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The effect of molar volume on the swelling of poly(dimethylsiloxane) in fluorocarbon fluids

Ferenc Horkay, William K. Waldron Jr and Gregory B. McKenna*
Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
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The vapour sorption of three fluorocarbon fluids (tetrafluoroethane, chlorotetrafluoroethane, and heptafluoropropane) has been measured in crosslinked and uncrosslinked poly(dimethylsiloxane) as a function of the temperature in the interval 35–105°C. For a given solvent, the swelling activity parameter, S, for the solvent/crosslinked polymer system decreases as both the degree of swelling and the temperature increase. The range of experimental conditions examined allowed consideration of S for different solvents, but constant molar volume, V_1. Plots of S as a function of degree of swelling can be reduced to families of curves at constant V_1 for the three solvents studied here. The dependence of S on solvent quality and temperature is then encompassed in its variation with V_1.

(Keywords: poly(dimethylsiloxane); fluorocarbon fluids; Frenkel–Flory–Rehner hypothesis; swelling activity parameter)

Introduction

There has been considerable recent activity in the search for alternatives to CF_3Br as a fire suppressant due to its high ozone depletion potential. An important part of this search is an understanding of the compatibility of storage vessel components with the different agents. Included in these components are elastomeric 'O'-ring seals. The seal compatibility is primarily determined by the polymer/liquid interaction and we have been performing isopiestic (constant vapour pressure) measurements to evaluate the compatibility of model, as well as commercial, elastomers with candidate substitute fire suppressant agents. Here we report on the swelling behaviour of poly(dimethylsiloxane) (PDMS) in a range of fluorocarbon fluids at various temperatures and pressures. As presented below, we find that, in contradiction to the Frenkel–Flory–Rehner (FFR) hypothesis, the swelling activity parameter S depends on the chemical quality of the solvent. Rather, it is shown that plots of S as a function of degree of swelling can be reduced to families of curves at constant molar volume V_1, independent of solvent quality. The dependence of S on solvent quality and temperature, then, are encompassed in its variation with V_1.

Theoretical considerations

Swelling is generally postulated to be describable within the context of the FFR hypothesis[1–3] that the free energy of mixing and the elastic free energy of the swollen network are additive. In isopiestic measurements Gee *et al.*[4] defined a quantity:

$$S = \lambda_s \ln(a_c/a_u) \tag{1}$$

where λ_s is the isotropic stretch of the network ($= \phi^{-1/3}$); a is the activity of the diluent; the subscripts c and u refer to the crosslinked and uncrosslinked polymers, respectively; ϕ is the volume fraction of polymer, and we refer to S as the swelling activity parameter. (It has also been referred to as the dilational modulus[5–7].) If the mixing contribution to the free energy for the uncrosslinked polymer and the network are the same, then S represents the elasticity of the network. In recent works[8–13], however, it has been shown that the mixing contributions to the free energy of the gel and the solution may be different. Here, we simply consider that S represents a difference in free energies between the crosslinked and uncrosslinked systems, whose full origins remain unexplained by current theories. It seems to depend upon such parameters as volume fraction, temperature, and degree of crosslinking, as well as solvent chemical composition.

Within the framework of the FFR hypothesis[1–3], and the use of the Flory–Huggins model[3] for the description of the thermodynamics of mixing, we can define the activities a_c and a_u of the crosslinked and uncrosslinked systems, respectively:

$$\ln(a_u) = \ln(P/P^0) = [\ln(1-\phi) + (1-1/n)\phi + \chi_u\phi^2] \tag{2}$$

$$\ln(a_c) = \ln(P/P^0) = [\ln(1-\phi) + \phi + \chi_c\phi^2] + V_1 w'(\lambda_s)/(RT\lambda_s^2) \tag{3}$$

where P is the vapour pressure that results in a given polymer volume fraction ϕ; P^0 is the saturation vapour pressure; n is the degree of polymerization; χ_c and χ_u are the Flory–Huggins interaction parameters for the crosslinked and uncrosslinked polymers, respectively; V_1 is the solvent molar volume; w is the elastic contribution to the Helmholtz free energy, and $w'(\lambda)$ is the derivative of w with respect to the stretch λ. In the case of swelling, λ_s is the isotropic stretch and is related to the volume

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* To whom correspondence should be addressed

fraction of the polymer in the swollen gel, as $\lambda_s = \phi^{-1/3}$. Then, the swelling activity parameter becomes:

$$S = (\chi_c - \chi_u)\lambda_s^{-5} + V_1 w'(\lambda_s)/(RT\lambda_s^2) \qquad (4a)$$

or, as used in our data analysis;

$$S/V_1 = [(\chi_c - \chi_u)\lambda_s^{-5}]/V_1 + w'(\lambda_s)/(RT\lambda_s^2) \qquad (4b)$$

If we accept that w' is a linear function of the temperature, equations (4a) and (4b) indicate that any temperature dependence of S (or S/V_1) comes from the mixing term (interaction parameters) or the temperature dependence of the molar volume. If χ_c and χ_u were equal, then S/V_1 would be a direct measure of the elasticity of the network and the volume fraction $\phi = \lambda_s^{-3}$. When other dependencies are observed, the FFR framework leads us to attribute them to the differences in the mixing between the crosslinked and uncrosslinked systems. Additionally, evaluation of S in the limit of zero swelling ($\lambda_s \rightarrow 1$) permits evaluation of the contributions to mixing thermodynamics alone, as $w'(1) = 0$. The importance of these observations becomes clear when we examine the experimental results.

In the following analysis no *a priori* assumption is made for the form of the elastic free energy function. S is derived from the difference of the amount of diluent absorbed by the crosslinked and the uncrosslinked polymers at the same vapour pressure. This is the standard procedure followed in differential sorption measurements[4]. The novelty of the present work lies in the ability to vary the molar volume of the swelling agent and the interaction energy between the polymer and the solvent in a controlled way. We were able to do this by varying the temperature in a range spanning from far below to close to the critical temperature of the diluent.

Experimental conditions

Three fluorocarbon fluids, tetrafluoroethane* (Allied Signal), chlorotetrafluoroethane* (Du Pont), and heptafluoropropane* (Great Lakes), were used in the present study. The purity of these compounds was reported by the suppliers as being 99.9 vol% or higher. The fluids were admitted to the measuring system without further purification.

Crosslinked and uncrosslinked poly(dimethylsiloxane)* (PDMS) samples were used for the vapour sorption measurements. The crosslinked polymer was prepared by vulcanization with 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexane* at 150°C for 2 h. The ratio of the monomer units of the polymer to the crosslinker could be estimated from the swelling measurements as approximately 200.

Vapour sorption isotherms were obtained in an isopiestic apparatus, which is similar to that used by McKenna and Crissman[12,13] but modified for high pressure and temperature use. The details of the current apparatus are described elsewhere[14]. A pressure charging and recovery system was built to allow the admission of the fluid into the previously evacuated vessel. The dry polymer samples were placed on quartz pans suspended from quartz springs. After pressure and temperature equilibrium were attained, the displacements of the springs were measured using a cathetometer. Mass uptakes of the polymer samples were obtained from the measured displacements of the quartz springs, corrected for buoyancy. Vapour sorption data were obtained at three temperatures (35, 70 and 105°C) and spanned a pressure range from the 0 to 2.5 MPa. For the calculation of the polymer volume fraction, ϕ, the densities of the pure poly(dimethylsiloxane)[15] and the fluorocarbon liquids (listed in *Table 1*) were used. Additivity of volumes of the solvent and polymer was assumed throughout.

Results and discussion

In *Figure 1*, the swelling activity parameter S is shown as a function of the polymer volume fraction, $\phi^{-2/3}$, for PDMS swollen in chlorotetrafluoroethane at three different temperatures (35, 70 and 105°C). The data points were obtained from the relationship:

$$S = \lambda_s \ln(P^c/P^u) \qquad (5)$$

here P^c and P^u are the solvent vapour pressures that cause a given degree of swelling (ϕ^{-1}) in the crosslinked polymer network and the uncrosslinked polymer solution, respectively. The values of P^u were interpolated at the appropriate volume fraction from a fit of the solution data to equation (2).

In *Figure 1* it can be seen that for each temperature there is a different swelling (as $\phi^{-2/3}$) dependence of S. This finding seems to be contrary to the prediction of the Frenkel–Flory–Rehner theory. As noted previously, if $\chi_c = \chi_u$, then, according to equation (4a), S is the elasticity of the network and should depend only on the swelling of the polymer, independent of the temperature. However, $S(\phi^{-2/3} = 1) > 0$, consistent with prior observations[8–13] that there are differences in the mixing thermodynamics in the gel and the solution. The results in *Figure 1* suggest that the differences between the gel and the solution decrease with swelling and that details of the differences are dependent on temperature.

Examination of equations (4a) and (4b) suggests that there might be some information to be gained by considering the molar volume of the individual solvents. Therefore, after looking at isothermal conditions (*Figure 1*), we now consider isomolar volume conditions by the appropriate choice of fluids and temperatures. In *Figure 2* we plot similar data to that of *Figure 1*, but now for constant molar volumes, rather than temperatures. As seen, the S/V_1 *versus* $\phi^{-2/3}$ data for chemically different

Table 1 Densities of fluorocarbon fluids at different temperatures

Chemical name	Temperature (°C)	Density (g cm^{-3})
Tetrafluoroethane[a]	35	1.167
	70	0.996
	105	0.622
Chlorotetrafluoroethane[a]	35	1.322
	70	1.181
	105	0.955
Heptafluoropropane[b]	35	1.351
	70	1.196

[a] Reference 16

[b] Reference 17

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* Certain commercial materials are identified in this article to specify the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, or that the materials identified are necessarily the best available for the purposes described

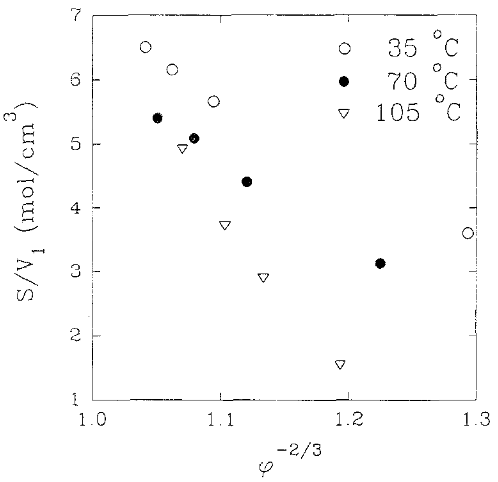

Figure 1 Plot of the swelling activity parameter, S, *versus* $\phi^{-2/3}$, for poly(dimethylsiloxane)/chlorotetrafluoroethane system at (○) 35, (●) 70 and (▽) 105°C

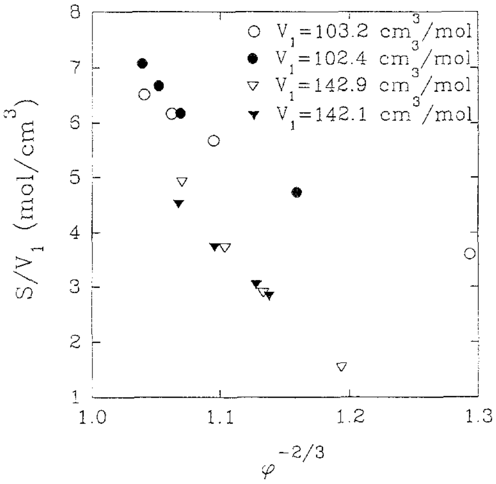

Figure 2 Plot of S *versus* $\phi^{-2/3}$ for poly(dimethylsiloxane) in different liquids. Symbols: (○) chlorotetrafluoroethane (35°C, $V_1 = 103.2\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$); (●) tetrafluoroethane (70°C, $V_1 = 102.4\,\mathrm{cm}^3\mathrm{mol}^{-1}$); (▽) chlorotetrafluoroethane (105°C, $V_1 = 142.9\,\mathrm{cm}^3\mathrm{mol}^{-1}$); (▼) heptafluoropropane (70°C, $V_1 = 142.1\,\mathrm{cm}^3\mathrm{mol}^{-1}$)

fluids having similar molar volumes collapse to the same curve. There appear to be two behaviours in *Figure 2*: one for a molar volume of $\approx 103\,\mathrm{cm}^3\mathrm{mol}^{-1}$ and one for a molar volume of $\approx 142\,\mathrm{cm}^3\mathrm{mol}^{-1}$, with the latter having a stronger dependence on $\phi^{-2/3}$.

In addition, the two sets of data seem to intercept the zero swelling line ($\phi^{-2/3} = 1$) at nearly the same point. Then, recalling equation (4b), we can comment that the non-zero value of $(\chi_c - \chi_u)$ at this point is consistent with the fact that the crosslinked PDMS has a different mixing thermodynamics from the uncrosslinked PDMS. As the network swells, S/V_1 decreases, as expected from equation (4b). However, the dependence on $\phi^{-2/3}$ is somewhat greater than might be expected for the λ_s^{-5} dependence given by the first term on the right hand sides of equations (4a) and (4b). This would suggest that $(\chi_c - \chi_u)$ decreases with swelling (increases with polymer concentration), consistent with prior results[8,9,11]. A detailed investigation of the reasons for this dependence remains the subject for a future study.

Conclusions

The solubility of fluorocarbon fluids (tetrafluoroethane, chlorotetrafluoroethane, and heptafluoropropane) in PDMS was measured in the temperature range 35–105°C. Plots of S as a function of the degree of swelling can be reduced to families of curves at constant V_1 for the solvents and temperatures studied here. The dependence of S on solvent quality and temperature then are encompassed in its variation with V_1. This reduction may be due to the fact that these solvents have very weak interactions with the PDMS elastomer.

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