Residual solvent removal and n-hexane sorption in blends of atactic and isotactic polystyrene

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Atactic polystyrene, isotactic polystyrene, and intermediate polyblend films of the homopolymers were cast from solutions of 1,3,5-trimethylbenzene (mesitylene) or *ortho*-chlorotoluene. Residual solvent content, glass transition temperatures, and densities of the polyblends were determined. Consequent to these preliminary characterizations, n-hexane absorption kinetics and equilibria in unannealed blends were determined; maxima in the plots of weight change *versus* time were apparent for all compositions. The maximum is a consequence of the 'unlocking' of previously trapped residual casting solvent consequent to plasticizing invasion by the n-hexane in the unannealed film specimens. Neutron activation analysis for chlorine confirmed that the o-chlorotoluene content in the films was reduced dramatically consequent to n-hexane absorption. Residual solvent content was also reduced by thermally annealing the films at 110°C for 48 h under a vacuum and, therefore, no maximum in the sorption/time behaviour was observed in thermally annealed samples nor in films previously contacted with n-hexane vapour and subsequently vacuum stripped. Both the rate of sorption and the apparent sorption equilibrium are greatly reduced as the isotactic polystyrene content is increased. Predominantly Case II or relaxation controlled absorption kinetics were observed in the polyblends consequent to thermal annealing and/or 'solvent' annealing. Although the form of the sorption kinetics was quite similar for absorption of n-hexane in thermally annealed or 'solvent-annealed' films, the sorption rate and amount of penetrant sorbed at apparent equilibrium were both larger for the thermally annealed films. These results suggest that the history dependence, which so frequently affects polymeric glasses, appears to confound a simple interpretation of the sorption experiments reported here. Consistent with observations in related systems, Super Case II kinetics were observed for the more slowly sorbing films which, in this case, contained isotactic polystyrene. Moreover, film whitening related to microvoiding accompanied n-hexane sorption in blends containing atactic polymer; however, the whitening in the isotactic polymer was less pronounced and densification, presumably related to solvent induced crystallization, occurred consequent to long term exposure of the isotactic polymer to n-hexane.

INTRODUCTION

There is a growing body of literature presenting experimental determinations of transport behaviour in polymer blends. Hopfenberg and Paul[1] have prepared a review of the historical and contemporary developments related to transport phenomena in polymer blends. Their review documents the intense current activity in this field.

Polystyrene was one of the first commodity polymers to be blended successfully with rubber compounds resulting in a multiphase structure with exceptional impact properties. These formulations known commonly now as high impact polystyrene (HIPS) were disclosed as early as 1913[2]. More recently, commercially successful blends of polystyrene and poly(phenylene oxide) have been introduced which are tough yet glassy polymers, also suitable for high impact applications.

During the past five years, Hopfenberg and coworkers have presented a series of papers[3-6] describing the complex sorption behaviour of n-hexane vapour and liquid in solu-

tion cast polystyrene/poly(phenylene oxide) blends.

Ito had previously determined the permeability and solubility coefficients related to the transport and sorption of CO_2 and nitrogen in polyethylene/polypropylene blends[7]. A distinct maximum was reported in a plot of the permeability coefficient of these blends to both CO_2 and nitrogen as a function of the polypropylene content of these blends. These results presumably reflect the interference of the admixed polymers on the crystallization processes which otherwise would proceed in the individual homopolymer specimens. Intermediate compositions result in lower levels of crystallinity and, therefore, higher permeabilities. In these studies, the tacticity and, therefore, crystallizability of the polypropylene is critical to the observed blend properties. In 1975, Overbergh, Berghman and Smets[8] described the sorption kinetics and equilibria of acetone and dichloromethane in homopolymer films of atactic and isotactic polystyrene. They observed that the sorption isotherms for the atactic and isotactic polystyrene virtually superimposed at low penetrant activities. However, at rather elevated activities the isotactic polymer deviated from the continuing monotonic isotherm of the atactic polymer, and the isotactic poly-

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mer exhibited consistently lower sorption than the atactic polymer over the range of elevated activities up to saturation. This more complex, non-monotonic behaviour exhibited by the isotactic polymer was attributed to solvent-induced crystallization of the isotactic polymer above a critically high penetrant concentration in the polymer.

The weight change *versus* normalized square root time plots of Overbergh *et al.*, representing the sorption kinetics in the isotactic homopolymer, all exhibited a pronounced maximum in the approach to an equilibrium penetrant content. The sorption in the atactic polymer did not display these maxima. The authors speculated that the maxima in the kinetic plots and the lower sorption at elevated activities were related to the crystallinity which develops in the isotactic polymer in the same time scale as the sorption experiments.

The work reported here relates not only to the recent studies of Overbergh *et al.*[8] but also to the large body of work on sorption, diffusion, and permeation in and through polymer blends. Whereas Overbergh and coworkers compared only the homopolymers, and virtually all of the work in the field of blends deals with polymers of dissimilar composition, this present study involves the characterization of films of blends containing equal weights of isotactic and atactic polystyrene. Observations consistent with the complex behaviour reported by Overbergh *et al.* are reported although an alternate fundamental mechanism is offered to explain these somewhat complicated kinetics and equilibria.

This study is an extension of the earlier work reported from these laboratories relating to the sorption and relaxation in atactic polystyrene[9-12] and in polystyrene/poly(phenylene oxide) blends[3-6]. Consistent with the earlier work, the blends of these tactic polystyrenes were prepared by casting from suitable solvents. Normal hexane was selected as a model penetrant because of the wealth of related sorption data available for n-hexane in atactic polystyrene and in polystyrene/poly(phenylene oxide) blends[3-6].

Solvents with high boiling points and, therefore, rather large charcteristic molecular dimensions were required to dissolve the crystallizable isotactic polystyrene. The large molecular size of the suitable casting solvents required somewhat elaborate procedures to ensure that residual casting solvent was indeed removed consequent to casting and prior to characterization of the equilibrium and kinetic behaviour of the resulting films. The objectives of this investigation included, therefore, the determination of the effect of residual solvent on the kinetics of penetration of these blends. In addition, the varied effects of thermal annealing and 'solvent annealing' (actually vapour phase solvent extraction) on the resulting properties of the solvent-denuded films were compared. Ultimately, characterization of n-hexane sorption kinetics and apparent equilibria in the resulting solvent-free films was complemented by density determinations and thermal characterizations of the homopolymers and the tactic blend.

EXPERIMENTAL

Materials

Atactic polystyrene (APS) supplied by the Dow Chemical Company and isotactic polystyrene (IPS) supplied by the Arco Polymers Inc. were used as received to prepare the film casting solutions. Mesitylene (1,3,5-trimethylbenzene) (b.p. 165°C) and o-chlorotoluene (b.p. 159°C) were used as solvents to prepare the casting solutions.

High boiling solvents were selected to permit relatively

rapid dissolution, at elevated temperatures, of the isotactic component of the blend. *Ortho*-chlorotoluene was selected as an alternate casting solvent since the chlorine atom on the o-chlorotoluene permitted detection of the suspected residual chlorinated solvent by neutron activation analysis (n.a.a.). The residual o-chlorotoluene content in the films was determined to ±0.01 wt % by n.a.a.

The penetrant, n-hexane, had a listed purity of at least 99% (molar basis). Dissolved gases were removed from the n-hexane by successive freeze—thaw cycles.

Apparatus and procedures

Film casting. Polystyrene films were cast from two solutions, a 15 wt % solution of polymer in mesitylene and a 7 wt % solution of polymer in o-chlorotoluene. The solutions, maintained at 93°C, were cast on a glass plate also maintained at 93°C on an enclosed hot plate. The temperature was held constant for 15 min and the plate was subsequently removed from the hot plate and cooled to room temperature. The films were stored at ambient conditions until used in the requisite experiments.

Glass transition temperature determination. Glass transition temperatures were determined with a Perkin—Elmer Model TMS-1 Thermomechanical Analyzer and Perkin—Elmer Model DSC-1B differential scanning calorimeter. In both cases a scan rate of 5°C/min was used.

Density determination. A 40 cm sodium chloride/water gradient column was maintained at 23° ± 0.1°C in a constant temperature bath. The column was prepared according to the procedure described by Payne and Stephenson[13] to produce a linear density gradient along the length of the column. The density gradient column was calibrated with standard glass floats of known densities acquired from Techne of Princeton, New Jersey. The density range of the column was 1.0300 to 1.0900 g/cm^3.

Residual solvent determination. The residual mesitylene or o-chlorotoluene content in the films was determined by heating the as-cast films under vacuum until a constant weight was obtained. The weight change was assumed to be due to release of residual solvent. In addition, the o-chlorotoluene content was determined by neutron activation analysis.

Annealing. The samples were annealed at 110°C for a specified time under vacuum. The film samples were placed between two aluminium frames to prevent the films from curling during annealing at temperatures in excess of the T_g. Vacuum annealing was used to prevent oxidation of the sample at the elevated annealing temperature. Samples were removed from the oven and allowed to cool to room temperature immediately after the specified annealing time.

Vapour sorption. Vapour sorption kinetics were carried out using the McBain[14] microbalance technique with helical quartz springs supplied by Ruska Instrument Corporation, Worden Quartz Products Division of Houston, Texas. The vacuum apparatus was serviced by a mercury diffusion pump and mechanical vacuum pump. The temperature of the sorption cell was maintained to ± 0.05°C by circulating constant temperature water through a suitable water jacket. Portions of the vacuum apparatus were wrapped with heating tape to prevent condensation of the penetrant and to maintain a constant partial pressure throughout the experiment. The system, including the chamber containing the film sample,
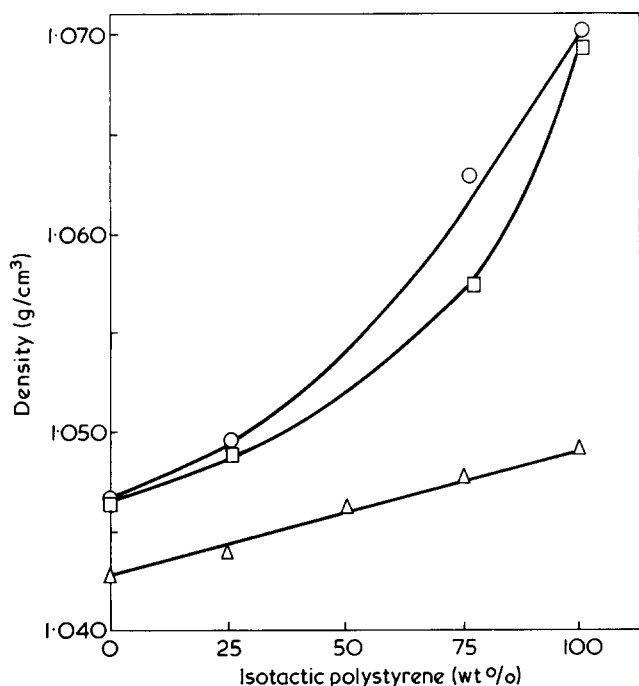
Figure 1 The density of atactic/isotactic polystyrene blends as a function of composition and annealing time. (Densities measured at 23°C) O, Annealed 121 h; □, annealed 48 h; △, unannealed

was evacuated to a pressure less than 10^{-5} mmHg and maintained for at least 15h or until a constant sample weight was achieved. Normal hexane was bled into the evacuated system at a fixed undersaturated pressure and the deflection of the spring was monitored with an optical reader as a function of time.

RESULTS AND DISCUSSION

Preliminary characterization of the blends.

The glass transition temperatures of the parent homopolymers prior to film casting were determined by thermomechanical analysis to be 88°and 92.5°C for isotactic polystyrene and atactic polystyrene, respectively. The T_g of the atactic polystyrene, measured by differential scanning calorimetry (d.s.c.) was 92°C. Unannealed atactic polystyrene films, cast from mesitylene had T_gs ranging from 71°–82°C as determined by d.s.c.

Densities of unannealed films and films annealed for 48 to 121 h, respectively, are plotted in *Figure 1* as a function of blend composition. In all cases, the density increased consequent to annealing although the density increase was much more pronounced in the isotactic rich, and therefore crystallizable, compositions.

Preliminary differential scanning calorimetry results, obtained to date, suggest that crystallinity is indeed developed consequent to annealing, and that crystallinity increases monotonically with annealing temperature and with increasing isotactic polystyrene content. These morphological studies will be pursued further in cooperation with the Laboratory of Polymer Technology and Rheology in Naples, Italy. Highly sensitive differential scanning calorimetry, X-ray diffraction, scanning and transmission electron microscopy will be used to give a better understanding of the interaction between thermal and swelling history on the resulting blend morphology.

Normal hexane sorption in unannealed films

The complex sorption kinetics of n-hexane in films cast from mesitylene solutions of atactic polystyrene, isotactic polystyrene, and an equal weight mixture of these parent homopolymers are presented in *Figure 2*. The kinetics were determined at 35°C and the n-hexane vapour, surrounding the film samples, was maintained at a fixed relative pressure (activity) of 0.876. In all cases, the plots describing these sorption kinetics reveal a pronounced maximum in the approach to a constant sample weight.

Michaels, Bixler, and Hopfenberg[15] have reported similar maxima in plots describing iso-pentane sorption in atactic polystyrene films containing several wt % of essentially trapped n-heptane. They speculated that the sorbed iso-pentane plasticized the glassy polymer, which permitted back diffusion of the otherwise trapped solvent along its independent concentration gradient. The qualitative similarity between the results obtained in this work and the results of Michaels *et al.*[15] coupled with the observed reduction in T_g of the polymer samples consequent to film preparation, suggested that n-hexane induced liberation of trapped casting solvent (mesitylene) might be responsible for the maxima observed in the plots characterizing the sorption kinetics in these mesitylene-cast films.

To test the hypothesis regarding n-hexane induced liberation of casting solvent, films were cast from *o*-chlorotoluene which is also a suitable solvent for the homopolymer and the intermediate blends. The molecular structure of the *o*-chlorotoluene is quite similar to mesitylene, but the chlorine substitution permits direct analysis for *o*-chlorotoluene in the films, at various stages of solvent/thermal history of the films, by neutron activation analysis. Films cast from *o*-chlorotoluene were similarly exposed to n-hexane at 35°C and a relative n-hexane pressure of 0.876. The resulting sorption kinetics are presented in *Figure 3*. The results are qualitatively identical to the earlier results of Michaels *et al.* and the results obtained here describing the complex sorption kinetics in mesitylene-cast films. In the plots describing these kinetics, the sample weight approached a final value which in all cases was less than the original sample weight, confirming that extraction of originally present casting solvent contributes to the observed overall kinetics.

The results of the analysis for *o*-chlorotoluene in these films, before and after sorption, are presented in *Table 1*. Strikingly, the films originally all contained a significant
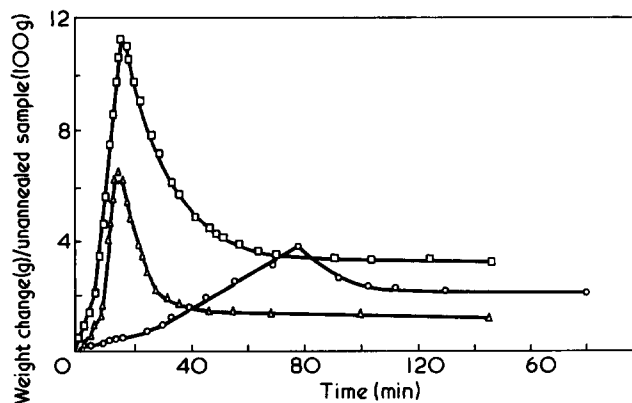

Figure 2 Time-dependent gravimetric change consequent to n-hexane sorption in unannealed polystyrene blends as-cast from mesitylene: □, 100% APS, 3.7 mils; △, 50% APS/50% IPS, 2.8 mils; O 100% IPS, 2.2 mils n-hexane sorption, p/p_0 = 0.876, T = 35°C

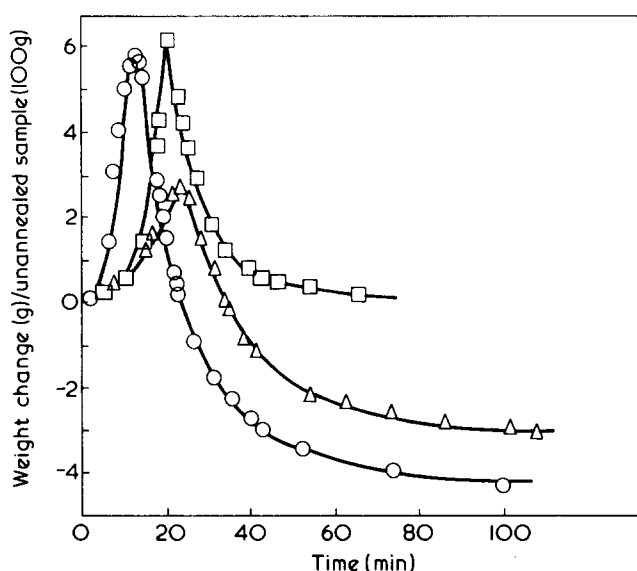*Figure 3* Time-dependent gravimetric change consequent to n-hexane sorption in unannealed polystyrene blends as-cast from o-chlorotoluene, n-hexane sorption, p/p_0 = 0.876, T = 35°C, □, 100% APS 2.5 mils; △, 50% IPS/50% APS, 4.5 mils; ○, 100% IPS, 6.6 mils

Table 1 Residual o-chlorotoluene content in the polystyrene blends before and after contacting with n-hexane determined by neutron activation analysis

Composition	o-Chlorotoluene content before n-hexane contact (%)	o-Chlorotoluene content after n-hexane contact (%)
APS	1.61	0.023
50% APS/50% IPS	1.31	0.048
IPS	2.68	0.314
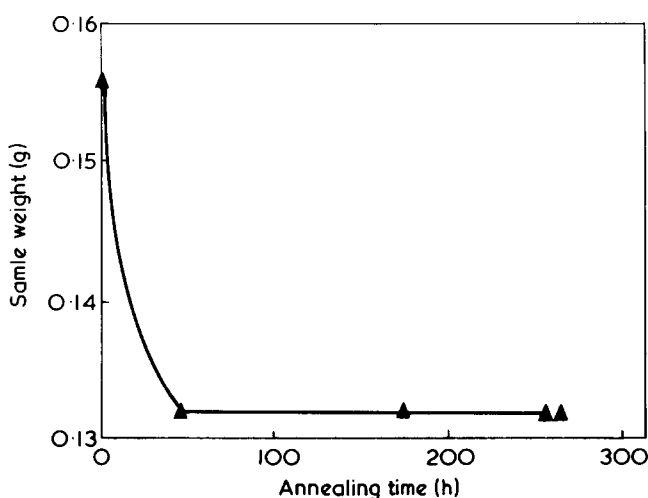
Figure 4 The effect of annealing time on the gravimetric change of atactic polystyrene cast from mesitylene. (annealing temperature = 110°C)

quantity of o-chlorotoluene and, after prolonged contact with n-hexane (equivalent to the time scale and boundary conditions of the sorption experiments), the o-chlorotoluene content in the films was reduced by an order of magnitude. The essence of these results was confirmed by gravimetry experiments wherein the samples were heated above the T_g to 110°C and the weight of the sample was monitored as a

function of time under these annealing conditions. Gravimetry results are presented for mesitylene and o-chlorotoluene in *Figures 4* and *5*, respectively. Neutron activation analyses before and after the annealing are presented in *Table 2*.

The percentage weight loss (based on original film weight) of these specimens, consequent to subjecting the samples to annealing conditions for protracted time periods were 15.5 and 11.7% for the mesitylene and o-chlorotoluene, respectively. The quantitative discrepancy between the gravimetry results for o-chlorotoluene and the neutron activation analysis results most likely is related largely to the significantly longer times which were arbitrarily inherent in the storage protocols for samples ultimately subjected to neutron activation analysis. Specifically, the samples submitted for neutron activation analysis were stored for several weeks whereas the samples ultimately characterized by thermogravimetry and n-hexane sorption were analysed only a few days after film formation.

Nevertheless, both neutron activation analysis and gravimetry convincingly demonstrate that significant amounts of either solvent are initially trapped in all the film specimens and that these particular solvents are virtually eliminated from the film specimens by either contacting with n-hexane vapour ('solvent annealing') or by more conventional thermal annealing.

After a reasonably constant sample weight was achieved, consequent to exposure to n-hexane vapour, the sample was again exposed to a dynamic vacuum and the desorption history was monitored. These results are presented in *Figure 6* for the atactic sample. After constant weight was again achieved, n-hexane vapour was readmitted into the thermostated sample chamber and the resorption kinetics were
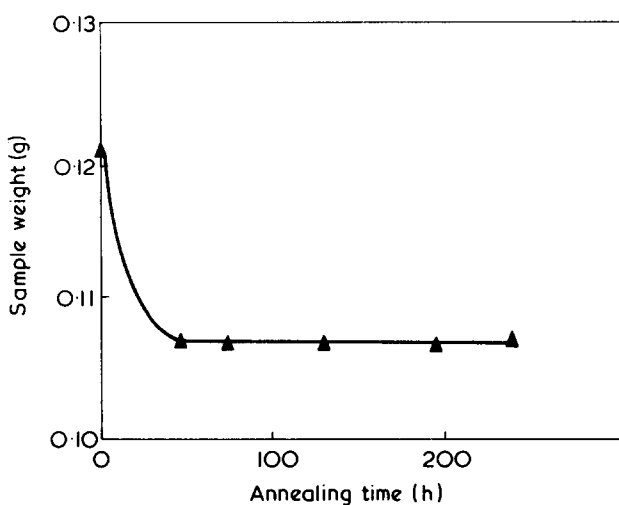

Figure 5 The effect of annealing time on the gravimetric change of atactic polystyrene cast from o-chlorotoluene (annealing temperature = 110°C)

Table 2 Residual o-chlorotoluene content in the polystyrene blends before and after annealing at 110°C determined by neutron activation analysis

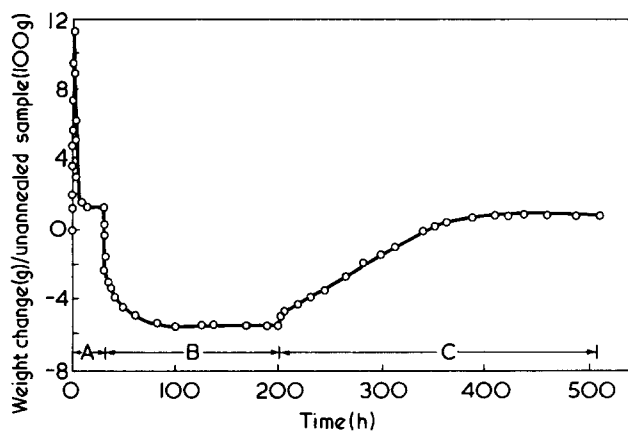| Composition	o-Chlorotoluene content before annealing (%)	o-Chlorotoluene content after annealing (%)
APS	2.28	0.0031
50% APS/50% IPS	1.31	0.0040
IPS	4.42	0.024

Figure 6 Sequential sorption and desorption of n-hexane in atactic polystyrene as-cast from mesitylene. A, Sorption; B, desorption; C, resorption. n-Hexane sorption, p/p_0 = 0.876, vacuum desorption, T = 35°C
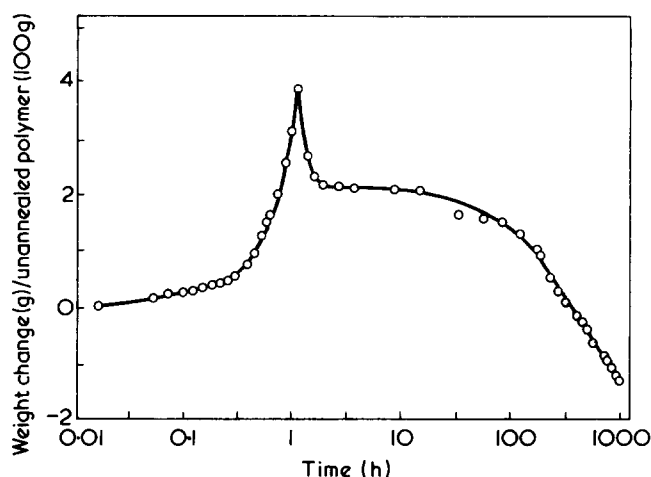

Figure 7 Time-dependent gravimetric change consequent to n-hexane exposure in unannealed isotactic polystyrene as-cast from mesitylene. n-Hexane absorption, p/p_0 = 0.876, T = 35°C

consequence of the liberation of solvent species used in the complex synthesis and casting histories of their particular polymer specimens. Their samples were prepared by quite dissimilar techniques and the presence of the 'maxima' in their plots characterizing the absorption kinetics of acetone and dichloromethane in the isotactic specimen only may be a somewhat fortuitous consequence of the dissimilar solvent types and contents which might complicate the history and, in turn, the subsequent sorption kinetics in their atactic and isotactic films. Overbergh et al.[8] did not provide sufficient information describing preparative techniques in their recent work[8] nor in the referenced earlier papers[16,17] to provide a rational basis for dogmatism on this point. Nevertheless, n-heptane was apparently used in the synthesis of their isotactic polymer which is coincidently the trapped species allegedly extracted by iso-pentane in the Michaels et al.[15] study.

Normal hexane sorption in annealed films

The thermogravimetry results suggested that the vexing maxima should, indeed, be eliminated by annealing the as-cast films, above T_g, for suitable periods. The n-hexane sorption kinetics in films annealed at 110°C for 48 h are presented in *Figure 8*. The films were originally cast from mesitylene.

In all cases, the kinetics are essentially of the Case II form; the slower sorbing isotactic film does, however, exhibit Super Case II kinetics[18] consistent with the earlier speculations regarding development of long term acceleration in relatively slow-sorbing glassy films. The acceleration has been attributed to the overlapping of Fickian 'tails'[19] which plasticizes the polymer at the critical boundary region between swollen and essentially unpenetrated polymer. The increased penetrant content of the swelling boundary accelerates the rate controlling relaxations and, in turn, the sorption rate.

Most importantly, however, there are no maxima apparent in the sorption kinetics of the annealed films. Consistent with the thermogravimetry results and the neutron activation analyses, these sorption results suggest that elimination of trapped solvent was effected by the annealing. In addition, the sorption kinetics in the isotactic sample do not involve a 'maximum'. This explicit demonstration of sorption in an
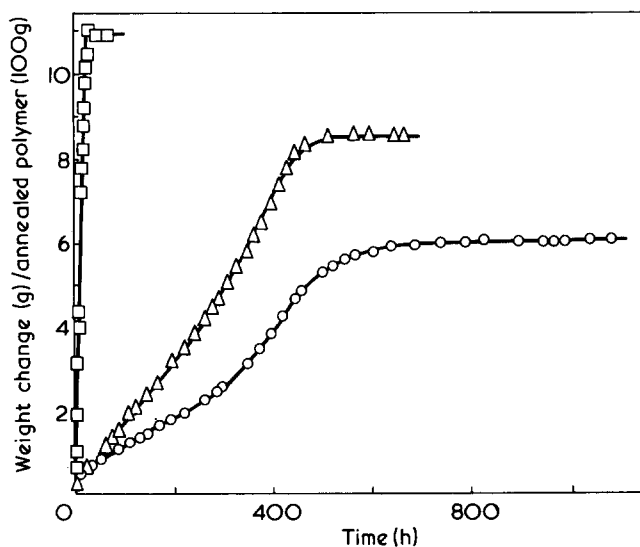
monitored. Whereas the initial sorption kinetics were confounded by complex behaviour involving a maximum in the sorption-film plots, the resorption kinetics showed virtually ideal Case II sorption and were not at all complicated by a maximum value of sorption preceding equilibrium. These resorption results are gratifyingly consistent with the developing evidence for trapped solvent liberation, causing the complex sorption behaviour apparent during initial sorption in unannealed films.

Unfortunately, this explicit additional experimental confirmation of the 'trapped solvent hypothesis' was not practical for the isotactic sample since the experimental times were prohibitive. The initial sorption history in the isotactic sample is presented in *Figure 7*. The sample continues to lose material after 1000 hours of contact with n-hexane. The attainment of a sample weight, less than the original weight of the cast, unannealed film testifies rather conclusively to the n-hexane induced liberation of casting solvent.

Whereas Overbergh, Berghmans and Smets[8] observed this type of maximum in plots characterizing absorption kinetics from the vapour phase for their isotactic polystyrene samples only, it seems reasonable to speculate that their results, although accompanied by a discernible and unequivocal development of crystalline structure, are in fact a more direct

Figure 8 Vapour sorption kinetics of n-hexane in annealed polystyrene blends at 35°C. n-Hexane sorption, p/p_0 = 0.876, T = 35°C. □, 100% APS, 1.9 mils; △, 50% APS/50% IPS, 2.3 mils; O, 100% IPS, 1.0 mils
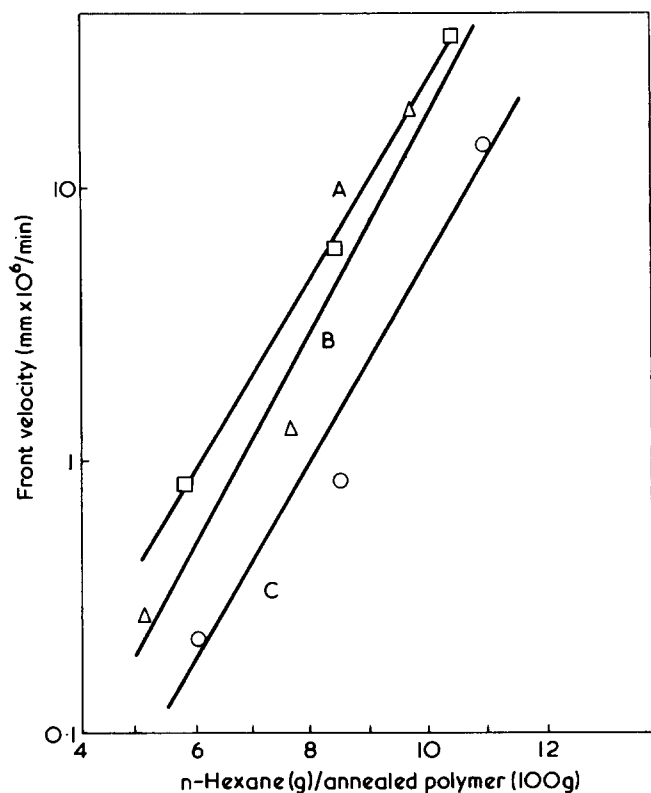
Figure 9 The effect of equilibrium penetrant solubility on the Case II front velocity in annealed polystyrenes blends. A, 45°C; B, 40°C; C, 35°C

isotactic sample without a maximum provides additional support for the emerging hypothesis that the 'maxima' are related to trapped solvent release rather than expulsion of previously sorbed penetrant. In addition, tacticity and the related possibility of crystallization does not seem to affect the tendency to develop a 'maximum' in the sorption experiments in unannealed films nor is there a qualitative, tacticity-related difference in the kinetics observed in the annealed films.

In a more straightforward way, increasing the atactic content of these samples increases not only the equilibrium sorption content but also the rate of absorption. Presumably, sorption is restricted in the isotactic-containing samples since there is more ordered, non-sorbing polymer in the glassy matrix.

Jacques and Hopfenberg[5] observed a close relationship between Case II front velocities and equilibrium n-hexane solubility in PS/PPO blends. Presumably, increased penetrant solubilities generate steep, rate determining, osmotically active concentration gradients and, in turn, more rapid sorption. In this regard, semi-logarithmic plots of swelling front velocity versus equilibrium n-hexane content are presented for three temperatures in *Figure 9*.

Apparent activation energies for sorption were determined from the slopes of the Arrhenius plots of *Figure 10*. These results are all in the range of previously reported activation energies associated with Case II sorption constants measured in the related PS/PPO system. The activation energies are higher than those typically observed for diffusion-controlled absorption.

A comparison between the effects of thermal annealing and solvent annealing

The n-hexane absorption kinetics in atactic films, freed of original mesitylene by thermal annealing and solvent an-

nealing, are compared in *Figure 11*. Whereas both films show qualitatively identical absorption kinetics, following virtually ideal Case II sorption kinetics, there is a significant difference in the actual magnitude of the rate of sorption as well as the apparent equilibrium penetrant content in these seemingly comparable glasses.

Although these equilibrium results are somewhat disquieting in the light of classical thermodynamics, there is a growing body of evidence suggesting that glassy polymers are subject to history-induced differences which survive even the most patient experimental protocol. Quite simply, within the
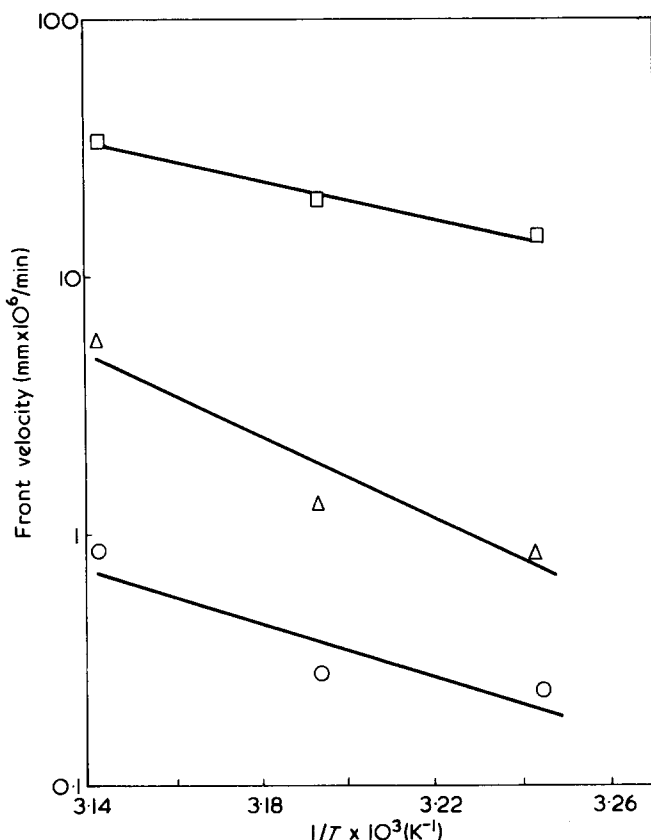

Figure 10 Arrhenius plots of Case II front velocty for n-hexane sorption in annealed polyblends. n-Hexane sorption, p/p_0 = 0.876. □, 100% APS, E_a = 18 kcal/gmol; △, 50% APS/50% IPS, E_a = 38 kcal/gmol; ○, 100% IPS, E_a = 24 kcal/gmol
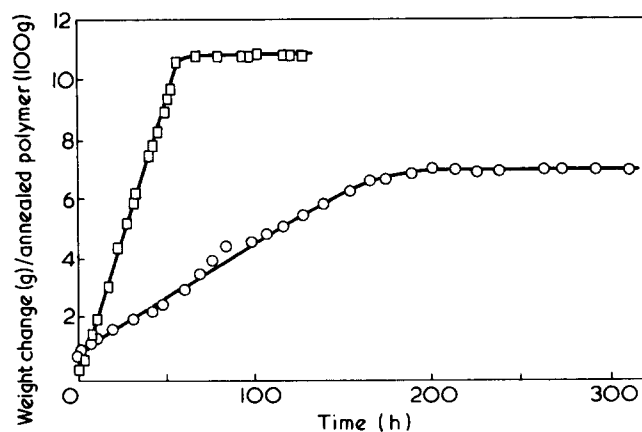

Figure 11 Sorption kinetics of n-hexane in thermally and 'solvent' annealed atactic polystyrene. n-Hexane sorption, p/p_0 = 0.876, T = 35°C. □, Thermally annealed 4.0 mils; ○, 'solvent annealed', 3.7 mils

time scale of reasonable experimentation, these samples, with subtle differences in their respective histories, exhibit measurable differences in their kinetic responses and in their apparent sorption equilibria.

Berens[20,21] and Enscore, Hopfenberg, and Stannett[22,23] have exploited the ultra-small dimensions of emulsion polymerized poly(vinyl chloride) and polystyrene, respectively, to carry out experiments relating to history effects in these polymeric glasses. The small (sub-micron) particle size permitted equilibration in hours rather than months. History effects, quite consistent with the quantitative differences observed here, were reported in the more elaborate study of history effects by Berens[20,21] and Enscore *et al.*[22,23].

Some observations on penetrant-induced morphological changes

Both atactic and isotactic polystyrene are susceptible to penetrant-induced morphological changes. Hopfenberg[12] has reported that a series of n-alkanes (n-pentane to n-nonane) are crazing agents for polystyrene. Moreover, Overbergh *et al.*[8] present convincing evidence for solvent-induced crystallization in isotactic polystyrene.

Crystallization of isotactic polystyrene densifies the overall matrix, while crazing in the atactic polymer results in voiding and, therefore, a significant density reduction.

In this study, samples exposed to liquid n-hexane whiten; the whitening is discernably less pronounced for the isotactic polymer, however. For example, at 35°C, appreciable whitening was apparent after 44 min of immersion of the atactic films in n-hexane liquid. Similar whitening was developed, under comparable immersion conditions, in 98 min for the 50/50 atactic/isotactic blend and no whitening was detectable after protracted immersion of the isotactic homopolymer. The whitening may be exclusively related to solvent-induced crystallization in the isotactic sample whereas the samples containing atactic polymer are still quite susceptible to voids. The density of the isotactic sample prior to contact with n-hexane was 1.0493 g/cm³ and increased to 1.0543 g/cm³ at the end of the experiment. Atactic films contacted with n-hexane typically suffered a 15% decrease in apparent bulk density[4].

These morphology studies are focal to the continuing experimentation with this intriguing system. It is quite possible that isotactic polymer retards crazing of the atactic component whereas atactic polymer may interfere with the crystallization of the isotactic rich formulations. The continuing experimentation will, therefore emphasize X-ray diffraction, microtomy, scanning and transmission electron microscopy, pychnometry, and differential scanning calorimetry.

ACKNOWLEDGEMENTS

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