Polymethyltrifluoropropylsiloxane: polymer–solvent interaction, solubility and network swelling

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The degree of swelling of polymethyltrifluoropropylsiloxane (PMTFPS) networks and the solubility of the linear polymer have been determined in a variety of solvents (hydrocarbons, halogenated hydrocarbons, ethers, ketones, esters, alcohols, nitriles and nitro compounds) at 25°C, and, in some of them (ethyl acetate (EtOAc), n-butyl acetate (BuOAc), tetrahydrofuran (THF) and butyl chloride (BuCl)), as a function of temperature (range 15–45°C). The polymer–solvent interaction parameter χ has been obtained from the degree of swelling, applying Flory's elasticity theory: χ is practically constant in EtOAc, BuOAc and THF (good solvents), and varies appreciably with T in BuCl (poor solvent). From these χ results, Hildebrand's solubility parameter for PMTFPS has been obtained as $\delta = 8.8$ (cal cm^{-3})$^{1/2}$. The better solvents are aliphatic ketones and acetates, having $-CH_2-CO-$ groups in the molecule. All solvents consist of polar molecules. It is argued that the polar trifluoropropyl side chain, being articulated, effectively shields the chain from interactions with the solvent unless the solvent molecules are sufficiently polar.

(Keywords: polymethyltrifluoropropylsiloxane; swelling equilibrium; interaction parameter; solubility)

INTRODUCTION

The thermodynamic properties of polydimethylsiloxanes (PDMS) in solution and especially their polymer–solvent interaction parameters have been extensively studied[1–5]. Some studies of solution properties have also been carried out on other polysiloxanes with alkyl substituent higher than methyl and with phenyl substituents[6–11]. However, very few data have been published on fluoroalkylsiloxanes such as polymethyltrifluoropropylsiloxane (PMTFPS)[12].

The properties of fluorine-containing polymers are of special interest. The introduction of fluorinated substituents has profound influence on the solubility and interaction properties of the polymer. In the present paper we report on such properties of PMTFPS in a variety of solvents at 25°C and also in some of them as a function of temperature (15–45°C). The liquids studied as possible solvents cover a wide range of chemical groups: hydrocarbons, halogenated hydrocarbons, ethers, ketones, esters, alcohols, nitriles and nitro compounds. The results obtained are compared with results for other siloxane polymers, PDMS and polymethylphenylsiloxane (PMPS), and analysed with regard to the influence of the fluoro group on polymer–solvent interactions.

One of the methods available for studying the solvent power of liquids for a given polymer and for determining the polymer–solvent interaction parameter is equilibrium swelling of the crosslinked polymer[13]. The swelling of networks is usually interpreted assuming additivity of the mixing and elastic contributions to the chemical potential of the solvent, so that at equilibrium both contributions cancel each other. This assumption of additivity of contributions appears to be adequate provided the degree of swelling of the network is not too low[14].

The mixing contribution to the chemical potential contains a combinatorial and a non-combinatorial or residual part[13]. This residual part is usually written as $RT\chi v_2^2$, where RT is the thermal energy, v_2 is the polymer volume fraction and χ is the interaction parameter[15]. This χ parameter can be obtained from swelling experiments by using the equality between mixing and elastic contributions to the solvent chemical potential if one knows how much that elastic contribution is. To obtain it one has to resort to the theory of elasticity. Here, we use the theory of Flory[16], which appears to be the most adequate at the present moment.

Any elasticity theory contains parameters that depend on the characteristics of the networks. In some cases,

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these parameters are determined in the same swelling experiment by calibrating with a solvent whose polymer–solvent parameter χ is known[17]. Here, we calculate the elastic contribution by an independent method. We take the parameters characteristic of the network from a fit of independent stress–strain measurements performed on the dry network and previously reported[18]. In this way, the interaction parameter values obtained can be termed absolute, since they do not depend on previous calibration with a known χ.

The method of network swelling yields χ parameter values which can be considered truly representative of the polymer–solvent interaction if the crosslinks have a negligible effect. This requires that the density of crosslinks be sufficiently low. The networks studied here comply with this requirement, having chains with an average molecular weight between crosslinks greater than 10^4.

EXPERIMENTAL

Polymer

Two PMTFPS networks were obtained from linear PMTFPS using dicumyl peroxide as crosslinking agent. The linear PMTFPS, containing approximately 0.5% of vinyl groups distributed randomly, was kindly supplied by Dow Corning Co.

The molecular weight between crosslinks, M_c, of both networks was determined by stress–strain measurements[18]. The values of M_c are given in *Table 1*.

Solvents

These were supplied by Carlo Erba RPE. They were used without previous treatment.

Swelling degree

The volume fraction of polymer, v_2, in the swelling equilibrium has been obtained by weighing. Once swelling equilibrium was reached, the swollen gel was blotted with a filter paper, introduced in a closed vessel, and weighed.

If ω is the mass of solvent per unit mass of dry network we can write (assuming volume additivity)

$$v_2=(1+\omega\rho_2/\rho_1)^{-1}$$

where ρ_1 and ρ_2 are the densities of the liquid and the polymer respectively.

The swelling degree was always determined after 48 h.

To determine v_2 as a function of the temperature, each network was introduced in the solvent at the lower temperature (15°C) to reach the swelling equilibrium. Then, v_2 was determined by first increasing and then decreasing the temperature over the same sample of network. The values of v_2 were found to be reproducible.

Table 1 Molecular weight between crosslinks, M_c, and parameters ζ and κ (Flory's elasticity theory) of PMTFPS networks

Network	M_c	ζ^a	κ^a
1	34800	0	6.0
2	24250	0	3.5

^{a}Ref. 18

Table 2 Density of the liquids, ρ_1, as a function of the temperature t (expressed in °C). (Parameters A and B of the equation $\rho_1=A-Bt$)

Solvent	A (g cm^{-3})	B ($\times 10^3$) (g cm^{-3} deg^{-1})
EtOAc	0.9242	1.04
BuOAc	0.9012	1.03
THF	0.9097	1.10
BuCl	0.9086	1.11

Density

The density of the solvents, ρ_1, as a function of the temperature has been determined with an Anton Paar 55 digital densimeter with distilled water and air as calibrating substances. The temperature in the measuring cell was regulated to ±0.001°C.

The density as a function of the temperature, t, shows linear behaviour ($\rho=A-Bt$) in the solvents studied. The parameters A and B obtained by least-squares analysis are given in *Table 2*.

The density of the polymer, ρ_2, has been taken from data of partial specific volumes of the linear polymer reported elsewhere[19]. The temperature variation of ρ_2 has been considered similar to that of the liquids used as solvents (*Table 2*). The equation used to obtain ρ_2 (in g cm^{-3}) is[19]:

$$\rho_2=1.2809-10^{-3}(t-25)$$

Solubility

To perform the solubility test of linear PMTFPS, we prepare polymer/liquid mixtures with a fixed proportion of 2% (w/w) polymer. These solutions were kept at room temperature for 48 h.

The results are shown in *Table 3*, where (+) represents a perfect homogeneous solution of the PMTFPS after the 48 h test and (−) represents a two-phase system remaining after the same time.

RESULTS AND DISCUSSION

Solvent power

In *Table 3* are shown the results of the polymer volume fraction at swelling equilibrium, v_2, determined at 25°C for network 1 of PMTFPS, swollen with various liquids. The liquids belong to different chemical families: (1) ketones, (2) esters, (3) ethers, (4) halogenated hydrocarbons, (5) hydrocarbons, (6) alcohols and (7) nitrogen-containing compounds.

The degree of swelling, v_2^{-1}, of a polymer network is directly related to the solvent power of the liquid swelling the network[13]. Therefore, the results of v_2 in *Table 3* allow us to discuss the affinity of PMTFPS with liquids having a great variety of chemical groups.

Table 3 also contains the results of the solubility tests performed on the linear PMTFPS polymer. These results are complementary to those of network swelling and allow the distinction between clear solvents and non-solvents or marginal solvents. As we can see, only a few liquids give a positive result in the solubility test. They are the following ones: (a) aliphatic ketones (methyl ethyl ketone (MEK) and dimethyl ketone (DMK), but not acetophenone); (2) acetates (but not other esters such as benzoate, phthalate or malonate); (3) tetrahydrofuran (THF) (but not other ethers such as diethyl ether (DEE)

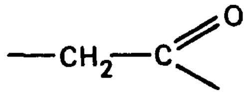
Table 3 Polymer volume fraction at swelling equilibrium, v_2, and interaction parameter, χ, of PMTFPS network 1 in different solvents. Test of solubility of the linear PMTFPS polymer and solubility parameter values, δ, of the different liquids used

Solvent	v_2	χ	Test	δ^a ((cal cm^{-3})$^{1/2}$)
Dimethyl ketone	0.127	0.498	(+)	9.77
Methyl ethyl ketone	0.115	0.472	(+)	9.27
Cyclohexanone	0.184	0.533	(+)	9.88
Acetophenone	–	–	(+)	9.68
Methyl acetate	–	–	(+)	9.49
Ethyl acetate	0.158	0.514	(+)	9.10
n-Butyl acetate	0.147	0.485	(+)	8.50
n-Pentyl acetate	0.156	0.488	(+)	8.50
iso-Pentyl acetate	0.144	0.472	(+)	8.32
Diethyl malonate	–	–	(–)	9.50
Methyl benzoate	–	–	(–)	10.50
Ethyl benzoate	–	–	(–)	8.2
Dibutyl phthalate	–	–	(–)	9.30
Diethyl ether	0.624	0.903	(–)	7.62
Dioxane	0.717	1.060	(–)	9.87
Tetrahydrofuran	0.153	0.517	(+)	9.52
Methoxybenzene	–	–	(–)	9.40
Dichloromethane	–	–	(–)	9.93
Trichloromethane	0.730	1.080	(–)	9.21
1,2-Dichloroethane	–	–	(–)	9.76
n-Chlorobutane	0.313	0.620	(+)	8.46
1,2-Dichlorobenzene	–	–	(–)	9.98
Benzene	0.791	1.234	(–)	9.15
Toluene	0.686	0.998	(–)	8.91
o-Xylene	–	–	(–)	9.0
n-Hexane	–	–	(–)	7.24
Cyclohexane	–	–	(–)	8.20
Methanol	–	–	(–)	14.5
Ethanol	–	–	(–)	12.92
Benzyl alcohol	–	–	(–)	11.97
Acetonitrile	0.555	0.823	(–)	11.90
Nitrobenzene	–	–	(–)	10.62
Aniline	–	–	(–)	11.02
Pyridine	–	–	(–)	10.61
N,*N*-Dimethylformamide	–	–	(+)	12.14

[a] Ref. 28

or dioxane (Dox)); (4) butyl chloride (BuCl) (but not other halogenated hydrocarbons); and (5) dimethylformamide (DMF).

According to the values of the degree of swelling shown in *Table 3*, the solvents that interact most favourably with PMTFPS are the aliphatic ketones and the acetates. These two families have in common the chemical structure



Other ketones and esters, such as acetophenone and benzoate, which have an aryl group directly attached to the carbonyl instead of the $-CH_2-$ in α, are not solvents of the polymer. It appears essential for a good solvent power of PMTFPS that the carbonyl group of the solvent molecule be in an aliphatic chain separated from any electron-donating group such as aryl. The malonate having two CO groups is also not a solvent. Lately, anomalous high solubility of CO_2 in PMTFPS as compared with other siloxane polymers has been attributed to specific interactions between the CO_2 molecules and the fluorine atoms[20].

In the case of ketones (MEK and DMK), an anomalous behaviour of PMTFPS networks has been observed. On long contact of the network with the ketones (MEK and DMK), the network structure is damaged in such a way that it disappears, passing to the state of solution. This behaviour is subject to further investigation. In view of this anomaly, the values of v_2 corresponding to MEK and DMK in *Table 3* are only indicative of the degree of swelling reached by PMTFPS network 1 after 48 h of contact with the liquid, but not of swelling equilibrium properly.

In group (3) corresponding to ethers, only THF is a good solvent of PMTFPS, while the other two ethers, DEE and Dox, are not. Of the rest of the liquids appearing in *Table 3*, only BuCl behaves as a solvent, albeit a poor one according to its low value for the degree of swelling, v_2^{-1}.

The results obtained for the PMTFPS polymer can be compared with the ones known for the other siloxane polymers. The ketones MEK and DMK are not good solvents of PDMS[21],[22]. MEK is a θ solvent at 20°C[21]. But for PMPS, which differs from PDMS in that a methyl group is replaced by phenyl, DMK has a better solvent quality[23]. The ethers, Dox, DEE and THF, as well as the hydrocarbons benzene (Bz) and toluene (Tl) and also chloroform (Cl_3CH), are all very good solvents of PDMS and of PMPS. From this we can see that PMTFPS has a behaviour very different from that of the other siloxane polymers with respect to its interaction with solvents.

The molecule of PMTFPS differs from those of PDMS and PMPS in that its polarity should be notably higher ($\langle\mu^2\rangle_{PDMS}/nm^2 = 0.37$ and $\langle\mu^2\rangle_{PMPS}/nm^2 = 0.31$)[24,25], due to its lateral trifluoropropyl group ($-CH_2-CH_2-CF_3$). Hence, in contrast with PDMS and PMPS, it interacts favourably with liquids having highly polar groups such as C=O in ketones and acetates. THF has a polarity similar to that of acetates ($\mu = 1.75$ D)[26], while Dox and DEE are of lower polarity ($\mu_{Dox} = 0.4$ D, $\mu_{DEE} = 1.15$ D)[26], which can explain why PMTFPS interacts favourably with THF but not with the other two ethers. The interaction of PMTFPS with halogenated hydrocarbons, Cl_3CH and CuCl, is not very favourable, but, in contrast with PDMS and PMPS, the solvent power of BuCl is notably higher than that of Cl_3CH. Again, the explanation can be found in the difference in polarity between both liquids ($\mu_{Cl_3CH} = 1.15$ D, $\mu_{BuCl} = 1.96$ D)[26].

The high solvent power of DEE towards PDMS and PMPS has been attributed before[27] to the similarity between the siloxane backbone and the ether structure (–Si–O–Si– and –C–O–C–). In the case of PDMS and PMPS the substituents attached to the Si–O chain are rigid (Me and Ph), but in the case of our PMTFPS the lateral group ($-CH_2-CH_2-CF_3$) besides being highly polar is also articulated so that it can coil back towards the backbone.

If this back-coiling occurs, it would effectively hinder the chain from possible interaction with the solvent. The polymer would come into solution only when the solvent is polar enough to interact or compete with the also polar fluorinated $-CF_3$ group protecting the chain.

Polymer solubility is usually interpreted in terms of cohesive energy density or solubility parameter, δ[13]. According to regular solution theory, the best solvent power should be obtained with liquids having δ values closest to the δ of the polymer. The solubility parameter values of the liquids studied here are given in *Table 3*. The δ value of PMTFPS is not known. We can try to estimate it from the information contained in *Table 3* by looking at the δ values of the liquids giving highest degrees of swelling. They comprise the range $\delta = 8.32$–9.52 $(\mathrm{cal\,cm^{-3}})^{1/2}$. A better criterion to estimate the solubility parameter of the polymer can be based on the knowledge of the interaction parameter χ and of its temperature variation, as we shall discuss later.

Interaction parameter

The mixing contribution to the chemical potential of a solvent swelling a network is[13]:

$$(\Delta\mu_1)_{\mathrm{mix}} = RT[\ln(1-v_2)+v_2+\chi v_2^2] \qquad (1)$$

Here, χ is a phenomenological coefficient, expressing deviations from purely combinatorial terms. It is concentration-dependent. The elastic contribution to the chemical potential of the solvent in the network is, according to the theory of Flory[16]:

$$(\Delta\mu_1)_{\mathrm{el}} = RT\frac{\rho_2}{2M_c}\frac{V_1}{\lambda}[1+(\tfrac{1}{2}\phi-1)^{-1}K(\lambda^2)] \qquad (2)$$

where V_1 is the solvent molar volume, and ϕ the network functionality. In the case of a tetrafunctional network $(\frac{1}{2}\phi-1)=1$. Also $\lambda = v_2^{-1/3}$ in swelling deformation.

The function K interpolates between the affine and the phantom limits. According to the theory of Flory, it is given by[15]:

$$[1+K(\lambda)^2] = B[\dot{B}(B+1)^{-1}+g(\dot{g}B+g\dot{B})(gB+1)^{-1}] \qquad (3a)$$

where

$$g = \lambda^2[\kappa^{-1}+\zeta(\lambda-1)]; \qquad \dot{g} = \kappa^{-1}-\zeta(1-\tfrac{3}{2}\lambda) \qquad (3b)$$

$$B = (\lambda-1)(1+\lambda-\zeta\lambda^2)/(1+g)^2 \qquad (3c)$$

$$\dot{B} = B\{2\lambda(\lambda-1)^{-1}+(1-2\zeta\lambda)[2\lambda(1+\lambda-\zeta\lambda^2)]^{-1} - 2\dot{g}(1+g)^{-1}\} \qquad (3d)$$

Parameter κ takes into account the constraints on fluctuations of crosslinks, and parameter ζ measures network imperfections[15]. The values of these parameters κ and ζ, as well as the values of M_c and ρ_2, corresponding to the networks studied here had been determined before by means of stress–strain measurements without solvent[18]. The values obtained are given in *Table 1*.

At swelling equilibrium:

$$(\Delta\mu_1)_{\mathrm{mix}} + (\Delta\mu_1)_{\mathrm{el}} = 0 \qquad (4)$$

Thus, from the determination of v_2 for networks whose structural parameters are known, we obtain the value of χ corresponding to the polymer concentration v_2. In this way we have determined the polymer–solvent interaction parameter χ of PMTFPS in various solvents, at 25°C (network 1). The results are shown in *Table 3*.

With four of the solvents included in *Table 3* we have determined the equilibrium swelling as a function of the temperature, in the range 15–45°C (networks 1 and 2). Of the four liquids, three are good solvents of the polymer, viz. ethyl acetate (EtOAc), n-butyl acetate (BuOAc) and THF; and one is a poor solvent, viz. BuCl. These four cover almost all the possibilities available within the collection of liquids explored and listed in *Table 3*.

The results of v_2 for the two networks as a function of temperature are shown on *Figure 1*. Results obtained on increasing temperature are denoted by empty symbols and those obtained on decreasing T by filled ones. As we can see, there is good reproducibility.

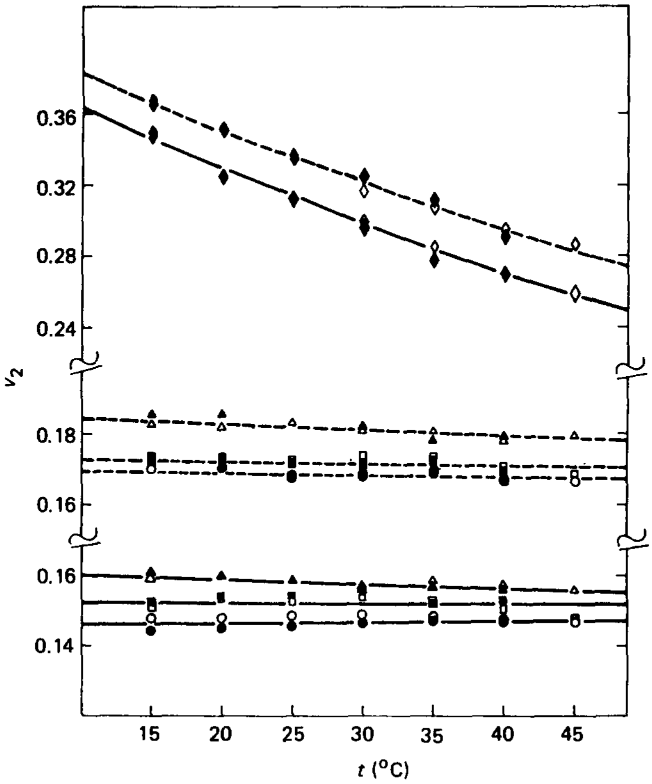


Figure 1 Polymer volume fraction at swelling equilibrium, v_2, of PMTFPS networks 1 and 2, as a function of temperature in different solvents: circles, BuOAc; squares, THF; triangles, EtOAc; and diamonds, BuCl. Empty and filled symbols represent values of v_2 obtained by increasing and decreasing temperature respectively. Curves through the points are drawn to fit the experimental points: full curve, network 1; and, broken curve, network 2

The values of v_2 for network 2 are higher than the corresponding ones for the network 1. This is natural, since network 2 has a higher density of crosslinks (*Table 1*).

The temperature dependence of v_2 is important only in the case of the poor solvent BuCl. For the other three solvents, v_2 remains practically constant on variation of T.

The values of χ obtained from these v_2 values are shown on *Figure 2*. Each χ corresponds to the mean v_2 when two determinations are available for the same temperature.

As we can see, the behaviour of χ as a function of temperature is very similar to that of v_2. In the case of EtOAc, BuOAc and THF, χ is practically independent of temperature, confirming the good solvent character of these three liquids. In the case of BuCl, χ decreases notably on increasing T, as is typical of a poor or θ solvent.

The concentration dependence of χ can also be seen in *Figure 2*. For a given temperature and solvent, χ is larger in the network giving the higher v_2 (network 2). This indicates that χ increases with polymer concentration. This behaviour is typical of PDMS also[1–5]. The concentration dependence is larger in the poor solvent (BuCl) than in the good ones, as can be seen in *Figure 2*.

The variation of χ as a simultaneous function of temperature T and concentration v_2 can be expressed by an equation of the form:

$$\chi = a + \frac{b}{T} + \left(c + \frac{d}{T}\right)v_2 \qquad (5)$$

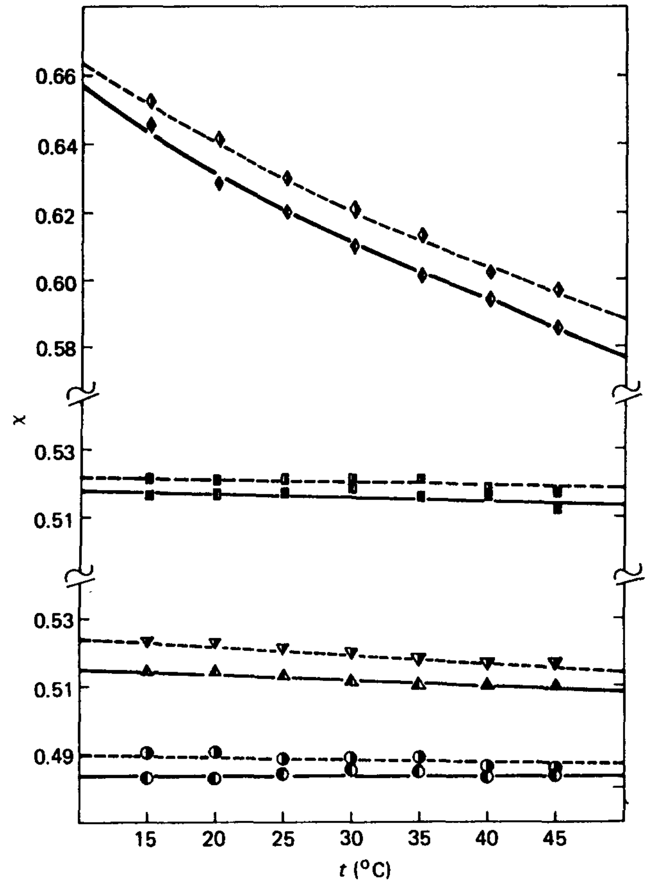


Figure 2 Interaction parameter of PMTFPS, χ, as a function of temperature in different solvents: circles, BuOAc; triangles, EtOAc; squares, THF; and, diamonds, BuCl. Curves through the points are drawn to fit the experimental points: full curve, network 1; and, broken curve, network 2

valid in a narrow range of the two variables. The values of the coefficients of this equation fitted to the data obtained in the four solvents EtOAc, BuOAc, THF and BuCl are given in *Table 4*.

The enthalpic and entropic parts of the interaction parameter, χ_H and χ_S, respectively, can be obtained from the temperature dependence of χ through[13]:

$$\chi_H = -T(\delta\chi/\partial T)v_2 \tag{6}$$

$$\chi_S = \chi - \chi_H \tag{7}$$

The enthalpic part is the one that is related to the solubility parameter difference between polymer and solvent[13]:

$$\chi_H = (V_1/RT)(\delta_1 - \delta_2)^2 \tag{8}$$

We obtain χ_H be deriving equation (5) with the coefficients of *Table 4*. The values of χ_H thus determined yield the solubility parameter of the polymer, δ_2, by using equation (8). With each solvent a different δ_2 value is obtained. The results corresponding to 25°C, given in $(\text{cal cm}^{-3})^{1/2}$, are as follows:

$$\delta_2 = 8.55 \text{ (in EtOAc)}$$

$$\delta_2 = 8.80 \text{ (in BuOAc)}$$

$$\delta_2 = 9.08 \text{ (in THF)}$$

$$\delta_2 = 9.56 \text{ (in BuCl)}$$

It has been observed before that the solubility parameter value obtained for a given polymer depends significantly on the class of liquids in which it has been obtained[29].

Table 4 Interaction parameter χ of PMTFPS networks as a function of polymer volume fraction, v_2, and temperature, T (in K) (coefficients *a*, *b*, *c* and *d* of equation (5))

Solvent	*a*	*b* (deg^{-1})	*c*	*d* (deg^{-1})
EtOAc	0.3288	36.49	0.7898	−121.6
BuOAc	0.8686	−124.7	−2.546	827.1
THF	0.4257	17.10	0.4075	−56.38
BuCl	0.4282	15.78	0.0542	149.4

Besides the specific influence of the chemical nature of the solvent, there should also be a dependence of δ_2 on polymer concentration. In equation (8) the left-hand side is v_2-dependent; therefore the right-hand side should give δ_2 also v_2-dependent. The results of δ_2 for PMTFPS shown above have been calculated using the equilibrium v_2 for each solvent (actually, the mean value between the two networks). The v_2 values are very similar in EtOAc, BuOAc and THF, and so the δ_2 values obtained in these three solvents are comparable. But v_2 is about double in BuCl, so the value of δ_2 obtained in BuCl is not comparable with the other ones. We therefore conclude that the best estimate of δ_2 (corresponding to the v_2 obtained in EtOAc, BuOAc and THF) is $\delta_{\text{PMTFPS}} = 8.8$ $(\text{cal cm}^{-3})^{1/2}$. This is a much higher value than $\delta_{\text{PDMS}} = 7.6$ owing to the polarity of the fluoropolymer.

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