMENTAL

Sample Preparation

Polystyrene films with a weight-average molecular weight of 1,880,000 were prepared according to the procedure of Baird⁴ by casting a dilute solution of polystyrene in benzene onto a mercury surface and allowing the benzene to evaporate slowly at room temperature. The films were air dried for at least three days and subsequently placed in frames and annealed at 115°C for 24 hr. Uniaxially oriented samples were obtained by controllably stretching 2×5 -cm strips of previously annealed film in an Instron tensile tester at 110–120°C. After given elongations of 50%, 100%, and 200% had been obtained, the samples were rapidly cooled to freeze the orientation.

Polystyrene films with a weight-average molecular weight of 250,000 were prepared by casting a dilute solution of polystyrene in trichloroethylene onto a glass plate. The films were vacuum dried at 55°C for three days, but not annealed above the T_g . A commercial biaxially oriented polystyrene film (Trycite 1000) was used as received.

Birefringence Measurements

The optical birefringence of uniaxially oriented films was measured using a Leitz polarizing microscope and a Berek Compensator with a monochromatic light source. The greatest errors in the birefringence determination are in the film thickness measurements. Film thicknesses were measured

with an Ames No. 25M film micrometer and were reproducible to within $\pm 5\%$.

Solvent Crazing

Samples approximately 2 cm² were cut from the centers of each of the polystyrene films. From each of these samples, 2 mm² were used in the birefringence measurements. One half of the remaining portion was immersed in liquid *n*-hexane at 45°C \pm 1°C until the film was observed to suddenly shrink in the direction of the previously applied stretch. This time was recorded to within 10% of the total immersion time. The remaining sample was subsequently immersed in liquid *n*-hexane at 45° \pm 0.1°C for 50% of the time it took the first sample to shrink. After immersion for these specified times, the sample was quickly removed from the *n*-hexane and quenched in iso-octane at 0°C for 15 min to extract the *n*-hexane. The samples were allowed to dry at room temperature for 24 hr and were subsequently examined by scanning electron microscopy (SEM).

Scanning Electron Microscopy

Preparation for SEM involved mounting squares of previously crazed film approximately 4 mm in length on a brass specimen mount. Silver paint was brushed around the edge of the film, and the entire surface was metallized with a 250-Å vapor deposit of aluminum in a Denton vacuum evaporator at 10⁻⁶ torr. An accelerating voltage of 10 kilovolts was used in the SEM. Preliminary micrographs were obtained at 630-diameter enlargements, and subsequent observation of individual crazes was made at an enlargement of 6300 diameters.

RESULTS AND DISCUSSION

Craze Morphology

Scanning electron micrographs of individual micropores found on the surfaces of dried polystyrene films previously crazed by *n*-hexane are presented in Figures 1 and 2. Figure 1 shows micropores in polystyrene films with a molecular weight of 1,880,000 which were cast from benzene solutions, annealed 15°C above T_g for 24 hr, uniaxially elongated, and then rapidly quenched to freeze the orientation. One of the films in Figure 2 is a polystyrene film with a molecular weight of 250,000 which was cast from a trichloroethylene solution and then vacuum dried, but not annealed above T_g . The other film is a commercially available biaxially oriented polystyrene film. All of the samples were subjected to the same conditions to induce solvent crazing.

The differences in the sizes and shapes of the micropores shown in Figures 1 and 2 are striking. The average micropore length for the uniaxially oriented samples changes from ca. 1 μ to 21 μ as the sample elongation increases from 50% to 200%. The unoriented trichloroethylene-cast sample displays spherical microvoids with diameters ranging from less than 0.1 μ

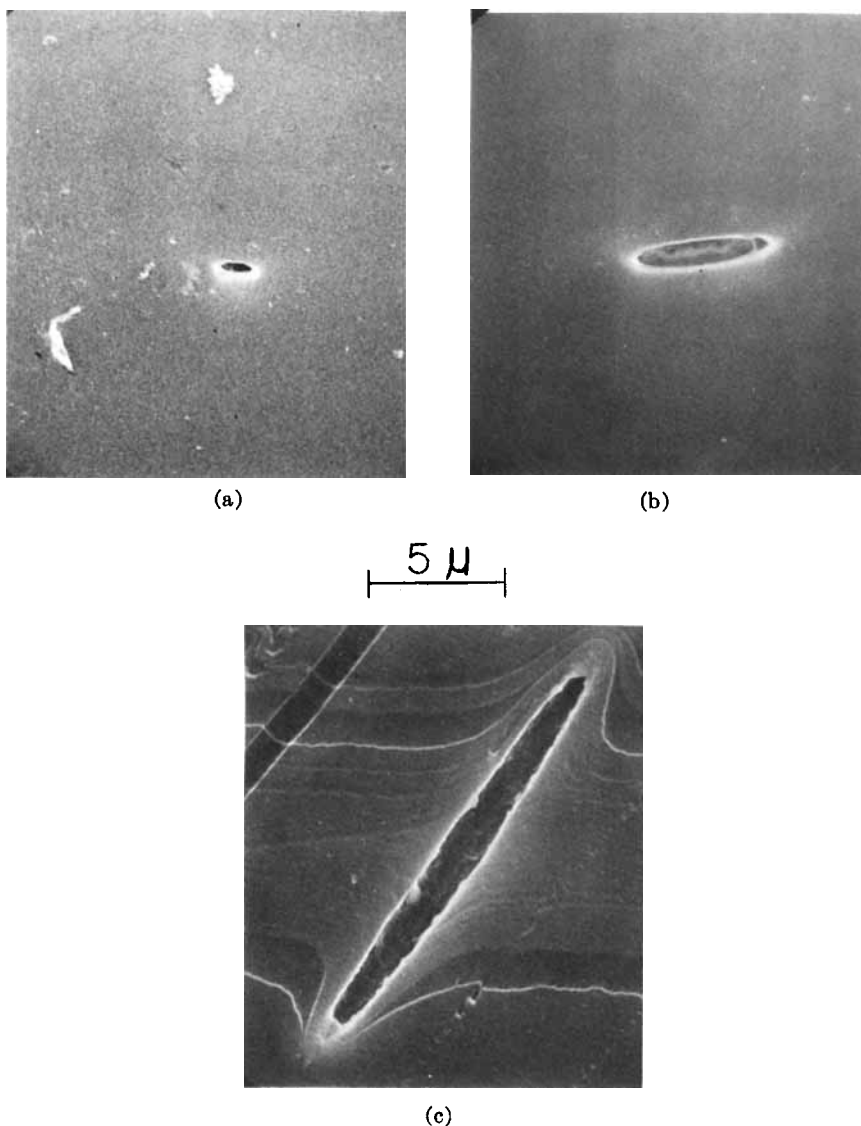


Fig. 1. Scanning electron Photomicrographs on surface micropores on uniaxially oriented polystyrene films previously immersed in liquid *n*-hexane at 45°C (mag. 6300×): (a) 50% uniaxial elongation; (b) 100% uniaxial elongation; (c) 200% uniaxial elongation.

to 3 μ . No surface micropores were observed in the benzene-cast, annealed sample with 0% elongation. Although the size of any particular micropore varied by as much as a factor of 2 for the uniaxially oriented samples and by a factor of 30 for the unoriented trichloroethylene-cast samples, the ratio of the major to minor axis of the ellipsoidal micropores in a given sample remained relatively constant. The axial ratio of the micropore dimensions is plotted as a function of uniaxial elongation in

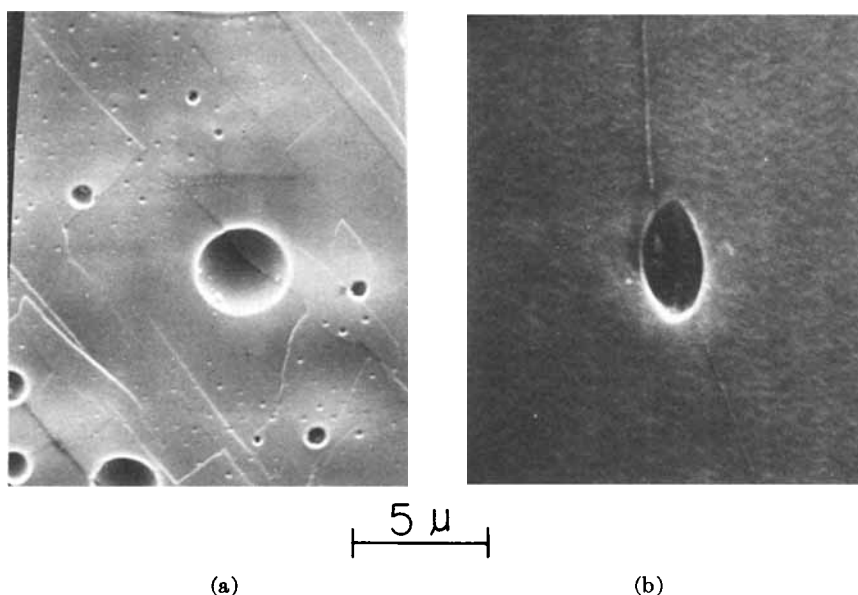


Fig. 2. Scanning electron photomicrographs of surface micropores on polystyrene films previously immersed in liquid *n*-hexane at 45°C: (a) unoriented, unannealed sample (mag. 6300 \times); (b) biaxially oriented sample (mag. 6300 \times).

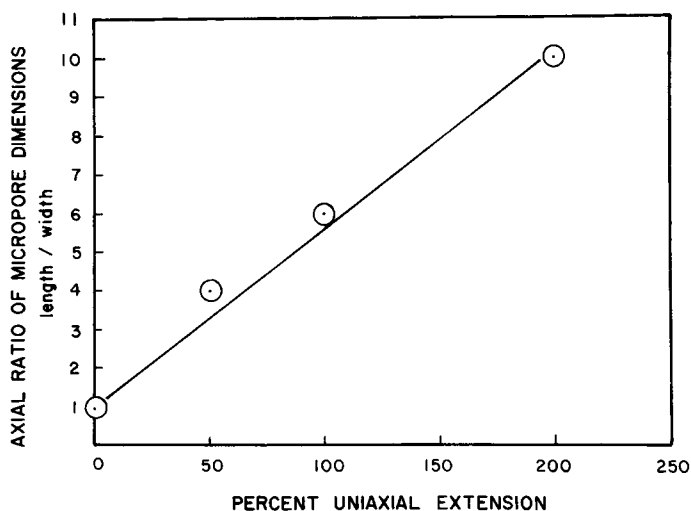


Fig. 3. Axial ratio of micropore dimensions as a function of film elongation for micropores formed on polystyrene films previously immersed in liquid *n*-hexane at 45°C.

Figure 3. A monotonic relationship appears to exist between polymer orientation and the major axis-minor axis ratio of the ellipsoid. Micropores in the unoriented polystyrene film are spherical in shape, i.e., the axial ratio is unity. The axial ratio of the ellipsoidal micropores in the uniaxially oriented samples vary from 4/1 to 10/1 as the film elongation is increased from 50% to 200%.

During a sorption experiment, the outer swollen gel, though plasticized, is still constrained by the inner glassy core. The shape of any microvoids formed in the gel will therefore reflect the degree of orientation in the glassy core. The absence of uniaxial orientation in the trichloroethylene-cast sample allows the micropores formed in the gel to assume a stable spherical shape. Micropores formed in the gel of the uniaxially oriented samples exhibit an elongated shape, with the longer dimension of the micropore corresponding to the direction of elongation frozen in the glassy core. The 2/1 length-to-width ratio of the micropores formed in the biaxially oriented films presumably reflects the draw ratio used in the processing of the film.

Crazing Rates

Previous investigators have shown that the rate of crazing in annealed and oriented polystyrene films is independent of time as a result of a discontinuous swelling boundary moving through the films at a constant velocity.¹⁻⁵ At some time after immersion in liquid *n*-hexane, the uniaxially oriented samples used in this study suddenly shrank along the axis of orientation. Shrinkage of the film is a manifestation of the relaxation of the strains frozen into the films by orientation and corresponds to the advance of penetrant fronts from each face of the film to the film midplane. Since the velocity of the swelling boundary moving through the film is constant, the craze front velocity can be measured by dividing the film half-thickness by the time observed for shrinkage to occur.

Craze front velocities for a series of uniaxially oriented polystyrene films are presented as a function of optical birefringence in Figure 4. The orientation of a polystyrene film is directly related to the optical birefringence of the film.¹¹ It can be seen that a monotonic relationship exists between craze front velocity and the uniaxial orientation of the film. The velocity of the craze front moving through the sample which was elongated

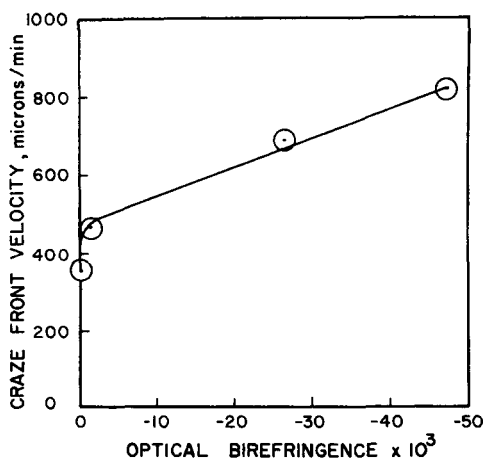


Fig. 4. Craze front velocity as a function of optical birefringence for a series of uniaxially oriented polystyrene films crazed by liquid *n*-hexane at 45°C.

to 200% is more than twice that of the unoriented sample. This confirms the observations of Hopfenberg, Holley, and Stannett^{2,3} and Baird et al.⁴ that an increase in film orientation leads to an increased rate of sorption and solvent crazing.

The higher crazing rates exhibited by the oriented films is evidently due to the coupling of orientation stresses frozen into the glassy film and swelling stresses which are produced at the boundary between the swollen, crazed, outer regions of the film and the residual glassy core. The superposition of these stresses promotes a more rapid relaxation at this boundary. Thus, the relaxation controlled case II sorption and concurrent crazing rates are increased with an increase in polymer orientation.

Craze Formation

Crazing may occur upon either sorption or desorption of a crazing agent from a glassy polystyrene film depending upon subtle variations in the preparation and the thermal/mechanical history of the film. Only extensively annealed (24 hr at 115°C) polystyrene films cast from benzene appear to craze during desorption of *n*-hexane from the partially swollen films. Unannealed films cast from trichloroethylene and commercial biaxially oriented polystyrene films craze during the sorption of liquid *n*-hexane at 45°C.

Many large cracks but relatively few micropores exist on the surface of dried samples of well annealed films which appeared to craze upon de-

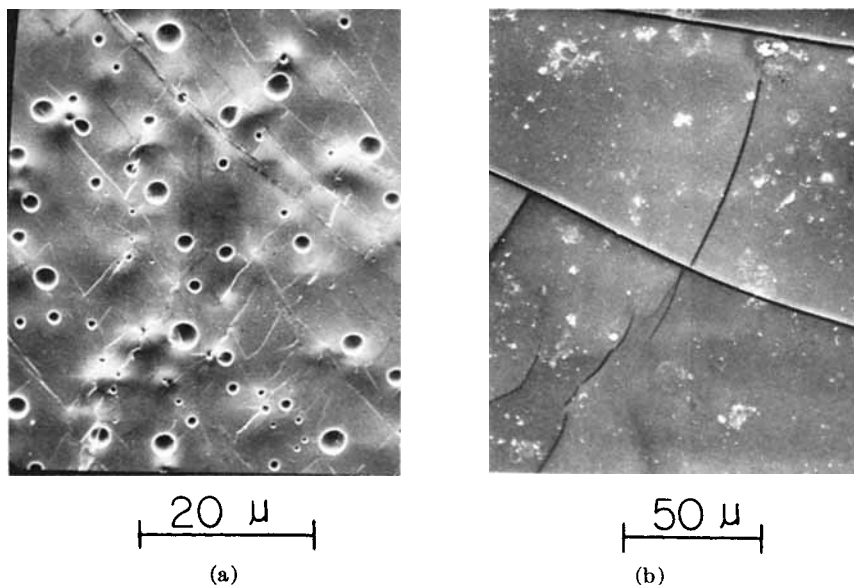
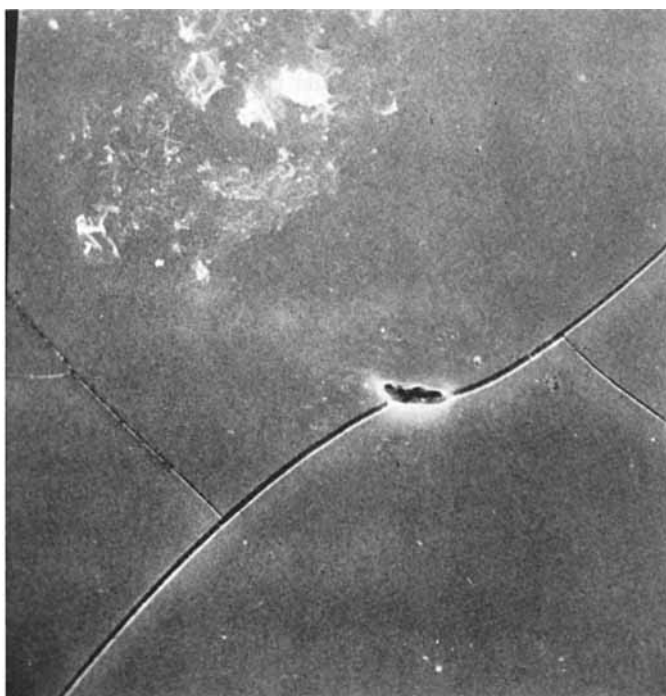


Fig. 5. Scanning electron photomicrographs of polystyrene films previously immersed in liquid *n*-hexane at 45°C: (a) unannealed film which appeared to craze during sorption (mag. 1890×); (b) well-annealed film which appeared to craze upon desorption (mag. 630×).



20 μ

Fig. 6. Scanning electron photomicrograph of a crack initiated by a micropore in well-annealed polystyrene film.

sorption. Conversely, films which appear to craze during sorption display surfaces with many microvoids and few, if any, large cracks. Surface characteristics describing these various crazing patterns are shown in the scanning electron photomicrographs of Figure 5.

It is tempting to speculate that individual spherical micropores form at the boundary between the swollen gel and glassy core during the sorption of liquid *n*-hexane by polystyrene films. As the film absorbs *n*-hexane, the volume expansion necessary to accommodate the swelling agent creates tensions on the residual glassy core. At the partially plasticized boundary, these tensile stresses are large enough to overcome the local strength of the polymer and cause micropore formation. These micropores are probably nucleated by inhomogeneities present in the polymer matrix which act as stress concentrators. Murray and Hull⁷ have observed similar voids, nucleated by impurities, preceding fracture in polystyrene bars.

Relatively few micropores are formed in the well-annealed samples even if the annealing is followed by uniaxial orientation. Extensive annealing of these films above T_g reduces anisotropic molecular orientation and may

drive off volatile impurities which would act as nuclei for micropore formation. Maxwell and Rahm⁸ reported that residual strain and impurities including excess monomer, solvents, oxygen, catalysts, or inhibitors increased crazing. The high molecular weight (1,880,000) of the well-annealed samples may also retard formation of large microvoids. Nielsen⁹ has suggested that the ease and intensity of crazing is increased by decreasing the molecular weight of polystyrene. Rudd¹⁰ has demonstrated that higher molecular weight polystyrenes have a more gradual stress relaxation than lower molecular weight samples and suggested that actual bond breakage may be necessary for failure to occur in very high molecular weight films.

Partially swollen, well-annealed films are, however, susceptible to cracks formed during the desorption process. The abrupt removal of *n*-hexane from the polymer film creates severe tension at the film surface. The weak, plasticized regions of the film, constrained between the residual glassy core of the partially swollen film and the contracting surface of the film, develop a network of fine cracks extending from the film surface to the point of maximum penetrant advance upon quenching, leaching, and drying. Films which are immersed sufficiently long so that no residual dry core exists do not develop cracks upon desorption of the crazing agent.

The low concentration of micropores formed during sorption in the well-annealed samples may even act as crack initiators for the large cracks which appear during desorption, as Figure 6 suggests. Unannealed samples in which many micropores are formed during sorption of the crazing agent are less susceptible to large scale cracking during desorption, since the numerous micropores present can terminate as well as initiate crack propagation (see Fig. 5.)

SUMMARY AND CONCLUSIONS

The results of this investigation are summarized in Table I. In more detail, these may be described as follows:

1. *Sorption and concurrent crazing rates* are directly proportional to the uniaxial orientation frozen into the polystyrene films. Residual orientation stresses couple with swelling stresses to increase the observed rate of relaxation-controlled sorption and crazing.

2. The *sizes and shapes* of micropores formed on the surfaces of partially crazed polystyrene films are dependent upon the orientation remaining in the residual glassy core. A constant length-to-width ratio exists for micropores in a sample with a given orientation history even though the gross dimensions of individual micropores may vary by more than a factor of 30. The ratio of micropore dimensions changes from 1/1 (spherical) for an unoriented film to 10/1 (ellipsoidal) for a film with a 200% uniaxial elongation. The asymmetric micropores are a consequence of restraint of the craze-containing rubbery shell by the still rigid and oriented central core.

TABLE I
Summary of Results

Sample	Optical birefringence	Craze front velocity, microns/min	Ratio of micropore dimensions, length/width	Average micropore length, microns	Crazing occurred during	Type of crazing
Annealed 0% Extension $M_w = 1,880,000$ Film thickness = 0.10 mm	0.0	360	none seen on sample		desorption	cracks
Annealed 50% Extension $M_w = 1,880,000$ Film thickness = 0.075 mm	-1.8×10^{-3}	470	4/1	1.3	desorption	many cracks, few micropores
Annealed 100% Extension $M_w = 1,880,000$ Film thickness = 0.060 mm	-26.6×10^{-3}	690	6/1	5	desorption	many cracks, few micropores
Annealed 200% Extension $M_w = 1,880,000$ Film thickness = 0.045 mm	-47.0×10^{-3}	820	10/1	21	desorption	many cracks few micropores
Unannealed Unoriented $M_w = 250,000$ Film thickness = 0.040 mm	Not Measured	440 ^a	1/1	0.1 to 3	sorption	few cracks, many micropores
Biaxially oriented (Trycite 1000) Film thickness = 0.133 mm	Not Measured	570 ^b	2/1	4	sorption	few cracks, many micropores

^a From reference 12.

^b From reference 2.

3. The *formation* of microvoids during the sorption of *n*-hexane by polystyrene films occurs at the boundary separating the outer swollen regions of the film from the residual glassy core. Cast but unannealed and biaxially oriented polystyrene films are highly susceptible to microvoid formation and appear to craze during the sorption of a crazing agent into the film. Conversely, well-annealed polystyrene films in which few microvoids are formed during the sorption process craze during desorption only and may form large cracks during desorption of *n*-hexane from the partially penetrated films. Extensive annealing of the films above T_g reduces anisotropic molecular orientation and may also drive off volatile impurities which could act as sites for micropore initiation. The major effect of annealing, therefore, may be the elimination of nucleating sites for crazes which would otherwise form during sorption. The annealed samples only manifest crazing and cracking upon desorption.

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