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Antiplasticization and Volumetric Behavior in Glassy Polymers

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ABSTRACT: A model is proposed for understanding changes in the volumetric and the free-volume properties of a glassy polymer upon addition of a low molecular weight diluent. The proposed theory for volumetric behavior appears to describe the negative departures from volume additivity that have been observed experimentally in glassy polymer–diluent systems. An expression is derived for the concentration dependence of the specific hole free volume in a glassy polymer–diluent mixture. This expression is used to explain antiplasticization behavior in glassy polymers and to rank the antiplasticization effectiveness of various diluents that are added to a particular polymer glass.

Introduction

When certain low molecular weight materials are added to glassy polymers, motions in the polymer chain appear to be retarded, and the mechanical behavior of the material is the opposite of that observed when plasticizers are added to a polymer. This type of behavior has been termed antiplasticization, and it is thought that this phenomenon is somehow related to a loss in free volume and a subsequent suppression of motions in the polymer chain.[1-4] Volumetric data for polymer–diluent mixtures have shown a significant negative departure from volume additivity,[2,3] and its seems reasonable to suppose that this leads to a loss in the free volume of the system. Although this general picture appears plausible, there has been no comprehensive attempt to provide a quantitative description of the volumetric and free-volume behavior of glassy polymer–diluent systems. The objective of this article is thus to propose a model for understanding changes in the volumetric and the free-volume properties of a glassy polymer upon addition of a low molecular weight diluent.

Since glassy polymer properties are history dependent, this model is necessarily restricted, in the strictest sense, to polymer–diluent samples that are prepared in a prescribed manner. However, the sample preparation history that will be utilized is a reasonable one, and, furthermore, the formulation of a quantitative model leads to a better general understanding of antiplasticization and of volumetric behavior in glassy polymers even when different sample preparation histories are used. The assumptions used in the model are listed in the second section of the paper, and predictions of the theory are developed in the third section. A comparison of the theory with experimental data is presented in the final section.

Assumptions of the Model

The following assumptions are used in the development of a theory describing the volumetric behavior of polymer–diluent systems in the glassy state:

(1) Transport behavior in the glassy polymer–diluent mixture is governed by the amount of specific hole free volume in the polymeric system.

(2) For most of the calculations carried out in this article, the various volumes required for the theory are calculated by using thermal expansion coefficients that are approximated by average values in the temperature range under consideration. Furthermore, for all expansion coefficients utilized in the theory and for the temperature intervals of interest, it is assumed that approximations of the type

$$\exp[\alpha_2(T - T_{g2})] = 1 + \alpha_2(T - T_{g2}) \qquad (1)$$

are sufficiently accurate. In this equation, α_2 is the thermal expansion coefficient for the equilibrium liquid polymer, and T_{g2} is the glass transition temperature of the pure polymer.

(3) The theoretical development is simplified if it is assumed that the rapid change in the expansion coefficient of the pure polymer in the vicinity of T_{g2} can be idealized as a step change from α_{2g}, the thermal expansion coefficient of the glassy polymer, to α_2 at T_{g2}.

(4) The specific volume, $\hat{V}$, of the equilibrium liquid mixture is given by

$$\hat{V} = \omega_1 \hat{V}^0_1 + \omega_2 \hat{V}^0_2 \tag{2}$$

at a given concentration at temperatures both above and below T_{gm}, the glass transition temperature of the polymer–diluent mixture. Here, $\hat{V}^0_1$ is the specific volume of the pure liquid diluent, $\hat{V}^0_2$ is the specific volume of the pure equilibrium liquid polymer, and ω_I is the mass fraction of component I. It is thus assumed that the equilibrium liquid structure is formed from pure polymer and pure diluent with no volume change on mixing. It is of course not generally possible to observe the equilibrium liquid structure below T_{gm} for transport experiments of conventional duration since a nonequilibrium liquid or glassy structure exists in this temperature range.

(5) At temperatures below T_{gm}, the polymer–diluent system exists as a nonequilibrium liquid structure at a given concentration, and it is assumed that this structure remains effectively invariant during any experiments carried out on the polymer–diluent mixture. Furthermore, it is assumed that the glassy polymer–diluent system is formed such that there is no volume change on mixing at each concentration and temperature. Hence, the specific volume of the mixture is computed by assuming that the volumes contributed by the diluent and by the glassy polymer are additive at a particular concentration:

$$\hat{V} = \omega_1 \hat{V}^0_1 + \omega_2 \hat{V}^0_{2g} \tag{3}$$

In this equation, $\hat{V}^0_{2g}$ is the appropriate specific volume of the glassy polymer used to form the nonequilibrium mixture at some temperature below T_{gm}. The volumetric properties of the nonequilibrium liquid or glassy polymer–diluent mixture are thus computed by using the glassy volumetric behavior of the pure polymer and the equilibrium liquid volume of the diluent. The temperature of the system is taken to be higher than the glass transition temperature of the diluent.

(6) The value of $\hat{V}^0_{2g}$ that is to be used in eq 3 will depend on how the polymer-solvent system is prepared because of the history dependence of the properties of glassy polymers. It is supposed here that the polymer–diluent system is formed by first mixing the materials at some temperature above T_{gm}, and then the mixture is cooled to the desired temperature below T_{gm} by using a conventional experimental time scale. This procedure is certainly a plausible one for forming glassy polymer–diluent mixtures, but there are of course other expeirmentally feasible possibilities for preparing glassy polymer samples. For the particular sample history described above, it is proposed that $\hat{V}^0_{2g}$, the specific volume of the pure glassy polymer at some temperature T below T_{gm}, is given by the following equation:

$$\hat{V}^0_{2g} = \hat{V}^0_2(T_{gm})[1 + \alpha_{2g}(T - T_{gm})] \tag{4}$$

Here, $\hat{V}^0_2(T_{gm})$ is the specific volume of the equilibrium liquid polymer at T_{gm}, and α_{2g} is the same thermal expansion coefficient that is measured for the glassy state as the pure polymer is cooled below T_{g2}, its glass transition temperature. There exists some experimental justification for using eq 4 with a *single* value of α_{2g} to calculate $\hat{V}^0_{2g}$ below the glass transition temperature at all diluent concentrations of interest. It can be easily shown that the following equation can be derived for $\Delta\alpha$, the difference in the thermal expansion coefficients for the polymer–solvent system above and below the glass transition temperature of the mixture:

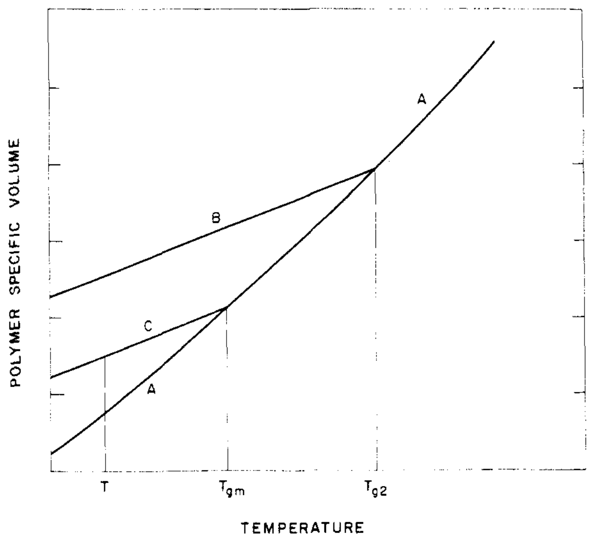

Figure 1. Volume–temperature behavior of an amorphous polymer: A, volume of equilibrium liquid; B, volume of pure polymer glass; C, volume of polymer glass in mixture of polymer and diluent.

$$\Delta\alpha = \alpha^+_m - \alpha^-_m = \phi_2(\alpha_2 - \alpha_{2g}) \tag{5}$$

In this equation, α^+_m is the thermal expansion coefficient of the polymer–diluent system in the liquid state at T_{gm}, α^-_m is the thermal expansion coefficient of the mixture in the glassy state at T_{gm}, and ϕ_2 is the volume fraction of polymer. From eq 5, it is clear that $\Delta\alpha$ will be linear in ϕ_2 if it is assumed that a single value of α_{2g} describes the jump in expansion coefficients for all solvent concentrations. It has been proposed previously[5] that $\Delta\alpha$ should be linear in the volume percent of diluent added, and Jenckel and Ueberreiter[6] have presented volume contraction data for the polystyrene–paraffin oil system that are in reasonable agreement with eq 5. We thus conclude that eq 4, with the same value of α_{2g} for all diluent concentrations, satisfactorily describes the volumetric behavior of the glassy polymer in a mixture below T_{gm}, where the combined polymer–diluent system is a glass. Finally, the equilibrium specific volume of the polymer is given by the expression

$$\hat{V}^0_2 = \hat{V}^0_2(T_{gm})[1 + \alpha_2(T - T_{gm})] \tag{6}$$

at a temperature T either above or below T_{gm}. The volumetric behavior of the polymer, as described in the proposed model, is illustrated in Figure 1.

Theory

The model for the glassy state presented in the previous section will now be used to explain the significant negative departures from volume additivity that have been observed[2,3] experimentally for polymer–diluent systems. Also, it is shown why the partial specific volumes of diluents in glassy polymer–diluent mixtures are significantly smaller than the specific volumes of the pure liquid diluents and also smaller than diluent partial specific volumes measured in diluent–diluent mixtures.[2,3] In addition, an expression is derived for the concentration dependence of the specific hole free volume in the glassy polymer–diluent mixture.

Before these results are presented, it is useful to comment on the volume additivity assumption introduced above for a nonequilibrium liquid structure. For a diluent–diluent mixture, it is sometimes assumed that the partial specific volumes of the two components are essentially independent of concentration at a particular temperature. This assumption immediately leads to the result that there is no volume change on mixing (volume additivity) at all concentrations. For the glassy polymer–diluent mixture, it is assumed here that there is volume additivity at *each* concentration in the sense that the volumes contributed by the pure solvent and by the glassy polymer can be added together. However, since T_{gm} must of course depend on the concentration of diluent, it is clear from eq 4 that $\hat{V}^0_{2g}$ is a function of concentration. This concentration dependence of $\hat{V}^0_{2g}$ is simply a result of the fact that the molecular structure of the glassy polymer is different at each concentration. Furthermore, since the structure of the nonequilibrium liquid changes as the concentration of diluent is increased, it is not strictly permissible to utilize the usual formulas to extract polymer and diluent partial specific volumes from specific volume–mass fraction data for the mixture. In general, the specific volume of a glassy polymer–diluent system is a function of molecular structure or molecular order, temperature, pressure, and concentration,[7] so that the usual thermodynamic relationships cannot be directly utilized.

An ideal or additive specific volume for a glassy polymer-diluent mixture can be defined as[2]

$$\hat{V}(\text{ideal}) = \omega_1\hat{V}^0_1 + \omega_2\hat{V}^0_{2g}(\omega_1=0) \tag{7}$$

so that the excess specific volume, $\Delta\hat{V}$, at a particular mass fraction ω_1 for the glassy polymer–diluent system can be determined from the following expression:

$$\Delta\hat{V} = \omega_1(\hat{V}_1 - \hat{V}^0_1) + \omega_2[\hat{V}^0_{2g}(\omega_1) - \hat{V}^0_{2g}(\omega_1=0)] \tag{8}$$

Here, $\hat{V}_1$ is the partial specific volume of the diluent in the mixture. It has been assumed above that $\hat{V}_1 = \hat{V}^0_1$, the specific volume of the pure liquid diluent. Furthermore, the value of $\hat{V}^0_{2g}$ at a particular mass fraction can be computed by using eq 4. This equation can be simplified by using the following equation to relate $\hat{V}^0_2(T_{gm})$ to $\hat{V}^0_2(T_{g2})$

$$\hat{V}^0_2(T_{gm}) = \hat{V}^0_2(T_{g2})[1 - \alpha_2(T_{g2} - T_{gm})] \tag{9}$$

and by introducing a linear approximation for the concentration dependence of T_{gm}:[8]

$$T_{gm} = T_{g2} - A\omega_1 \tag{10}$$

The coefficient A depends on the nature of the diluent used to depress the glass transition temperature for a particular polymer.

Combination of eq 4, 9, and 10 produces the equation

$$\hat{V}^0_{2g} = \hat{V}^0_2(T_{g2})[1 - A\alpha_2\omega_1 + \alpha_{2g}(T - T_{g2} + A\omega_1)] \tag{11}$$

and utilization of this expression in eq 8 gives the following result for $\Delta\hat{V}$:

$$\Delta\hat{V} = -A\omega_1\omega_2\hat{V}^0_2(T_{g2})(\alpha_2 - \alpha_{2g}) \tag{12}$$

Clearly

$$\Delta\hat{V} < 0 \tag{13}$$

and the negative departure from volume additivity is simply a consequence of the particular form of the concentration dependence of $\hat{V}^0_{2g}$. A comparison of experimental values of $\Delta\hat{V}$ with those computed from the theory is presented below.

For a diluent–diluent system for which the specific volume of the mixture is a function only of temperature, pressure, and composition, the partial specific volumes, $\hat{V}_1$ and $\hat{V}_2$, of the components of the mixture can be calculated by using the following two equations, if data are available for the concentration dependence of the specific volume of the mixture:

$$\hat{V} = \omega_1\hat{V}_1 + \omega_2\hat{V}_2 \tag{14}$$

$$(\partial\hat{V}/\partial\omega_1)_{T,p} = \hat{V}_1 - \hat{V}_2 \tag{15}$$

These two equations yield the following explicit result for $\hat{V}_1$:

$$\hat{V}_1 = (1 - \omega_1)(\partial\hat{V}/\partial\omega_1)_{T,p} + \hat{V} \tag{16}$$

As noted above, it is not generally possible to utilize these equations directly in the determination of the partial specific volumes for glassy polymer–diluent systems. The specific volume for a glassy polymer–diluent mixture depends on molecular structure[7] as well as on temperature, pressure, and composition, and the structure or molecular order of the polymer generally changes as the composition is varied at fixed temperature and pressure. Consequently, it is not in general possible to calculate the mass fraction derivative in eq 16 since the composition of the mixture cannot usually be changed at fixed values of the molecular ordering parameters.[7] Thus, it is to be expected that the calculation of $\hat{V}_1$ from eq 16 for a mixture of diluent and glassy polymer will give an anomalous result because a change in composition generally leads to a change in molecular order for glassy polymeric systems.

It is nevertheless instructive to see what result is obtained if eq 16 is used to calculate $\hat{V}_1$ for a glassy polymer–diluent system in the limit of zero diluent concentration:

$$\hat{V}_1(\omega_1=0) = (\partial\hat{V}/\partial\omega_1)_{\omega_1=0} + \hat{V}^0_{2g}(\omega_1=0) \tag{17}$$

For the mixture of diluent and glassy polymer, $\hat{V}$ is given by eq 3 and $\hat{V}^0_{2g}$ by eq 11. Utilization of these equations in eq 17 gives

$$\hat{V}_1(\omega_1=0) = \hat{V}^0_1 - A\hat{V}^0_2(T_{g2})(\alpha_2 - \alpha_{2g}) \tag{18}$$

Clearly, the calculated partial specific volume of the diluent can be significantly less than the specific volume of the pure solvent. Again, this anomalous result, which has been observed experimentally,[2,3,9] is simply a consequence of the particular form of the concentration dependence of $\hat{V}^0_{2g}$. For a diluent–diluent mixture, for which an equation of the form of eq 2 can be applied, it is clear that eq 17 will yield the usual result, $\hat{V}_1(\omega_1=0) = \hat{V}^0_1$.

We conclude this section by deriving an expression for the specific hole free volume, $\hat{V}_{FH}$, for the glassy polymer–diluent system. Below T_{gm}, the average hole free volume per gram of mixture can be expressed as

$$\hat{V}_{FH} = \omega_2(\hat{V}^0_{2g} - \hat{V}^0_2) + \omega_1\hat{V}_{FH1} + \omega_2\hat{V}_{FH2} \tag{19}$$

where $\hat{V}_{FH1}$ is the specific hole free volume of the pure solvent at the temperature of interest, T, and $\hat{V}_{FH2}$ is the specific hole free volume of the pure equilibrium liquid polymer at T. Substitution of eq 4 and 6 into eq 19 yields the expression

$$\hat{V}_{FH} = \omega_2\hat{V}^0_2(T_{gm})(T - T_{gm})(\alpha_{2g} - \alpha_2) + \omega_1\hat{V}_{FH1} + \omega_2\hat{V}_{FH2} \tag{20}$$

and introduction of eq 9 and 10 produces the following result:

$$\hat{V}_{FH} = \omega_2\hat{V}^0{}_2(T_{g2})(1 - A\omega_1\alpha_2)(T - T_{g2} + A\omega_1) \times (\alpha_{2g} - \alpha_2) + \omega_1\hat{V}_{FH1} + \omega_2\hat{V}_{FH2} \quad (21)$$

The effect of adding diluent on the hole free volume of the system can be assessed by evaluating the mass fraction derivative of $\hat{V}_{FH}$ at $\omega_1 = 0$:

$$(\partial\hat{V}_{FH}/\partial\omega_1)_{\omega_1=0} = -\hat{V}^0{}_2(T_{g2})(\alpha_2 - \alpha_{2g})(T_{g2} - T) \times [1 + A\alpha_2 + A/(T_{g2} - T)] + \hat{V}_{FH1} - \hat{V}_{FH2} \quad (22)$$

Expressions for $\hat{V}_{FH1}$ and $\hat{V}_{FH2}$, in terms of the free-volume parameters of the diluent and polymer, are presented elsewhere.[10]

Equation 22 provides a useful interpretation of the change in $\hat{V}_{FH}$ caused by the addition of diluent to a glassy polymer. The first term in eq 22 is obviously negative and reflects a loss in free volume in the system that is enhanced by the concentration dependence of $\hat{V}^0{}_{2g}$. Specifically, as is evident from eq 11, $\hat{V}^0{}_{2g}$ decreases with increasing diluent concentration. The term $(\hat{V}_{FH1} - \hat{V}_{FH2})$ in eq 22 is generally positive since the diluent usually possesses more free volume at a particular temperature T than does the polymer. Consequently, eq 22 contains terms with different signs, and whether $\hat{V}_{FH}$ decreases or increases initially depends on the relative magnitudes of these competing terms. For diluents with very low glass transition temperatures, $\hat{V}_{FH1}$ is generally much greater than $\hat{V}_{FH2}$ for a typical polymer, and the $(\hat{V}_{FH1} - \hat{V}_{FH2})$ term is often larger in magnitude than the negative first term in eq 22. This leads to an initial increase in specific hole free volume with increasing diluent concentration, and hence the diluent has a plasticizing effect. For diluents with relatively high glass transition temperatures, $\hat{V}_{FH1}$ is not much greater than $\hat{V}_{FH2}$ of the polymer since the glass transition temperatures of the two species will be closer together. In this case, $(\hat{V}_{FH1} - \hat{V}_{FH2})$ will be relatively small, and hence the negative first term in eq 22 often leads to an initial decrease in specific hole free volume with increasing diluent concentration. Hence, the diluent acts as an antiplasticizer. Consequently, for a particular polymer, diluents that have low values of $\hat{V}_{FH1}$ (and generally relatively high glass transition temperatures) will be good candidates for creating an antiplasticization effect for this polymer. Also, it is evident from eq 22 that, for a particular polymer and a given temperature, the negative term will have a larger magnitude if A is larger. Therefore, diluents that cause a significant initial decrease in the polymer glass transition temperature will tend to enhance the possibility of an antiplasticization effect.

Different effects of adding diluents to glassy polymers can be illustrated by presenting calculations for the mass fraction dependence of $\hat{V}_{FH}$ for two systems: polystyrene–toluene at 30 °C and polysulfone (PSF)–tricresyl phosphate (TCP) at 30 °C. These calculations were carried out by using eq 20 and estimates for the volumetric, free-volume, and glass transition properties of these two systems.[2,8,10-14] The $\hat{V}_{FH}$ versus ω_1 curves for the two systems are presented in Figure 2. For the polystyrene–toluene system, there is a monotonic increase of $\hat{V}_{FH}$ with increasing ω_1, so that toluene acts as a plasticizer for the glassy polymer. On the other hand, for the PSF–TCP system, there is a decrease of $\hat{V}_{FH}$ with increasing ω_1 up to a TCP mass fraction of approximately 0.1 before $\hat{V}_{FH}$ begins to increase with increasing ω_1. Hence, TCP acts as an antiplasticizer since there is a reduction of the specific hole free volume of the polymer–diluent system relative to that of the pure polymer over 20% of the concentration range. An important aspect of the difference in the behavior of these two systems is the significant difference in the free-volume characteristics of the two diluents. Toluene has a lower glass transition temperature than TCP[8] and hence a higher specific hole free volume at 30 °C (more than 2 times as large). Consequently, the $(\hat{V}_{FH1} - \hat{V}_{FH2})$ term in eq 22 is larger for the polystyrene–toluene system, and it leads to a positive mass fraction derivative for $\hat{V}_{FH}$. For the PSF–TCP system, the $(\hat{V}_{FH1} - \hat{V}_{FH2})$ term is smaller, and hence the negative first term in eq 22 produces an initial decrease of $\hat{V}_{FH}$ with increasing ω_1.

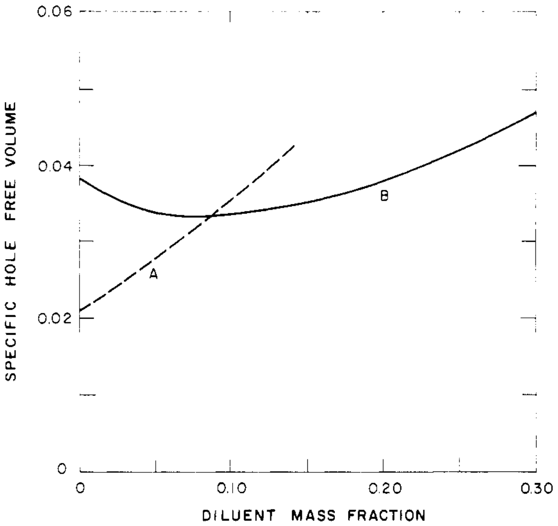

Figure 2. Mass fraction dependence of specific hole free volume for the polystyrene–toluene system at 30 °C (curve A) and for the PSF–TCP system at 30 °C (curve B).

Table I
Materials Used

name	abbreviation	physical characteristics at 30 °C
polysulfone	PSF	glassy polymer
4,4′-dichlorodiphenyl sulfone	DDS	solid
N-phenyl-2-naphthylamine	PNA	solid
tricresyl phosphate	TCP	liquid
poly(phenylene oxide)	PPO	glassy polymer
bis(2-ethylhexyl) phthalate	DOP	liquid
dioctyl sebacate	DOS	liquid

Data–Theory Comparisons

Some of the predictions of the theoretical results presented above are now compared with experimental data collected by Maeda and Paul.[2-4] It is important to emphasize that the glassy polymer–diluent samples used by Maeda and Paul were prepared by a solvent casting procedure that is of course a different sample preparation history than the one used above in the theoretical development. Consequently, a direct comparison of the theoretical predictions with the experimental results of Maeda and Paul is not strictly justified. However, we believe that such a comparison is instructive since no other theory for describing antiplasticization and volumetric behavior in glassy polymers is available and since the experimental data may not be overly sensitive to the exact nature of the sample preparation history. Furthermore, there is some similarity between the glassy polymer history used by Maeda and Paul and the one used to develop the theory.

Maeda and Paul[2,3] reported specific volume and excess specific volume data for the following six polymer–diluent systems: PSF–TCP, PSF–PNA, PSF–DDS, PPO–TCP, PPO–DOP, and PPO–DOS. A list of the materials used, their abbreviations, and their physical characteristics at 30 °C are presented in Table I. Since three of the diluents listed in this table are liquids at the temperature of in-

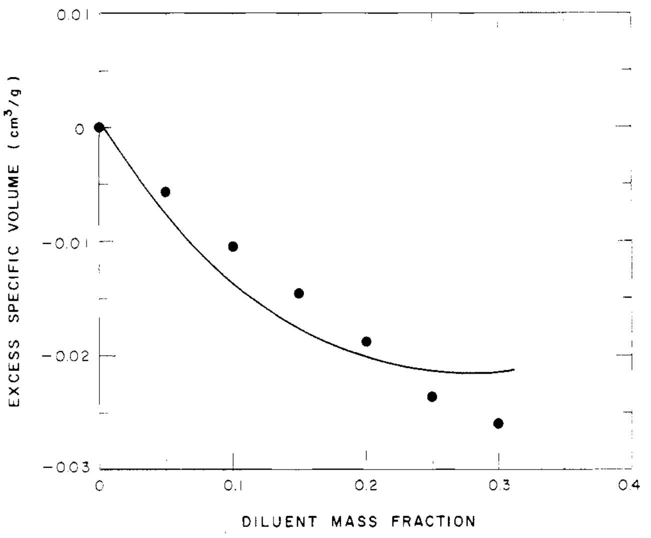

Figure 3. Mass fraction dependence of excess specific volume for the PSF–TCP system at 30 °C. The curve represents predictions of theory, and solid circles are data collected by Maeda and Paul.[2]

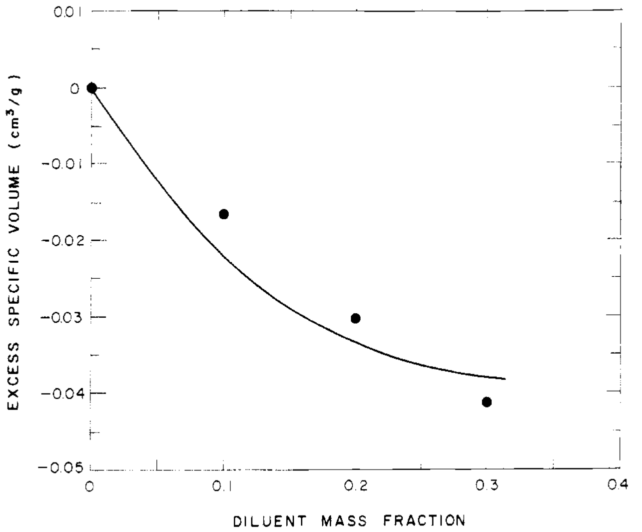

Figure 4. Mass fraction dependence of excess specific volume for the PPO–TCP system at 30 °C. The curve represents predictions of theory, and solid circles are data collected by Maeda and Paul.[3]

terest, 30 °C, it is possible to estimate the partial specific volume of the diluent by using $\hat{V}^0_1$ for these materials. Comparisons of the predictions of the theory with experimental data for four of the above systems are presented in Figures 3–6. The theoretical calculations were carried out by using available volumetric data for the pure polymer and data for the effect of diluent concentration on the glass transition temperature of the system.[2,3,14,15] The experimental results for $\Delta \hat{V}$ were in all cases computed by using the expression for the ideal volume of the mixture given by eq 7 with values of $\hat{V}^0_1$ taken to be the pure diluent specific volumes reported by Maeda and Paul.[2,3] It is evident from the comparisons presented in Figures 3–6 that there is reasonably good agreement between theory and experiment even though the sample preparation histories for the theory and experiment are different. It should also be noted that there may be some error introduced by the assumption that the partial specific volume of the diluent is equal to $\hat{V}^0_1$ since this is not generally true even for diluent–diluent systems. It is clear that the proposed theory for volumetric behavior appears to describe the negative departures from volume additivity observed in glassy polymer–diluent systems both qualitatively and, with reasonably good accuracy, quantitatively.

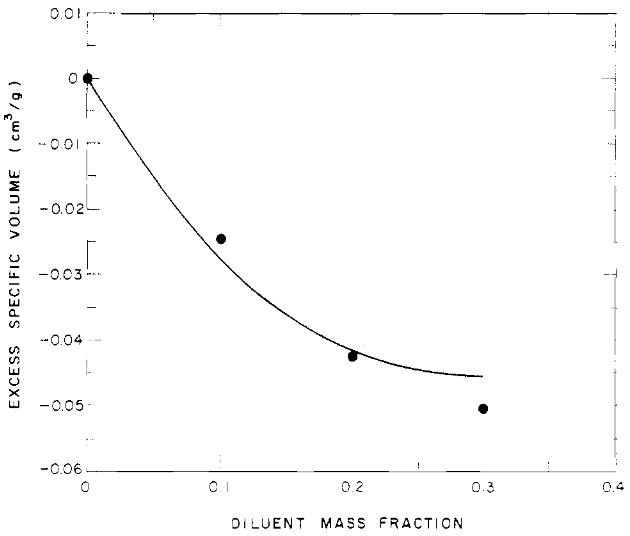

Figure 5. Mass fraction dependence of excess specific volume for PPO–DOS system at 30 °C. The curve represents predictions of theory, and solid circles are data collected by Maeda and Paul.[3]

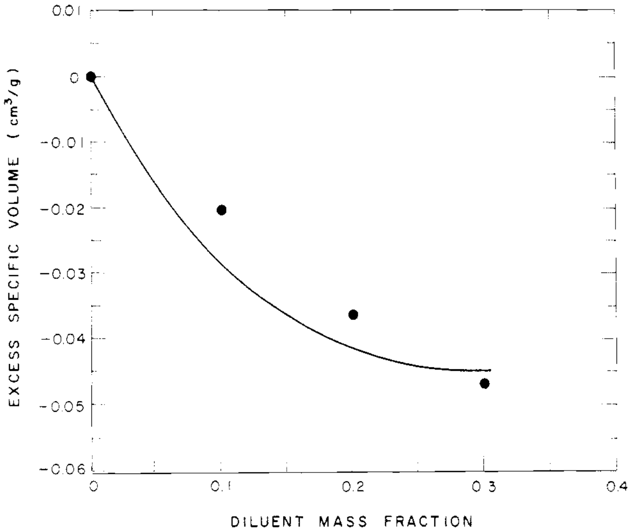

Figure 6. Mass fraction dependence of excess specific volume for PPO–DOP system at 30 °C. The curve represents predictions of theory, and solid circles are data collected by Maeda and Paul.[3]

One important aspect of understanding antiplasticization behavior in glassy polymers is the explanation of why some diluents are better antiplasticizers for a particular polymer than others. If the hypothesis that the mechanical and transport behavior in a glassy polymer depends strongly on the specific hole free volume of the system is accepted, then it is clear that the better antiplasticizers are those that lead to a larger decrease in free volume as the diluent is added to the polymer. Consequently, at small diluent concentrations, eq 22 can be used to rank antiplasticizers. Diluents that are antiplasticizers will of course produce a negative value for the mass fraction derivative of $\hat{V}_{FH}$ that is given by eq 22. Among those diluents with negative derivatives, those with the larger absolute values will rank as better antiplasticization agents. In their study of antiplasticization in PSF and PPO, Maeda and Paul[2,3] used mechanical and transport data to obtain the following rankings for diluents for the extent of antiplasticization:

$$\text{PNA} > \text{DDS} > \text{TCP} \quad \text{for PSF} \tag{23}$$

$$\text{TCP} > \text{DOP} > \text{DOS} \quad \text{for PPO} \tag{24}$$

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Table II
Initial Concentration Dependence of $\hat{V}_{FH}$ for Six Systems at 30 °C

system	$[(1/\hat{V}_{FH})(\partial \hat{V}_{FH}/\partial \omega_1)]_{\omega_1=0}$
PSF–TCP	−2.25
PSF–DDS	−2.79
PSF–PNA	−2.99
PPO–DOS	−2.03
PPO–DOP	−2.51
PPO–TCP	−3.26

Calcultions based on eq 22 were carried out for the above six glassy polymer–diluent systems by using estimates for the volumetric, free-volume, and glass transition properties of these systems.[2,3,8,14,15] The results for the mass fraction derivative for $\hat{V}_{FH}$ at $\omega_1 = 0$ are presented in Table II, and it is evident that the theoretical predictions for antiplasticization effectiveness are equivalent to the rankings deduced by Maeda and Paul from their experiments. Consequently, it is fair to conclude that the free-volume equation proposed above appears to provide a reasonable description of antiplasticization effectiveness in glassy polymer–diluent systems.

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Registry No. DDS, 80-07-9; PNA, 135-88-6; TCP, 1330-78-5; PPO (homopolymer), 25134-01-4; PPO (SRU), 24938-67-8; DOP, 117-81-7; DOS, 2432-87-3.

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Thermolysis and Photochemical Acidolysis of Selected Polymethacrylates

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ABSTRACT: Thermal behavior and thermolytic deprotection catalyzed by photochemically generated $HSbF_6$ in the solid state have been investigated for atactic polymethacrylates having benzyl, α-methylbenzyl, α,α-dimethylbenzyl, and *tert*-butyl ester groups as well as cyclopropyl carbinol esters. Ease of thermolysis to convert polymethacrylates to poly(methacrylic acid) and to poly(methacrylic anhydride) is very much dependent on the ester groups. The dimethylbenzyl and dimethyl cyclopropyl carbinol esters are converted first to poly(methacrylic acid) and then to anhydride, while poly(*tert*-butyl methacrylate) is rather directly converted to the anhydride due to the higher deprotection temperature, poly(benzyl methacrylate) depolymerizes without much deprotection, and the methylbenzyl ester exhibits depolymerization and deprotection/dehydration. Sensitivity of these polymethacrylates to photochemically induced acidolysis is very much reflected by the thermal deprotection temperatures except for the cyclopropyl carbinol esters, which possess the lowest deprotection temperature in the series but suffer from concomitant rearrangement to a thermally stable primary ester. The thermal rearrangement of the cyclopropyl carbinol ester is more pronounced in the presence of acids. These polymethacrylate films containing a photosensitive acid generator such as arylsulfonium salts can be lithographically imaged in either positive or negative mode depending on choice of a developer solvent owing to the change in polarity resulting from conversion of nonpolar ester to polar acid. Poly(*tert*-butyl methacrylate) allows image reversal owing to its thermal stability at the temperature at which poly(methacrylic acid) and copolymers of methacrylic acid and *tert*-butyl methacrylate undergo anhydride formation.

Introduction

tert-Butyl esters and carbonates readily undergo A_{AL} 1-type acid-catalyzed deesterification in a reaction that does not require a stoichiometric amount of water to produce isobutene/acid and isobutene/carbon dioxide/alcohol, respectively. The polarity change induced by a radiochemically generated acid in the solid state has allowed the design of dual tone resist materials with a very high sensitivity due to the catalytic nature of the reaction (chemical amplification).[2–5] Such polymers included poly(*tert*-butyl methacrylate) (PTBMA), poly(*tert*-butyl *p*-vinylbenzoate) (PTBVB), and poly(*p*-(*tert*-butoxycarbonyloxy)styrene) (PBOCST). Ito et al.[5] have recently studied the effect of the structure of the esters on the photochemical sensitivity of poly(*p*-vinylbenzoates) sensitized with a sulfonium salt cationic photoinitiator and found that the thermal deprotection temperature of these poly(vinylbenzoates) is a good measure of the sensitivity.

PTBMA and poly(methacrylic acid) (PMAA) are converted thermally to poly(methacrylic anhydride) (PMAN) when heated to temperatures above 200 °C as first reported by Grant and Grassie.[6] Matsuzaki et al.[7] have

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