

## COUPLING OF MOLECULAR DIFFUSION AND POLYMER PROCESSING

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**Abstract** - An overview of the coupling of polymer formation and processing with molecular diffusion is presented. Specific cases are used to illustrate the importance of molecular diffusion in processing, and the reciprocal interaction in which processing influences migration in the finished product. Finally, a free-volume theory for predicting diffusion coefficients in concentrated polymer solutions at conditions of interest in polymer processing is presented.

### INTRODUCTION

From their inception as materials, it has been recognized that polymers have unique properties associated with their resistance to molecular penetration by other materials. This property led to many early applications in the coatings and film industry. It was natural that these applications further led to the study of diffusion in finished polymer products and their permeation properties. Consequently, the preponderance of diffusion studies in polymer systems have focused on the properties of solid polymers at temperatures and concentrations which reflect the conditions during the end use applications. A large data base which is concerned with diffusion and sorption in glassy polymers and elastomers near ambient conditions now exists (1,2). A second impetus for the study of molecular diffusion in polymer systems has been to use the molecular diffusion of small molecules in polymers as a molecular probe to elucidate molecular motion in macromolecular systems and morphology(3).

In addition to the studies concerned with the penetration of small molecules into solid polymers and elastomers, diffusion in dilute polymer solutions has received considerable attention, particularly in recent years. Although diffusion in dilute polymer solutions is not very important from an applications point of view, theoretical and experimental advancements have uniquely converged in this area. Quasi-elastic light scattering techniques have developed to permit detailed examinations of the rotational and translational diffusion of macromolecules in solutions. In the infinitely dilute limit, the polymer molecules are widely dispersed and the individual chains do not interact. Consequently, statistical mechanical techniques can be applied to an ensemble of individual polymer chains in a continuum of the solvent. Starting with the work of Kirkwood and Riseman (4), many advancements have been made in the theoretical description of molecular mobility in infinitely dilute and dilute polymer solutions (5). This convergence of theoretical and experimental developments has led to considerable interest and work in the region where the domains of the migrating polymer chains do not overlap but may interact hydrodynamically.

The above discussion indicates that of the considerable effort which has been concerned with the study of diffusion in polymer systems, very little has been directed to elucidating diffusion phenomena which are important in the production and processing of polymers. Unfortunately, the physical properties associated with heat and momentum transfer in polymeric systems under processing conditions have been studied almost to the exclusion of mass transfer properties. Diffusion in molten polymers far above the glass-transition, which is characteristic of many industrial processes, has been particularly neglected. There are several reasons for this state of affairs. As Fujita (6) has noted, it is a formidable task to conduct diffusion measurements in polymer systems at the elevated temperatures which are characteristic of industrial processes. The experimentation is further complicated by the strong dependence of diffusion coefficients on concentration and temperature which is exhibited by many systems of practical importance. Most polymer processing operations involve concentrated solutions of polymers and solvents which are far removed from the dilute region where theoretical advancements have been most significant. The complications associated with chain entanglements has held back theoretical advancements in this area. Although it is obvious that the first step in the analysis of processes involving molecular diffusion would be the measurement of the appropriate diffusion coefficients, the need for such measurements does not appear to have been generally recognized in the polymer industry. In the past, the emphasis in industry has been on the synthesis of new polymer materials and

the engineering of the polymer formation and fabrication processes has been a secondary concern. However, it appears that continued growth in the polymer industry will be more directly associated with sophisticated engineering which will lead to improved processes and new applications (7). Recently, the importance of mass transfer during polymer processing has become quite conspicuous due to the growing concern over the potential health problems associated with residual impurities in plastic containers, films, etc.

The importance of molecular diffusion during polymer formation and processing has not been generally recognized. The significance of mass transfer during formation and fabrication on the properties and performance of the final product has also been neglected. An overview of the coupling of molecular diffusion, polymer processing, and polymer applications will be presented in the next section. The state of the art of predicting molecular diffusion in polymer systems under conditions of interest in polymer processing will also be reviewed.

#### THE ROLE OF MOLECULAR DIFFUSION IN POLYMER PROCESSING

The diffusion of solvents, monomers, additives, and other relatively small molecules is critical in many polymer formation and processing operations. In the chemical industry which deals with the formation and processing of small non-polymeric molecules, the rate of processes which involve molecular diffusion can be accelerated by mixing or some other modification of the fluid mechanics. Consequently, in many cases, fluid mechanical considerations are of first importance and the actual values of the diffusion coefficients involved are secondary. However, the very high viscosities which are characteristic of polymer systems often eliminate the practicality of significantly enhancing mass transfer by modifications of the fluid mechanics. Under these conditions, diffusion coefficients can often be the dominant physical property in process analysis.

Mass transfer is perhaps most prominent in the initial formation of polymers. In many cases, the rate at which a polymerization reaction proceeds is controlled or strongly influenced by the molecular diffusion of monomers, initiators, long-chain radicals, dead polymer chains, or low molecular weight condensation products. In many step polymerization reactors, the removal of condensation products can influence the rate of polymerization (8). For reversible reactions, the condensation by-product must be removed in order to drive the polymerization reaction toward completion. For example, in the glycol condensation route for producing polyethylene terephthalate, the diffusion of the eliminated glycol molecule from the melt can control the rate of polymerization and the properties of the produced polymer. The recent study of the diffusion of water and caprolactam in molten nylon by Nagasubramanin and Reimsschuessel (9) exemplifies a situation where diffusivity data were required in order to design a polymerization reactor.

In idealized kinetic studies of polymerization reactions, diffusion effects can often be neglected. However, these effects become particularly important in the analysis of commercial polymerization reactors where sharp gradients in concentration often occur. As the polymer industry moves to more extensive use of bulk polymerization reactors with their inherently high yields per reactor volume, the importance of mass transfer and reactor design will become more prominent. For example, an ideal reactor for the production of a polymer by free-radical chain kinetics would be a continuous tubular flow reactor. In principle, monomer and initiator could flow in one end and a high concentration of polymer would be produced at the outlet. Such a reactor involves a complex coupling of fluid mechanics, polymerization kinetics, heat transfer, and molecular diffusion (10,11). At the high conversions which are desirable, the main problem is a buildup of polymer concentration near the tube wall which causes "plugging." This phenomena could be eliminated by a high diffusion rate of the monomer into this high polymer concentration region and correspondingly a high diffusion rate of the polymer into the monomer rich center of the tube. The modeling of this radial diffusion can be the critical step in the analysis of such reactors.

The use of a catalysis for polymer formation by chain polymerization kinetics will not eliminate the importance of monomer diffusion. Brockmeier and Rogan (12) have shown that the diffusion of monomer through a growing polymer shell around the catalyst can significantly influence the overall rate of polymerization in a polypropylene slurry reactor.

It is well known that the conventional low conversion free-radical kinetics do not apply over the entire conversion range in concentrated polymerizing systems. The termination step in such systems is diffusion controlled for a large range of conversions (13). Monomer molecules and long chain radicals compete for each free-radical, and when two long chain radicals come together by molecular diffusion, termination occurs. At high conversions, the decrease in the molecular diffusion of the long chain radicals cause a rapid increase in the rate of polymerization which is termed the autoacceleration or Trommsdorff effect. This phenomena is due to the difference in the concentration dependence of the diffusivities of the two competing species. Whereas mass transfer in most polymer formation and processing operations involves the mutual diffusion of the polymer with a relatively low molecular weight species such as the monomer, the Trommsdorff effect involves the diffusion of long

chain free-radicals. This process is controlled by the self-diffusion of long chains, whereas the mutual binary diffusion coefficient for a polymer solution is often insensitive to the self-diffusion coefficient of the high molecular weight species (15). Tulig and Tirrell (14) have recently considered the kinetics of high-conversion autoaccelerating free-radical polymerization, incorporating the reptation model of deGennes (16) for chain migration. This is one of the few cases in polymer processing where the mutual binary diffusion coefficient predicted by the free-volume theory presented in the following section is not applicable.

Today, one of the crucial problems of the polymer industry is the removal of small amounts of volatile residuals to meet environmental, health, and safety regulations. In the early days of the industry, polymer devolatilization was employed to recover the monomer and to control the properties of the polymers. Consequently, it was not particularly critical to attain very low concentrations of monomer or other volatile residuals. However, the recent concern with the potentially carcinogenic nature of some materials has placed an emphasis on reducing residual volatile concentrations to extremely low values. As shown in the next section, this is particularly difficult since the mutual binary diffusion coefficient will often decrease drastically at low solvent concentrations.

Vacuum or steam stripping are used in many different types of equipment such as wiped film evaporators and vented extruders to remove volatile residuals from polymer melts. Biesenberger (17) has shown that many of these operations can be modeled by a stagewise continuous process involving alternating steps of diffusion from a film coupled to a mixing stage. The success of such modeling depends on the availability of information concerning the concentration and temperature dependency of diffusion coefficients in polymer melts.

In many cases, polymer devolatilization does not involve a flowing melt, but diffusion from particles formed in emulsion and suspension polymerization processes. Again, many types of equipment such as stirred tanks and columns can be used to perform this stripping operation (18). Recent work with polyvinyl chloride has shown that the rate of monomer desorption is strongly influenced by the internal morphology of PVC particles (19). In this case we have an interesting coupling of diffusion phenomena. The porosity and other morphological characteristics of the polymer particle are fixed during the polymerization process, which involves coupling of a chemical reaction, molecular diffusion, and phase equilibria. This diffusion controlled structure then influences the diffusion of monomer out during devolatilization and the subsequent diffusion of plasticizers into the particle.

The control of polymer morphology by diffusion and phase equilibria phenomena during polymerization is a potentially powerful technique. The production of porous PVC particles and porous ion exchange resins are two examples of this technique.

A diffusion process can be used to control the morphology of a polymer independent of the polymerization process. A very specific morphology is desirable in polymer membranes for the separation of gases and liquids. The future of industrial membrane separation processes depends upon the formation of membranes which have high selectivity coupled with inherently high fluxes. One of the most promising approaches has been to produce membranes which have a very thin surface which provides high selectivity backed by a porous substrate to give mechanical strength. Diverse film morphologies can be produced by the coagulation of polymer solutions. Typically, the polymer structure is precipitated from a solution of the polymer in a good solvent in contact with a non-solvent. Cohen and co-workers (20) have shown that the pore structure formed during coagulation is controlled by simultaneous diffusion of several species coupled to the phase equilibria of the three component systems. Again, we have molecular diffusion during processing influencing the diffusion characteristics of the finished product.

It is well known that many processing operations can influence the diffusion characteristics of a polymer. Usually we have the processing operation altering the morphology or polymer structure, which in turn modifies the diffusion or mass transfer properties. Perhaps the most prominent area of this interaction between processing and diffusional characteristics has been observed in the dyeing of synthetic fibers. Orientation of the chains in the fiber can enhance tensile strength, but will often result in a detrimental reduction in the rate of dye diffusion.

Numerous investigators have demonstrated the coupling of process induced morphology on the diffusion of large dye molecules as well as low molecular weight materials. For example, Dumbleton, Bell, and Murayama (21) observed the relationship between the dynamic loss modulus and dye diffusivities. Takagi (22) measured dye diffusion parallel and perpendicular to the direction of chain orientation. Michaels (23), and Williams and Peterlin (24) observed the influence of orientation in polyolefins on the diffusion of small molecules.

#### PREDICTION AND CORRELATION OF DIFFUSION COEFFICIENTS

The previous section showed that molecular diffusion phenomena influences nearly all phases of polymer formation and processing; and concurrently, process operations influence the

diffusional characteristics of the final polymer product. It was further noted that diffusion in polymer melts under processing conditions has been a relatively neglected area. It could be argued that diffusion in polymer melts above the glass transition and melt temperatures is a natural starting place for the study of diffusion in polymer systems. At these conditions, the polymer is in a well defined equilibrium liquid state and the diffusion process is not complicated by an ambiguous morphology. A basic understanding of diffusional behavior in this relatively idealized state should lead to progress in other more complex areas. At first consideration, the behavior of diffusion coefficients for concentrated polymer solutions above  $T_g$  appear quite complex. Typically, diffusion coefficients for these systems show a very strong dependency on the solution concentration as well as temperature. Even more disconcerting is the fact that the literature is filled with many cases where anomalous diffusion has been observed. In this context, anomalous means that the observed mass transfer phenomena are not consistent with classical diffusion theory.

The anomalous behavior observed in concentrated polymer-solvent systems is related to the relaxation characteristics of macromolecules. In classical diffusion, theory, it is implicitly assumed that local equilibrium exists in all regions of the diffusion field. The conformation of a polymer chain in a solution must change as the diffusion induced concentration field changes. If the relaxation of the polymer chain to its new equilibrium state is slow compared to the diffusion process, the mass transfer process will involve coupling of relaxation and molecular diffusion. It has been noted (25) that the various types of diffusional behavior exhibited by polymer-solvent systems can be distinguished by the ratio of two characteristic times: a characteristic relaxation time for the polymer-solvent system, and a characteristic diffusion time. The situation is analogous to that encountered in the study of the flow behavior of viscoelastic materials, where the nature of the deformation depends on a ratio of characteristic times called the Deborah number (26). An analogous dimensionless group for diffusive processes has been defined as

$$DEB = \frac{\tau}{\theta} \quad (1)$$

where  $\tau$  is the characteristic relaxation time of the polymer system, and  $\theta$  is the characteristic time of the diffusion process. For example, a characteristic diffusion time for unsteady, one-dimensional mass transfer in a polymer film can be defined as

$$\theta = \frac{L^2}{D} \quad (2)$$

where  $L$  is the thickness of the film and  $D$  is the characteristic diffusion coefficient. According to this characterization, classical diffusion behavior can be expected when  $DEB \ll 1$  and small Deborah numbers can be attained by conducting experiments with thick samples. When the Deborah number is of the order of 0.1-10, complications due to coupling of relaxation to the diffusion process can be expected. At the present time, a theory does not exist which completely describes this coupling phenomena.

In the past, anomalous behavior was associated with the temperature region near or below the glass transition where polymer relaxation is slow. However, the Deborah number characterization indicates that anomalous behavior may be exhibited in systems significantly above  $T_g$  if the process time is very short. For example, in the devolatilization of polymer melts in vented extruders, the diffusion process has an oscillatory nature. The polymer melt circulates from the surface region where the mass transfer occurs to a mixing zone below the surface (17). The characteristic time of this circulation can be quite short and it is possible that polymer relaxation effects are important even at the elevated temperatures which are characteristic of such devolatilization processes. The following discussion will be confined to those systems where the characteristic Deborah number is small and classical diffusion behavior is anticipated.

As mentioned earlier, the complex nature of concentrated polymer solutions has frustrated the theoretical description of chain migration in these systems. The recent development of the reptation model (16) to describe polymer chain movement may lead to accurate formulations for the self-diffusion of the polymer species. However, the mutual binary diffusion process in the concentrated region which is of interest in most industrial operations, is dominated by the self-diffusion or migration of the low molecular weight solvent (15). The most successful approach for the description of molecular diffusion in concentrated polymer solutions has been based on free-volume concepts. Although formulations based on free-volume considerations can accurately predict and correlate the mutual binary diffusion coefficient over a wide range of concentration and temperature, this approach is not completely satisfactory from a theoretical point of view. Many of the parameters in the free-volume theory cannot be related to fundamental molecular properties, but are determined by correlating the viscous behavior of the pure components with free-volume theory. Since the theory does not include detailed information on intermolecular potentials, it is unrealistic to expect that expressions for viscosities and self-diffusion coefficients can be derived in terms of molecular parameters. Furthermore, the hole free-volume of a system available for molecular transport is a quantity which cannot be determined by methods which are independent of viscosity and self-diffusion measurements. The free-volume approach can, however, be used to develop methods which permit the use of a limited number of transport measurements to predict viscosities and diffusion coefficients at other temperatures and concentrations.

Free-volume theory can be a useful method for predicting the transport properties of a mixture from those of effectively pure components, since unknown molecular mechanisms are conveniently hidden inside parameters which are determined from transport data.

The basic concepts of free-volume theory will be reviewed in the following discussion. The details of the theory presented here are available in the literature (27-29). The discussion will be limited to binary diffusion coefficients for amorphous polymer-solvent systems.

According to free-volume concepts, the movement of solvent molecules or polymer chains in concentrated solutions is impeded by the presence of neighboring molecules. A molecule migrates by jumping into a void or a hole, which forms because the free-volume in the system is being continuously redistributed by thermal fluctuations. In the case of many relatively small solvent molecules, the jumping unit is the entire molecule. For flexible linear polymers, however, the jumping unit is some small part of the entire chain.

Two requirements must be fulfilled before a molecule or jumping unit can migrate in solution: a hole or free-volume space of sufficient size must appear adjacent to the molecule, and the molecule must have enough energy to move or jump into this void. The occurrence of a jump is based on the product of probability that a fluctuation in local density will produce a hole of sufficient size, and the probability that the jumping unit will acquire sufficient energy from the distribution of thermal energy to overcome attractive forces in order to jump into the void. These concepts have been used by several investigators (30,31) to derive self-diffusion coefficients for one component liquid systems.

For concentrated polymer systems, the mutual diffusion coefficient can be related to the self-diffusion coefficient of the solvent and to the thermodynamic properties of the mixture (15). In the most recent version of the free-volume theory, all thermal expansion coefficients needed to calculate the various volumes required for the theory are approximated by average values in the temperature range under consideration, and the influence of volume change during mixing on the free-volume of the system is considered negligible (27-29). Based on these assumptions, the mutual diffusion coefficient,  $D$ , for a polymer-solvent system, can be described in terms of the self-diffusion coefficient of the solvent  $D_1$ , and a thermodynamic factor,  $Q$ , by the following set of equations:

$$D = D_1 Q \quad (2)$$

$$D_1 = D_0 \exp(-E/RT) \exp \left[ - \frac{(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{\hat{V}_{FH}/\gamma} \right] \quad (3)$$

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1 \frac{\hat{V}_{FH}(1)}{\gamma} + \omega_2 \frac{\hat{V}_{FH}(0)}{\gamma} \quad (4)$$

$$\frac{\hat{V}_{FH}(0)}{\gamma} = \frac{K_{12}}{\gamma} (K_{22} + T - T_{g2}) \quad (5)$$

$$\frac{\hat{V}_{FH}(1)}{\gamma} = \frac{K_{11}}{\gamma} (K_{21} + T - T_{g1}) \quad (6)$$

If it is further assumed that the thermodynamics of the polymer-solvent system are described by the Flory-Huggins theory (33) with an interaction parameter,  $\chi$ , which is independent of concentration, the thermodynamic term becomes

$$Q = (1 - \phi_1)^2 (1 - 2\chi\phi_1) \quad (7)$$

In the above equations, the subscripts 1 and 2 refer to solvent and polymer respectively. Also,  $D_0$  is a constant preexponential factor,  $\omega_i$  is the mass fraction of component  $i$ ,  $\hat{V}_i^*$  is the specific critical hole free-volume of component  $i$  required for a jump, and  $\phi_i$  is the volume fraction of component  $i$ . Furthermore,  $T_{gi}$  is the glass transition temperature of component  $i$ ,  $K_{11}$  and  $K_{21}$  are free-volume parameters for the solvent,  $K_{12}$ ,  $K_{22}$  are free-volume parameters for the polymer, and  $\gamma$  is an overlap factor for free-volume. In addition,  $\hat{V}_{FH}$  is the hole free volume per gram of mixture,  $\hat{V}_{FH}(0)$  is the specific hole free volume of the pure polymer at temperature,  $T$ , and  $\hat{V}_{FH}(1)$  is the specific hole free volume of the pure solvent at  $T$ . Finally,  $\xi$  is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume for the polymer jumping unit, and  $E$  is the energy per mole that a molecule needs to overcome attractive forces, which hold it to its neighbor. The definitions of the free-volume parameters,  $K_{11}$ ,  $K_{21}$ ,  $K_{12}$ , and  $K_{22}$ , are given in the literature (27). These four constants are directly related to the WLF constants of the solvent

and polymer (24).

All the parameters in these relationships can be determined from density data, thermodynamic data, and viscosity data for the pure components except  $D_0$ ,  $E$ , and  $\xi$ . In the present state of development of the theory, a limited amount of diffusivity data is required to evaluate these parameters. Once these parameters have been established for a given system, the mutual binary diffusion coefficient can be predicted for a broad range of concentration and temperature. The predictive and correlative capabilities of this theory have been clearly demonstrated in the literature (29). For example, Figure 1 shows that a few data points at a low concentration can be used to determine parameters for the free-volume theory and hence predict diffusional behavior over a wide concentration range. The line represents the predic-

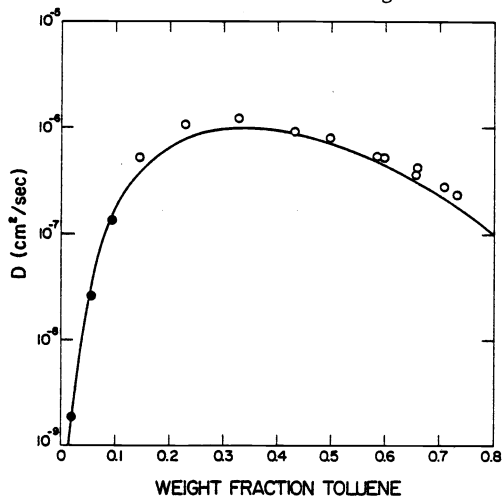


Figure 1. Demonstration of the predictive capabilities of the free-volume theory, using toluene-polystyrene diffusivity data at 110°C. Only data points represented by solid symbols were used to obtain the prediction represented by the line.

tion based on the data points represented by solid symbols in this figure. This theory has also been used to predict the concentration and temperature dependency of  $D$  from a few data points, and concentration dependency from information concerning only the temperature behavior of this transport coefficient (29).

The polystyrene-toluene system presented in Figure 1 exhibits diffusional behavior which is characteristic of many polymer-solvent systems. The rapid increase in diffusivity at low solvent concentrations is due to the high free-volume associated with the solvent. The coupling of the influence of the free-volume on the self-diffusion coefficient and the thermodynamic factor can cause the mutual binary diffusion coefficient to attain a maximum value at some intermediate concentration as shown in Figure 1. The relationships between the self-diffusion coefficient and the thermodynamic factor with concentration are shown in Figure 2 for this system.

Although the majority of investigations utilizing free-volume concepts to describe diffusional behavior have considered the polymer solution in an equilibrium liquid state above  $T_g$ . The theory has been extended to predict the influence of the glass transition on diffusivity (33). A glassy, non-equilibrium state is attained during cooling of a polymer solution when the rate of cooling is fast compared to the relaxation of the polymer chains. Consequently, below  $T_g$ , a non-equilibrium state exists which contains more free-volume than the equilibrium state. If the change in the expansion coefficient of the solution in the vicinity of  $T_g$  is idealized as a step change, then the free-volume theory can be used to predict a temperature dependency of diffusion coefficient for a trace amount of solvent in the polymer (33):

$$\ln\left(\frac{D(T)}{D(T_{g2})}\right) = \frac{\gamma V_2^* \xi}{K_{12}} \frac{T - T_{g2}}{K_{22}[(K_{22}/\lambda) + T - T_{g2}]} \quad (8)$$

All the parameters in this equation except  $\lambda$  can be determined from data obtained above the glass transition temperature. The parameter  $\lambda$  is related to the volume characteristics of the polymer above and below the glass transition. This parameter describes the character of the volume contraction which can be attributed to the glass transition (33). Clearly an infinite number of non-equilibrium liquid structures can be realized below  $T_g$  depending on

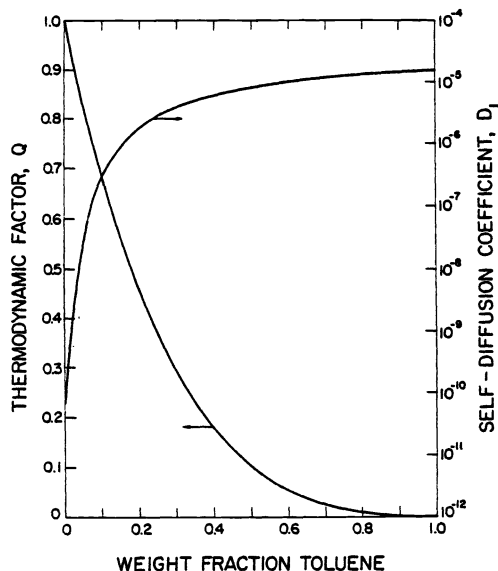


Figure 2. The concentration dependency of the self-diffusion and thermodynamic terms of the free-volume theory for the toluene-polystyrene system at 110°C.

the history of the material. If  $\lambda=1$ , the equilibrium liquid structure is realized at all temperatures above and below  $T_g$ . At the other extreme, if  $\lambda=0$ , the hole free-volume at  $T_g$  is available at all temperatures below this transition. The general characteristics of this free-volume theory are illustrated in Figure 3. If an equilibrium structure was maintained

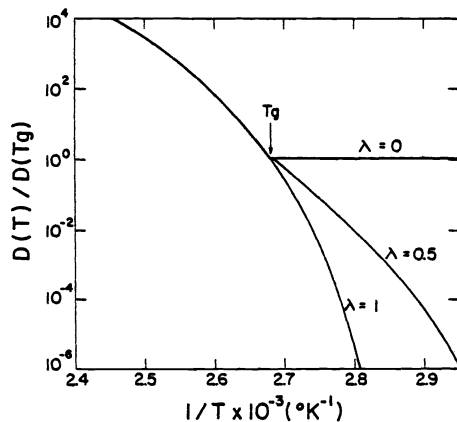


Figure 3. Free-volume theory prediction of the influence of the glass transition on the diffusivity of a trace amount of solvent in a polymer. Calculations are based on parameters which approximate the behavior of the polystyrene-toluene system. The parameter,  $\lambda$ , is related to the change in the thermal expansion coefficient of the polymer at  $T_g$ .

at all temperatures, a glassy state would not be attained and the diffusion coefficient would be a smooth function of temperature. On the other hand, if all the free volume available at  $T_g$  was maintained as the temperature was lowered, the diffusivity would not decrease with temperature. As Figure 3 indicates, actual behavior falls in between these two extremes where  $0 < \lambda < 1$ , and an abrupt change in the temperature dependency of  $D$  can be observed. The predictions of the free-volume theory for the influence of the glass transition on diffusion in amorphous polymers are consistent with the available data for amorphous polymer-solvent systems.

## CONCLUSIONS

The preliminary discussion clearly showed that molecular diffusion is an important phenomena in many polymer formation and processing operations. Most of these applications involve mutual binary diffusion in concentrated polymer solutions above the glass transition. Molecular diffusion in such systems can be described by a free-volume theory which utilizes pure component viscosity data as well as density and phase equilibria information to predict and correlate diffusion coefficients. Free-volume concepts can also be utilized to predict the influence of the glass transition on diffusion behavior. More work is needed to extend this theory to incorporate complications such as crosslinking, ternary diffusion with two solvent, and orientation effects.

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