Effects of orientation on the penetration, crazing, and dissolution of polystyrene by n-hexane

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(Received 18 October 1978)

Extruded, drawn, and quenched samples of polystyrene were subsequently immersed in liquid n-hexane at temperatures between 35° and 55°C for various time intervals. Samples were removed from the immersion bath, quenched and fractured. Subsequent microscopic examination of the cross-sections revealed a distinct boundary between a crazed outer shell and an essentially unpenetrated central core. The time dependence of the depth of penetration of the advancing craze front was measured at various temperatures for several draw ratios. The initial rate of penetration increased monotonically with draw ratio (orientation) and the advance of the penetrant front was completely controlled by diffusion for drawn samples at 55°C. More complex kinetics, involving relaxations at the moving boundary, describe the penetration at lower temperatures; a slight systematic variation in the relative contribution of diffusion and relaxation was observed with increasing draw ratio. An activation energy of 23.7 kcal/g-mole characterized thetemperature dependence of the initial penetration rate, independent of sample orientation. Gravimetric swelling experiments were confounded by sample dissolution in the case of the oriented samples. Intriguing swelling patterns, including discernable differences between the pronounced edge effects in the draw and tranverse directions, were apparent. Conversely, diffusion transverse to the orientation direction was accelerated by the orientation resulting in an increasing component of relaxation control in the penetration experiments and increased rates of dissolution in the oriented samples.

INTRODUCTION

At high penetrant activities solvent crazing (voiding) accompanies the absorption of n-hexane in polystyrene[1,2]. The gross morphology of the resultant voiding depends upon the preorientation which has been imposed upon the samples prior to immersion in n-hexane[1,3]. Intercommunicating microvoids develop in commercial, biaxially oriented polystyrene during n-hexane immersion whereas discrete, spherical microvoids result from similar immersion of cast, annealed films prepared from otherwise identical polymer[1].

The development of a clearly visible boundary between crazed outer layers and an essentially unpenetrated central core permits straightforward light microscopic determination of the penetration kinetics of n-hexane advance into glassy, polystyrene specimens. Whereas constant rate (Case II) kinetics describe the penetration and gravimetric absorption in thin films[1], the rate of penetration in thicker specimens drops monotonically with time since diffusional resistances develop in the swollen (and often rubbery) outer layers[4]. Moreover, a distinct separation between the form of the sorption kinetics and penetration kinetics is apparent because the invading fronts meet at the sample midplane before gravimetric equilibrium is achieved when diffusional resistances in the swollen shell contribute significantly to the overall resistances controlling absorption[5–8].

Earlier studies relating to the effect of orientation on absorption kinetics have been limited to thin film specimens involving arbitrarily imposed biaxial orientation[1] or under conditions of post-formed drawing[3]. The objectives of this research were to extend the experimental programme to thicker specimens and to include systematic variations in orientation achieved by conventional extrusion and drawing 'in-line'. Moreover, explicit attention has been focused upon sorption 'anomalies' relating to polymer dissolution which become apparent in drawn samples.

EXPERIMENTAL

Materials

Pure commercial polystyrene Edistir NA 107, was obtained from Montedison, S.p.A., and was degassed at 50°C under vacuum for 24 h before extrusion and drawing. Reagent grade n-hexane was obtained from Carlo Erba, S.p.A and was used without further purification in the penetration and sorption experiments.

Apparatus and procedures

Extrusion and drawing. The polystyrene pellets were fed to a single screw Negri–Bossi extruder, operating at 19 rpm delivering 400 g/min of polystyrene to the die exit section. The polystyrene exited at 175°C and the rectangular exit die dimensions were 3.2 mm and 20 mm. The molten ribbon was collected on a double roll take-up apparatus which im-

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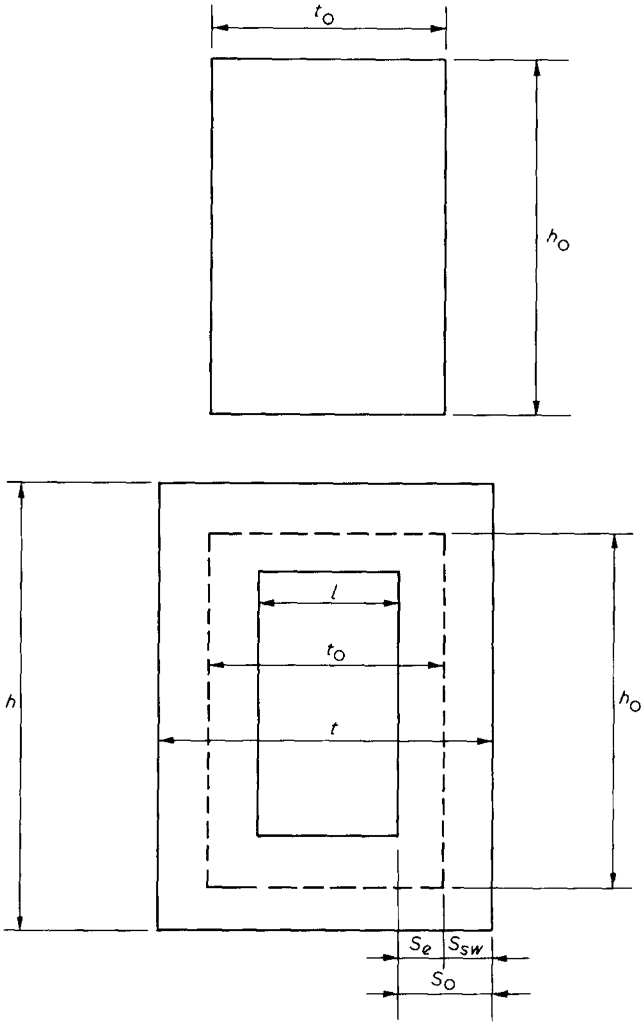

Figure 1 Schematic diagram of original and swollen sample cross-sections including symbolic designation of the relevant dimensions

posed preferred orientation in the direction of flow. The ribbon was water-quenched to 15°C in the region of the take-up rolls. The distance between the die exit and the quench bath was fixed at 80 cm and, therefore, the residence time above T_g varied between seven secs for a draw ratio equal to seven to 4 secs for a draw ratio of 16. The draw ratios were defined as S_0/S_1 where S_0 is the area of the die exit section and S_1 is the area of the drawn sample cross section. Values of S_1 were calculated from $W_1 = \rho l S_1$, where W_1 is the weight of a specimen of length, l, and ρ is the density of the polystyrene. The polystyrene density, measured for samples at different draw ratios, was found to be practically constant and equal to 1.05 g/cc. Samples with draw ratios of unity were obtained by compressing the melt at 175°C for 5 min at 5000 psi. Cooling at 15°C was achieved in 10 min by means of a water jacket.

Penetration kinetics

Polystyrene samples with different draw ratios were immersed in n-hexane, maintained at a predetermined temperature (±0.1°C) in the temperature range 35–55°C. The individual specimens were suspended in the n-hexane to avoid contact with the walls of the confining vessel. Immediately upon removal from the bath, the samples were fractured and the cross section was viewed with an optical reflectance microscope. A sharp boundary, easily detectable with the optical microscope, separated the apparently unpenetrated core from the morphologically altered swollen outer layers. The thickness of the central core and the overall specimen thickness were determined microscopically with a calibrated, Filar micrometer eyepiece.

Sorption kinetics and equilibria

Gravimetric liquid sorption experiments were performed by weighing samples repeatedly on a Sartorius 'Galileo' analytical balance following repeated immersion in n-hexane maintained at constant temperature. The samples were removed from the n-hexane, blotted, placed in a prepared weighing bottle, weighed, and then replaced in the constant temperature n-hexane pool. Apparent sorption equilibria were typically achieved within one day.

RESULTS AND DISCUSSION

Immersion of the polystyrene specimens in liquid n-hexane results in swelling of the samples. After immersion, the sectioned samples exhibit a clearly discernable boundary between a swollen (and crazed) outer shell and a central core of essentially unpenetrated polymer. The various dimensions used to characterize this concomitant expansion and penetration are presented schematically in *Figure 1*. The symbol t_0 is used to describe the initial sheet thickness; S_e designates the depth of penetration of the advancing front at any time, t; S_{sw} is used to abbreviate the linear increase in the half-sheet thickness; and S_0 is the apparent uncorrected depth of penetration based upon the dimensions of the swollen specimen.

The temperature dependence of the kinetics of liquid n-hexane penetration of polystyrene sheet specimens, characterized by draw ratios equal to unity and 16, are presented in *Figures 2* and *3*, respectively, in plots of penetration depth, S_e, *versus* time. Qualitatively similar plots were obtained for the intermediate draw ratios. In this regard, the kinetics of n-hexane penetration at 55°C into specimens of varying draw ratios are compared in *Figure 4*. In all cases, the plots deviate from linearity at relatively short times. These results suggest that, after initial Case II penetration, significant diffusional resistances are developed in the swollen outer regions of the sheet, providing an increasing overall kinetic resistance to continuing absorption, as the swollen outer shell becomes progressively thicker. These results are qualitatively consistent with earlier results reported from these laboratories on the n-hexane–polystyrene system and also with the large body of related work reported by Windle

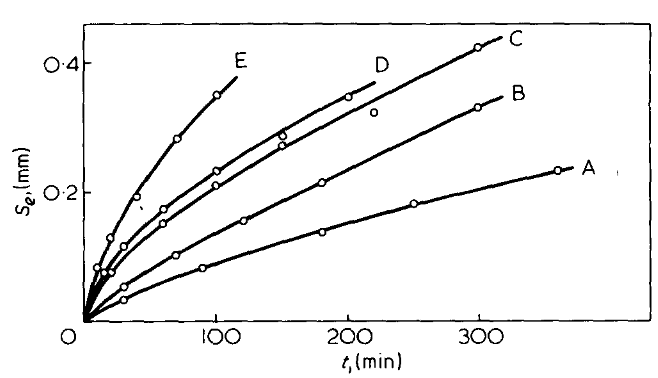

Figure 2 Temperature dependence of n-hexane penetration of polystyrene sheets. (Draw ratio = 1). A, 35°; B, 40°; C, 45°; D, 50°, E, 55°C

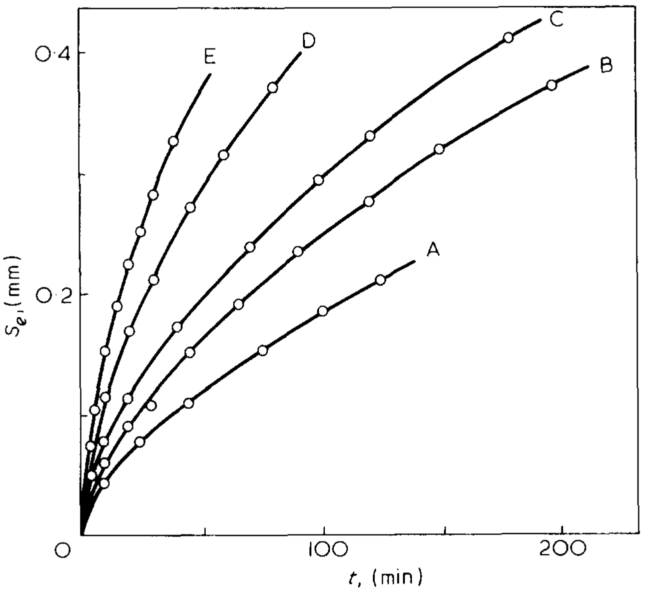

Figure 3 Temperature dependence of n-hexane penetration of polystyrene sheets (Draw ratio = 16). Key as *Figure 2*

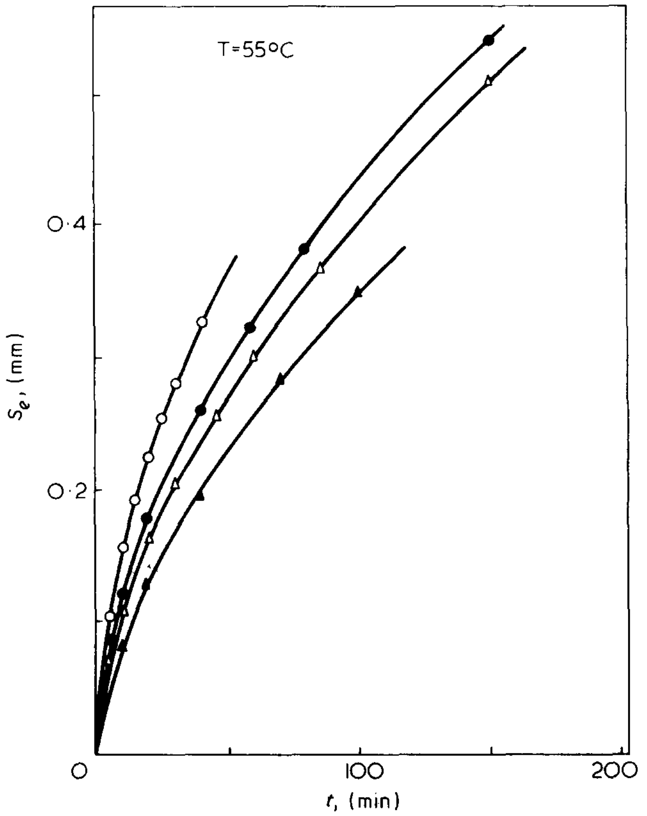

Figure 4 The effect of draw ratio on the penetration kinetics of n-hexane in polystyrene at 55°C. DR = ○, 16; ●, 11; △, 7; ▲, 1

and Thomas[6,8] describing the penetration of poly(methylmethacrylate) sheets by methanol.

Assuming that Case II transport does indeed control initial penetration of the sheets, the initial slopes of the penetration time plots reported, in *Figures 2* through *4* are proportional to the respective Case II relaxation constants. The initial penetration rates, V_0 have, therefore, been plotted in Arrhenius form in *Figure 5*.

As the draw ratio increases, the initial rate of penetration and, presumably, the Case II relaxation constant[9] increase. These results are consistent with generally observed effects of orientation on the absorption rate of alkanes in polystyrene[3,10]. Orientation stresses frequently couple with swelling stresses to give a tendency towards more rapid relaxations and, in turn, more rapid penetration, as the draw ratio is increased. The activation energy for initial penetration, calculated from the slopes of the Arrhenius plots of *Figure 5* is surprisingly independent of draw ratio, suggesting that the segment size cooperating in the rate-determining relaxations is essentially independent of orientation. The activation energy for initial penetration is 23.7 kcal/g-mole which is higher than the activation energies typically associated with purely diffusional processes[11].

The relative contributions of diffusion and relaxation are suggested by the value of the exponent, n, in the phenomenological relationship[12] between depth of penetration, S_e, and time, t, given by equation (1).

$$S_e = kt^n \qquad (1)$$

where k is a constant equal to the Case II penetration velocity for purely Case II penetration. The exponent, n, varies between unity, for a purely relaxation-controlled process, to 1/2 for a moving boundary phenomenon controlled strictly by diffusion to the advancing front. Intermediate behaviour, resulting from significant contributions from relaxation and diffusion is characterized by values of n which lie between 1/2 and unity.

The exponent, n, is conveniently determined by evaluating the slope of a log–log plot of S_e *versus t*. Representative logarithmic plots corresponding to draw ratios of unity and 16 are presented in *Figures 6* and *7*, respectively. The temperature dependence of the exponent, n, for each of the imposed draw ratios is presented in *Figure 8*. The exponent, n, decreases monotonically with temperature for each of

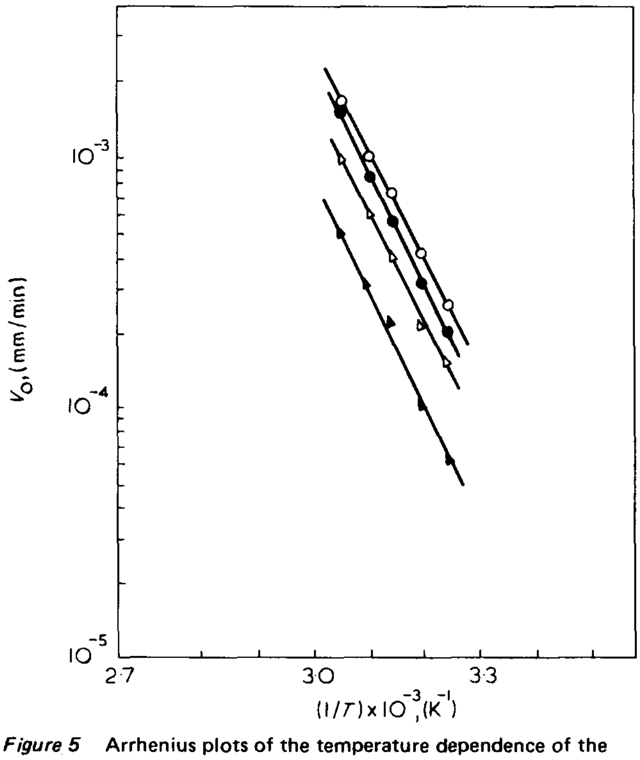

Figure 5 Arrhenius plots of the temperature dependence of the initial penetration velocity of n-hexane in polystyrene sheets characterized by varying draw ratios. Key as *Figure 4*

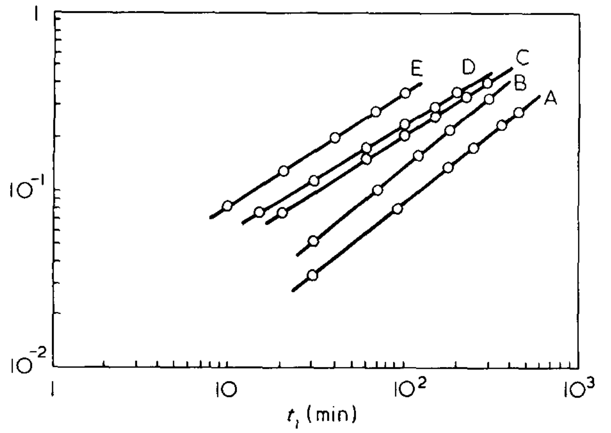

Figure 6 Logarithmic plots of the time dependence of n-hexane penetration in polystyrene sheets (Draw ratio = 1). Key as *Figure 2*

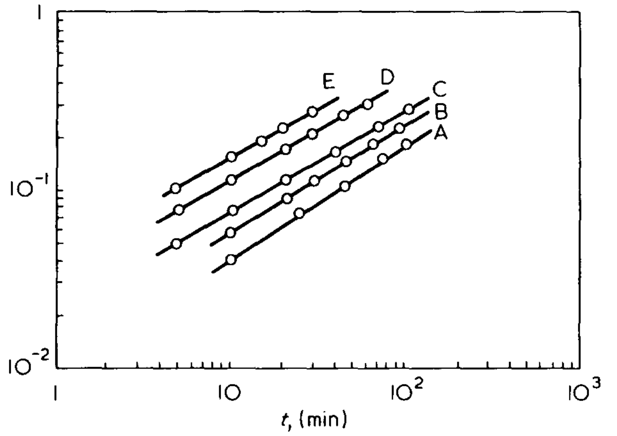

Figure 7 Logarithmic plots of the time dependence of n-hexane penetration in polystyrene sheets (Draw ratio = 16). Key as *Figure 2*

the respective draw ratios although there is a slight, albeit systematic, increase in the exponent, at a fixed temperature, as draw ratio is increased.

The monotonic decrease of n with increasing temperature results from the significant difference between the activation energy for relaxation and the activation energy for diffusion corresponding to n-hexane penetration of these polystyrene sheets[1]. At low temperatures, relaxation controlled transport dominates and, consequently the value of n approaches unity. The activation energy for n-hexane-induced relaxation reported here is approximately 24 kcal/g-mole, however the activation energy for n-hexane diffusion in polystyrene is significantly lower[11]. As temperature is increased, therefore, the relaxation processes become relatively rapid and the less activated diffusional processes become rate controlling. At sufficiently low temperatures (e.g. 20°C) perfect Case II transport has been reported for n-hexane in polystyrene[4]. Conversely, the diffusion controlled asymptote, corresponding to $n = 1/2$ is reached at temperatures in excess of 60°C. In this regard, the results presented here and the related results of Nicolais *et al.*[4] are quantitatively consistent.

Increasing the draw ratio presumably causes an increase in the diffusion coefficient as well as an increase in the relaxation rate constant[3]. The results presented in *Figure 8* relating to the effect of draw ratio on n (at a fixed temperature) suggest, moreover, that the diffusional processes are somewhat more strongly affected by orientation than are the relaxation processes. As draw ratio is increased, the value of n is increased indicating a larger contribution of relaxation to the rate determining step of the overall penetration process. These results would be expected if the diffusional processes are preferentially accelerated by drawing, resulting in penetration which is more completely controlled by the relaxation processes.

The apparent equilibrium sorption values presented in *Figure 9* were obtained by immersing the various specimens

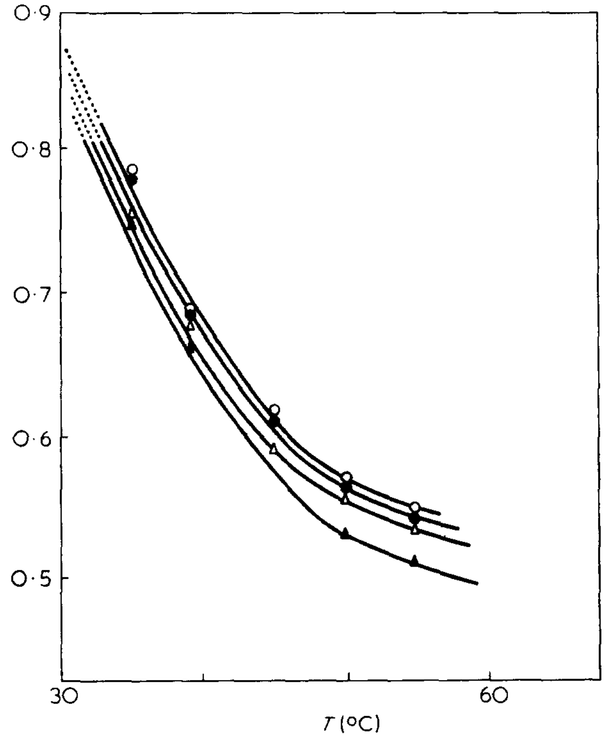

Figure 8 Temperature dependence of the exponent, n, in equation $S_e = kt^n$ which describes kinetics of penetration of n-hexane in polystyrene sheets. Key as *Figure 4*

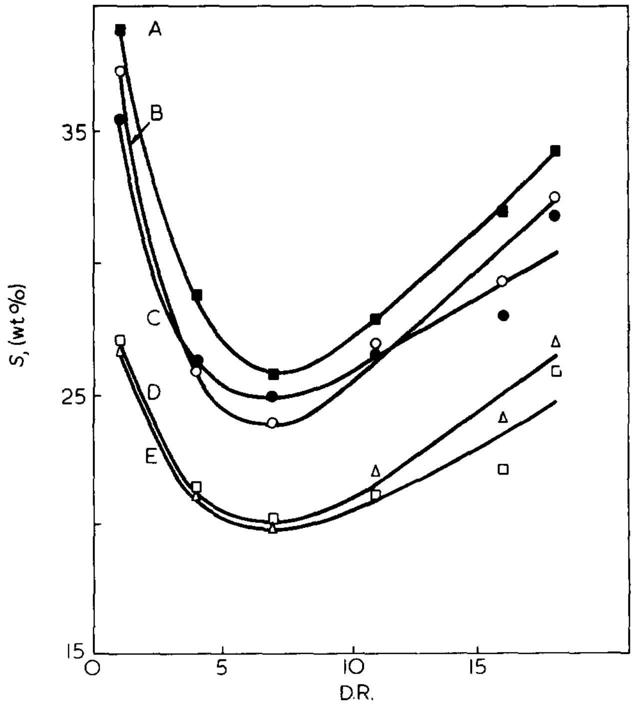

Figure 9 The effect of draw ratio and temperature on the apparent sorption equilibria of n-hexane in polystyrene sheets. Key as *Figure 2*

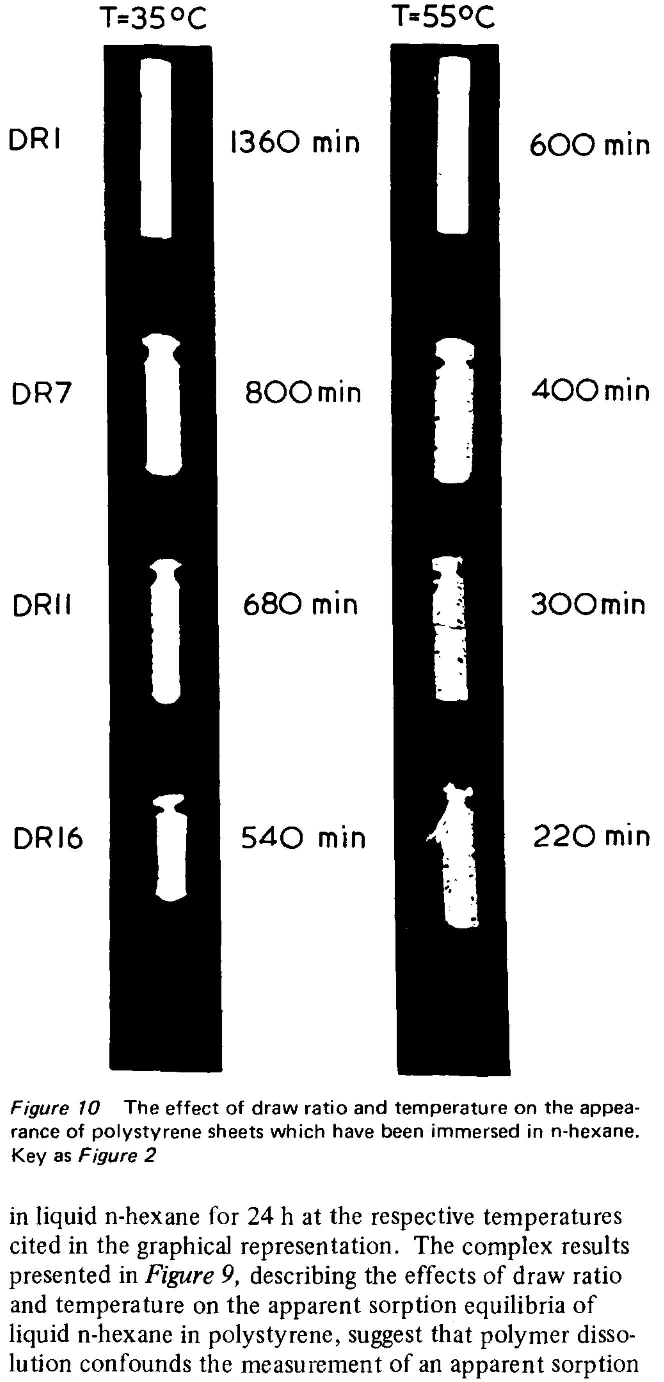

Figure 10 The effect of draw ratio and temperature on the appearance of polystyrene sheets which have been immersed in n-hexane. Key as *Figure 2*

in liquid n-hexane for 24 h at the respective temperatures cited in the graphical representation. The complex results presented in *Figure 9*, describing the effects of draw ratio and temperature on the apparent sorption equilibria of liquid n-hexane in polystyrene, suggest that polymer dissolution confounds the measurement of an apparent sorption equilibrium. In this regard, the results suggest an intriguing relationship between dissolution kinetics and drawing which requires explicit and independent determination of dissolution kinetics *per se*. These results have not been obtained to date since dissolution was not anticipated. The results presented in *Figures 9* and *10* are included here since they suggest rather important behaviour relating to the effects of orientation on swelling and dissolution.

The driving force for dissolution increases with draw ratio since the entropic component of the free energy change for dissolution increases monotonically with increasing draw ratio. The rates of relaxation controlled penetration and sorption also increased with draw ratio. The minimum in the various plots of apparent sorption equilibrium *versus* draw ratio presumably reflects this competition between n-hexane absorption and polystyrene dissolution. The ordinate values in *Figure 9* were calculated as apparent weight increase after 24 h of immersion, divided by the original dry weight of the polymeric specimen. True equilibrium was probably not achieved for samples undergoing significant dissolution.

The sense of the temperature dependence of the apparent equilibrium measurements is consistent with the suggestion that dissolution, resulting in competitive extraction of the polymeric matrix during immersion, confounds a straightforward interpretation of the 'sorption' data in *Figure 9*. Specifically, the amount of net apparent sorption drops with increasing temperature although alkane sorption in polystyrene is essentially athermal[13]. The rate of dissolution should increase with increasing temperature and, therefore, the apparent reduction in net sorption with increasing temperature reflects the increasing component of polymer dissolution to the overall mass transfer process as temperature is increased.

The qualitative results presented in *Figure 10*, describing the effects of draw ratio and temperature on the appearance of n-hexane immersed specimens are consistent with the implications of the sorption results. There is clear indication of polymeric dissolution in the swollen shell of drawn specimens immersed at relatively high temperature. The rate of dissolution appears to be directly and monotonically related to extent of drawing.

Quite intriguingly, the dissolution appears to be much more pronounced in the direction transverse to orientation than along the axis of drawing. At 55°C the penetration process is largely controlled by diffusion to the advancing boundary since the exponent, *n*, from equation (1) approaches 1/2 (see *Figure 8*). The rate determining step for dissolution is most likely a complex superposition of n-hexane absorption kinetics and concomitant chain untangling. These swelling patterns suggest, however, that diffusion along the orientation axis is retarded consistent with the increased component of long-range chain bending required for diffusion along the axis of the macromolecular chains.

The provocative results of *Figures 9* and *10* suggest a rewarding focus for continuing research into the complex phenomena of penetration, swelling, crazing, and dissolution of oriented organic glasses. Most importantly, independent and quantitative characterization of dissolution kinetics appear to be a pre-requisite to the quantitative interpretation of swelling and apparent equilibration in these and related systems.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the helpful suggestions offered by Dr John H. Petropoulos and Professor W. J. Koros. Part of this work was supported by the National Science Foundation through grant ENG 75-22437.

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