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Swelling of Model Networks[†]

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ABSTRACT: An approach is proposed for the treatment of equilibrium swelling of networks obtained by cross-linking poly(propylene glycol) (PPG) chains with a triisocyanate cross-linker, "Desmodur RF" (DRF). Three models are used for the analysis of swelling of these polyurethane networks in toluene and methanol. It is shown that the χ parameter of the copolymer network depends on the interactions between the solvent and the individual components of the network and between these components themselves. Swelling data in methanol and toluene appear to yield the same value for the interaction parameter of the network components provided (a) the differences in molecular surface area between the various building blocks of the systems and (b) the molecular association of methanol are taken into account. Two networks, identical in number-average chain length between cross-links but differing in chain length distribution, have identical enthalpic contributions to the effective interaction parameter but different entropic terms. The conclusions are affected neither by the choice of the model used for the front factors nor by possibly necessary corrections for the number of elastically active network chains. A simple solubility parameter treatment provides a fair prediction of swelling in mixtures of methanol and toluene.

Introduction

The swelling of a cross-linked polymer by a solvent is often used to assess either cross-link density or the polymer–solvent interaction parameter provided one of these two parameters is known from independent measurements. The theory of swelling proposed originally by Flory and Rehner[1] has been developed in parallel with the evolution of the theories of rubber elasticity. It is generally assumed that the Gibbs free energy of swelling is the sum of the free energy of mixing and the elastic free energy. The free energy of mixing is taken from the lattice theory of solutions and the elastic free energy from rubber elasticity theory.

Under certain simplifying conditions the elastic free energy change (ΔG) of network during deformation can be represented by the expression[2]

$$\Delta G_{\text{el}}/RT = (A\nu_{\text{e}}/2)(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - B\nu_{\text{e}} \ln \lambda_x\lambda_y\lambda_z \qquad (1)$$

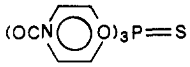
where R is the gas constant, T is the absolute temperature, ν_{e} is the number of elastically active network chains in moles per unit volume of dry rubber, and λ_i is the deformation ratio in direction i. Revision of the classic theory of rubber elasticity[3-5] has shown that the factors A and B, previously considered as constants, may depend on ν_{e} as well as on the degree of swelling. In the junction fluctuation model of Flory the limiting values of A and B are $(f_{\text{e}} - 2)/f_{\text{e}}$ and 0, respectively, for the phantom network limit (free fluctuations of cross-links), and 1 and $2/f_{\text{e}}$ for the limit of fully suppressed fluctuations of cross-links (original Flory–Wall model[6]). Here, f_{e} is the number-average functionality of an elastically active cross-link. Similar conclusions can be drawn from the tube models, although there the effect of interchain constraints is not limited by $A = 1$ (A may be >1). These models, however, have been much less thoroughly worked out than Flory's junction fluctuation model. Both models predict that $A \rightarrow (f_{\text{e}} - 2)/f_{\text{e}}$ and $B \rightarrow 0$ with increasing swelling and increasing tensile deformation. The concentration of elastically active network chains has an influence on this dependence.

There may also be an uncertainty in the value of ν_{e} if the network structure is not well defined. For *perfect* networks with ν_{e}^0 elastically active network chains and a density ρ, prepared from telechelic polymers, the molar mass between cross-links, M_{c}, given by

$$M_{\text{c}} = \rho/\nu_{\text{e}}^0 \qquad (2)$$

can be identified with the molar mass of the telechelic polymer. However, a state of network perfection is probably impossible to achieve and a very low level of imperfection may have a considerable effect on elastic properties.[7] Also, there may be a contribution to ν_{e} by permanent topological constraints—trapped entanglements—which may not disappear even at high degrees of swelling.

These points are raised to show that it is difficult to evaluate the polymer–solvent interaction parameter χ from swelling measurements. Another complication is represented by the usual assumption that the network contains a single type of interacting polymer segment. This assumption is not often fulfilled; the cross-links or bridging molecules and the elastomeric chains may have a different nature. As a consequence, the solvent–polymer interactions may be more complex than is usually assumed. Swelling of such "copolymer" governed by the interaction between the solvent molecules and the two types of polymer segments, and at least three χ parameters may be necessary to describe the system. We studied the swelling of such networks in order to find out whether, in spite of the complications described above, it might still be possible to separate the various χ parameters contributing to the effective interaction parameter χ_{ef}, characterizing the various interactions between the components in the swollen network. The treatment we developed was applied to polyurethane networks based on poly(propylene glycols) (PPG) and a triisocyanate, "Desmodur RF" (DRF), having the structural formula



Theory

The swelling equation derived for networks composed of a single type of segment, on the assumption of ΔG_{el}

[†] Dedicated to Professor Manfred Gordon on the occasion of his 70th birthday.

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being given by eq 1 and ΔG_{mix} by the expression of Flory,[8] Huggins,[9] and Staverman and Van Santen,[10] reads

$$\ln (1 - \phi) + \phi + \chi\phi^2 + \nu_e\tilde{V}_1(A\phi^{1/3} - B\phi) = 0 \qquad (3)$$

where ϕ is the volume fraction of the polymer in the swollen network and $\tilde{V}_1$ the molar volume of the solvent.

Swelling of the copolymer networks in this study involves three different interactions: between solvent and PPG units (χ_{12}), between solvent and DRF (χ_{13}), and between PPG units and DRF (χ_{23}). A classical analysis of such swelling data with eq 3 will produce an overall χ value, here designated by χ_{ef}. If the network is treated as a copolymer, then χ_{ef} might be considered as an average of two contributions[11,12]

$$\chi_{\mathrm{ef}} = \phi_2\chi_{12} + \phi_3\chi_{13} \qquad (4)$$

where ϕ_2 and ϕ_3 are the volume fractions of repeat units 2 and 3 in the dry network. This *two-parameter* model ignores a possible interaction between the repeat units 2 and 3 and has been found to be too simple an approximation to explain experimental data on solvent–copolymer solutions[13,14] and blends of homopolymers with copolymers.[15] A better treatment of the situation has been developed for copolymer solutions[16,17] and for blends containing copolymers,[15,18–20] and this leads to a *three-parameter* expression for χ_{ef}

$$\chi_{\mathrm{ef}} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23} \qquad (5)$$

The three-parameter model suggests that χ_{ef}, and thus the degree of swelling, will depend not only on interactions between solvent and the two repeat units but also on the attraction or repulsion between the repeat units themselves. If χ_{12} and χ_{13} are positive, then repulsion between repeat units 2 and 3 (positive χ_{23}) will enhance swelling (decrease χ_{ef}) in a given solvent. On the other hand, if 2 and 3 attract each other, specific interactions between 1 and 2 and/or 1 and 3 must be present for swelling to be sizeable. Although eq 5 is better than eq 4, it still has been found to be inadequate in some cases.[14]

Several possibilities exist for the modification of eq 5. One might consider the (branched) block copolymer character of the system in hand or, in a less extreme fashion, bring in deviations from the strictly regular mean field description underlying the analysis developed so far.[21–23] In this paper we investigate an alternative approach and introduce terms accounting for the differences between the coordination numbers (numbers of nearest neighbors) of the various repeat units in the system. We use a first approximation proposed many years ago by Staverman,[24] who suggested setting the numbers of nearest-neighbor contacts proportional to the attainable molecular surface areas. Application to the present system yields[20] (Appendix)

$$g_{\mathrm{ef}} = \phi_2 g_{12} + \phi_3 g_{13} - \phi_2\phi_3 g_{23}/\alpha \qquad (6)$$

where $\alpha = \phi_2 + S_{32}\phi_3$

$$g_{\mathrm{ef}} = \chi_{\mathrm{ef}}\{1 + (\beta - 1)\phi\}^2/\beta = \chi_{\mathrm{ef}}Q^2/\beta \qquad (7)$$

$$\beta = s_{21}\alpha$$

The introduction of disparity in contact involves an overall concentration dependence of the effective interaction parameter χ_{ef} determined from swelling equilibrium data with eq 3. As a consequence, χ_{ef} must be corrected (eq 7), and we denote the interaction parameters g_{ij} to distinguish between this *modified three-parameter* model and the three-parameter model defined by eq 5. The quantities s_{ij} stand for σ_i/σ_j, the ratios of molecular surface areas σ_i and σ_j.

The aim of this work is to examine the applicability of the three models expressed by eq 4–6 to real copolymer networks of different cross-link density and different composition ratios, i.e., different volume ratios of chains and cross-linker. With the two-parameter model we do not need to compare χ values between the two solvents; eq 4 does not contain the 2–3 interaction and linearity of $\chi_{\mathrm{ef}}(\phi_2)$ is the criterion for validity of the model. With the two three-parameter models, however, the criterion is much more demanding viz. agreement within experimental accuracy of the value of the 2–3 interaction parameter, obtained from swelling equilibrium in two different solvents.

In any theory of mixing molecules of different size the choice of the basic volume unit (BVU) in the system presents a nonnegligible problem. This is well-known for the rigid lattice model underlying eq 3 but equally true for other approaches. van der Waals demonstrated long ago that differences in molecular size constitute a factor of primary importance when dealing with thermodynamic properties of mixtures.[25] In the present study we have used two solvents with a large disparity in molecular size (methanol and toluene). If the comparison of the χ_{23} and g_{23} values between the two swelling solvents is to be meaningful, the data analysis with eq 3 must be carried out with the same value of the BVU, within the rigid lattice model identical with the size of the lattice sites. It would seem obvious to use the molar volume of methanol for the purpose, since it is the smallest of the various species. The Bondi[26] volumes for methanol, toluene, the PG repeat unit, and [$OCNC_6H_4O$] group are 20.56, 59.51, 34.39, and 64.55 cm^3/mol, respectively. Methanol, however, is known to associate and form quite stable trimers in the crystalline and liquid states,[27] and the molar volume of the liquid trimer must be a little larger than that of toluene. The molar volume of toluene would therefore seem to be a better choice for the BVU. The urethane groups are also known to be hydrogen bonded and might give rise to some association in the network. We see no obvious way to deal with this effect and neglect it, assuming that the evaluation procedure accounts for it, albeit in a formal way, in the term ν_e, variations in which are shown below not to affect conclusions about the interaction parameters in a general sense.

The preceding equations must be amended so that a direct comparison of χ or g values is possible. The Appendix contains some details of the necessary changes in the derivative of eq 3–6 which lead to the following expression for the modified Flory–Rehner equation:

$$\ln (1 - \phi) + \phi + m_1\chi_{\mathrm{ef}}\phi^2 + \nu_e m_1 V_b(A\phi^{1/3} - B\phi) = 0 \qquad (8)$$

where V_b is the molar volume of the BVU, $m_1 = V_1/V_b$, and $\chi_{\mathrm{ef}} = g_{\mathrm{ef}}\beta/Q^2$.

Experimental Section

PPG 425, PPG 1000, and PPG 2000 are poly(propylene glycols) obtained from Aldrich Chemical Co., and PPG 4000 is a poly(propylene glycol) obtained from Polysciences, Inc. They were dried by azeotropic distillation of added benzene and subsequently characterized for molar mass end hydroxyl functionality. Desmodur RF was kindly supplied by Mobay Chemical Corp. and was recrystallized from toluene. The NCO content agreed with the theoretical value. The networks were synthesized in bulk at 90 °C as described previously.[28] The molecular weight (MW) of the network chains was varied by variation of the MW of the glycols from about 470 to 3700. Five networks were synthesized: four of them were based on virtually monodisperse PPG with MWs 471, 1024, 2085, and 3696 with DRF (MW = 465). The fifth PPG was obtained by mixing the 471 and 2085 polyols in such a proportion that $M_n = 1024$ and $M_w = 1597$ ($M_w/M_n = 1.6$), the objective being the preparation of a bimodal network with the same M_n as that of one of the three unimodal networks. The

Table I
Results of Swelling in Toluene and Density of Dry Networks

polymer	M_c	ϕ_2	temp, °C	ϕ	ρ, g/cm^3
PPG 425/DRF	781	0.721	-13	0.648	1.237
			3	0.632	1.233
			23	0.629	1.228
			45	0.602	1.205
			60	0.587	1.190
PPG1000/DRF	1334	0.849	-13	0.424	1.150
			3	0.416	1.129
			23	0.401	1.112
			45	0.393	1.091
			60	0.383	1.077
PPG 2000/DRF	2395	0.920	-13	0.260	1.097
			3	0.257	1.078
			23	0.256	1.062
			45	0.251	1.042
			60	0.243	1.029
PPG 4000/DRF	4006	0.951	-22	0.197	1.074
			2	0.198	1.055
			22	0.198	1.040
			45	0.202	1.020
			60	0.201	1.007
PPG 1000/DRF bimodal	1334	0.849	-13	0.405	1.152
			3	0.399	1.132
			23	0.387	1.115
			45	0.376	1.094
			60	0.369	1.080

network based on PPG 3696 contained about 5% monofunctional species. The networks were designated by the polyols used as PPG 425/DRF, PPG 1000/DRF, PPG 2000/DRF, PPG 1000 bimodal/DRF, and PPG 4000/DRF.

Swelling was carried out in two solvents, one having a solubility parameter (δ) close to that of PPG (toluene) and another having a δ close to that of DRF (methanol). Swelling measurements were also carried out in mixed solvents. The temperature ranges usually were -13 to +45 °C for methanol and -13 to +60 °C for toluene. Volume changes were calculated from the weight increase after swelling and the densities of solvent and polymer. We determined the density of the dry networks at room temperature measuring the weight loss by immersion in water. Densities at other temperatures were calculated with thermal expansion coefficients determined on a Perkin-Elmer thermomechanical analyzer. Samples for swelling were disks, or squares, weighing about 1 g, cut from the cast sheet of a polymer, 2-4 mm thick.

The volume fraction of PPG chains (ϕ_2) and DRF (ϕ_3) in the networks can be calculated from the weight fractions if the densities of PPG and DRF in the networks are known. The latter can be found from the densities of two networks differing in DRF content. An error is introduced since the density of a network is not a linear combination of the component densities, i.e., because cross-linking introduces a decrease in free volume. Hence, average component densities depend on the pair of polymers chosen. We adopted average values of $\rho_{\mathrm{PPG}} = 1.005$ g/cm^3 and $\rho_{\mathrm{DRF}} = 1.713$ g/cm^3.

The drying of the networks after swelling was carried out at 90 °C under high vacuum for several days. Drying at higher temperatures or for longer times could cause some further chemical reaction (transurethanization).

Tables I and II show the equilibrium swelling data for polyurethane networks in toluene and in methanol, M_c was taken to be the molecular weight of the polyol plus two-thirds of the molecular weight of DRF. The functionality f_e was set equal to 3.

A study of the kinetics of swelling was undertaken to establish the time necessary to reach equilibrium. We show results for the PPG 2000/DRF system, which are fairly representative of all other systems. Sol fractions varied from 0% for PPG 425, 1.6% for PPG 1000, 2.4% for PPG 2000 to 2.3% for the bimodal network. In all cases swelling measurements were carried out on extracted networks.

The rate of swelling of PPG 2000/DRF in toluene was very rapid. Roughly one-third of the final swelling was achieved in the first minute, two-thirds of the process was completed in 2 h and the equilibrium value was reached after 15 h (Figure 1). The degree of swelling q, which is the reciprocal of the volume fraction ϕ, is plotted vs. time in Figure 1 (bottom). The function $q^4 = \kappa t$ fits the data fairly well. Most of the experiments lasted longer than 3 days.

Table II
Results of Swelling in Methanol

polymer	M_c	ϕ_2	temp, °C	ϕ
PPG 425/DRF	781	0.721	-13	0.680
			3	0.654
			23	0.638
			45	0.612
PPG 1000/DRF	1334	0.849	-13	0.578
			3	0.565
			23	0.545
			45	0.532
PPG 2000/DRF	2395	0.920	-13	0.421
			3	0.421
			23	0.418
			45	0.412
PPG 4000/DRF	4006	0.951	-18	0.355
			3	0.354
			22	0.355
			45	0.353
PPG 1000/DRF	1334	0.849	-13	0.561
			3	0.546
			23	0.529
			45	0.513

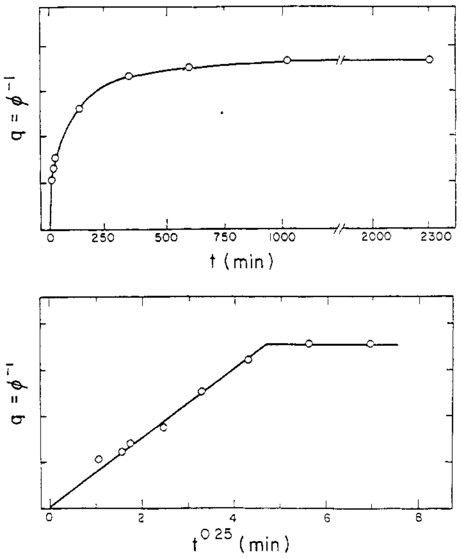

Figure 1. Swelling kinetics of PPG 2000/DRF: top, swelling ratio q vs. time t; bottom, q vs. $t^{1/4}$.

Evaluation of Interaction Parameters

In order to evaluate the swelling experiments with respect to the interaction models an estimate must be made of ν_e and of the front factors A and B.

If the networks were perfect, eq 3 or 8 could be used. However, the sol fractions are not negligible, except with network PPG 425/DRF. Using a universal relationship between the equilibrium number of network chains and the gel fraction, derived earlier on the basis of branching theory[29] and applied to polyetherurethane networks,[30] one can estimate that ν_e should be corrected by a decrease of 25% and 40% for networks PPG 1000/DRF and PPG 2000/DRF, respectively. We incorporate such corrections in the A and B values (then denoted by an asterisk) and use the perfect ν_e value calculated with eq 2. Further, using $A = {}^1/_3$ and $B = 0$ (see below), we have adapted A^* values of ${}^1/_3$ ($= {}^1/_3 \times 1$), ${}^1/_4$ ($= {}^1/_3 \times 0.75$), and ${}^1/_5$ ($= {}^1/_3 \times 0.6$) for the three networks, respectively.

There may also be a contribution to ν_e from trapped entanglements which, according to an estimate based on

Table III
Three-Parameter Model (Eq 5)

BVU	A^*	B^*	χ_{23}[a] methanol	χ_{23}[a] toluene
toluene (meth 3)	1	$^2/_3$	−5.7; −5.7; −4.1; −4.5	−2.1; −2.5; +0.2; −1.3; −2.0
toluene (meth 1)			−14; −14; −10; −10	−2.1; −2.5; +0.2; −1.3; −2.0
methanol (3)			−6.5; −6.5; −4.7; −5.1	−2.4; −2.9; +0.2; −1.5; −2.3
methanol (1)			−5.3; −5.3; −3.8; −4.1	−0.8; −1.0; +0.1; −0.5; −0.8
toluene (meth 3)	$^1/_3$	0	−4.5; −4.6; −3.3; −3.7	+0.6; +0.3; +2.0; +0.8; +0.4
toluene (meth 1)			−13; −13; −9; −9	+0.6; +0.3; +2.0; +0.8; +0.4
methanol (3)			−5.4; −5.5; −3.9; −4.3	+0.7; +0.3; +2.2; +0.9; +0.4
methanol (1)			−4.9; −4.9; −3.6; −3.9	+0.2; +0.1; +0.7; +0.3; +0.1
toluene (meth 3)	1.3	0.9	−6.0; −6.0; −4.3; −4.8	−3.4; −3.8; −0.6; −2.2; −3.0
toluene (meth 3)	var[b]	0	−4.7; −4.8; −3.7; −4.1	+1.4; +1.0; +2.5; +1.4; +1.1
toluene (meth 3)	$A(\phi)$	$B(\phi)$	−4.7; −4.8; −3.4; −3.7	+12; +0.8; +2.6; +1.3; +0.9

[a] χ_{23} values from left to right for lower to higher measuring temperatures (Tables II and III). [b] var means different A^* values for networks PPG425/DRF($^1/_3$), PPG1000/DRF ($^1/_4$), AND PPG2000/DRF ($^1/_5$).

data in ref 30, may amount to ca. 30% in the case of PPG 2000/DRF. To see how this feature affects the interaction parameters, we include a calculation on the basis of estimated values for A^* (=1 × 1.3) and B^* (=0.9 = 1.3 × $^2/_3$).

The dependence of A and B on the swelling ratio is roughly approximated by linear functions of ϕ and is also included in the analysis with an appropriately amended elastic contribution to the equation for swelling equilibrium (Appendix).

Sets of χ_{23} and g_{23} values have been calculated for the two solvents on the basis of various A/B combinations.

Two- and Three-Parameter Models

In the two- and three-parameter models the coordination numbers of all species in the system are assumed to be identical and χ_{ef}, calculated with eq 8, can be used to test eq 4 and 5. We base the evaluation on toluene as the BVU and assume the trimer of methanol to be stable within the full range of temperatures used; i.e., we set the molar volume of methanol at these temperatures equal to 3 times the literature value for monomeric methanol. Then the number of occupied BVUs per trimer is $m_1 = 3V_1$(methanol)/V_1(toluene). Figure 2 demonstrates the inadequacy of the two-parameter model, which requires χ_{ef} to be linear in ϕ_2. Though the deviation from the straight line may not be significant with toluene, the data on methanol leave no doubt that the 2–3 interaction has to be taken into account. The same result is obtained when monomeric methanol is used as BVU.

Using the data on systems 1–3 we can solve eq 5 for χ_{12}, χ_{13}, and χ_{23}. Thus we find at −13 and +45 °C, $\chi_{23} = -5.7$ and -4.5 for methanol and $\chi_{23} = -2.1$ and -1.3 for toluene ($A = 1$; $B = {}^2/_3$). It is clearly not possible to describe both the toluene and methanol data with the same value of χ_{23}. Hence, the three-parameter model cannot be valid.

Neither the particular choice of the A and B values in Figure 2 ($A = 1$, $B = 2/f = {}^2/_3$) nor that of the BVU is significant for the rejection of the three-parameter model for the systems in hand. Table III lists some examples for other combinations of A, B, and m_1, and the conclusion remains unaltered. Detailed listing of values for χ_{12} and χ_{13} was therefore not considered meaningful.

Table IV
Modified Three-Parameter Model (Eq 6)[a]

σ_{1M}, 10^9 cm^2/mol	g_{23} methanol	g_{23} toluene
10.74	−0.2; −0.3; +0.1; −0.2	−3.5; −3.7; −1.6; −2.5; −3.3
8	−1.2; −1.3; −0.6; −0.9	
6[b]	−3.2; −3.3; −2.2; −2.6	

[a] BVU: toluene; methanol: trimer; $A = 1$; $B = {}^2/_3$. [b] Value of σ_{1M} for which agreement for g_{23} between methanol and toluene is obtained.

Table V
Modified Three-Parameter Model[a]

BVU	σ_{1M}	g_{23} methanol	g_{23} toluene
methanol (3)	10.74	−0.2; −0.3; +0.2; −0.2	−4.0; −4.2; −1.9; −3.0; −3.9
	8	−2.0; −2.2; −1.3; −1.6	
	6[b]	−3.7; −3.8; −2.5; −3.0	
methanol (1)	3.58	−5.7; −5.9; −4.1; −4.6	−1.3; −1.4; −0.6; −1.0; −1.3

[a] $A = 1$; $B = {}^2/_3$. [b] Value of σ_{1M} for which agreement for g_{23} between methanol and toluene is obtained.

Another reason for caution in this respect is the experimental accuracy obtainable in χ_{ef}. Measurements of the sample weights had possible errors not exceeding 0.001 g. However, when the sample was tested in a range of temperatures a hysteresis loop was observed; i.e., the degree of swelling depended on the previous history of the sample. We estimate the probable error in χ_{ef} from this and other error sources to amount to about ±0.01 units. Four series of specimens of PPG 2000/DRF, which were taken from two different lots of the sample, have shown variations of χ_{ef} within these limits. We shall see that the present data allow conclusions to be drawn about the ϕ_2 and T dependence of χ_{ef} and/or g_{ef}, but the values of the individual interaction parameters are not significant enough to justify detailed specification. We make an exception for χ_{23} and g_{23} but are interested in their values only to find out which model makes them roughly identical for the two solvents.

Modified Three-Parameter Model

Use of eq 6 presupposes knowledge of the molecular surface areas. We draw on Bondi's estimations[26] and have the following values, expressed in 10^9 cm^2/mol: toluene, $\sigma_{1T} = 7.45$; methanol, $\sigma_{1M} = 3.58$; PG, $\sigma_2 = 4.65$. There is some ambiguity with regard to the DRF units. Bondi's data do not allow estimations for the S=P group, which, anyway, may largely be shielded by the three bulky groups attached. We ignore a possible S=P contribution and estimate $\sigma_3 = 7.2 \times 10^9$ cm^2/mol for each of the three groups in DRF.

Another question arises regarding the surface area of trimeric methanol. Multiplying σ_{1M} by 3 will surely overestimate the attainable surface area. We use σ_1 as a parameter and find that a reasonable decrease by about 40% to 6×10^9 cm^2/mol brings the g_{23} values for methanol and toluene close enough together to consider them identical in view of the experimental uncertainties involved. Table IV shows a few combinations. In Table V we demonstrate that (a) setting the BVU equal to $3V_1$(methanol) does not change the results and (b) use of monomeric methanol as BVU does not lead to agreement in g_{23} at all. These results indicate that the modified three-parameter model provides a meaningful treatment of the present data provided the association of methanol is accounted for.

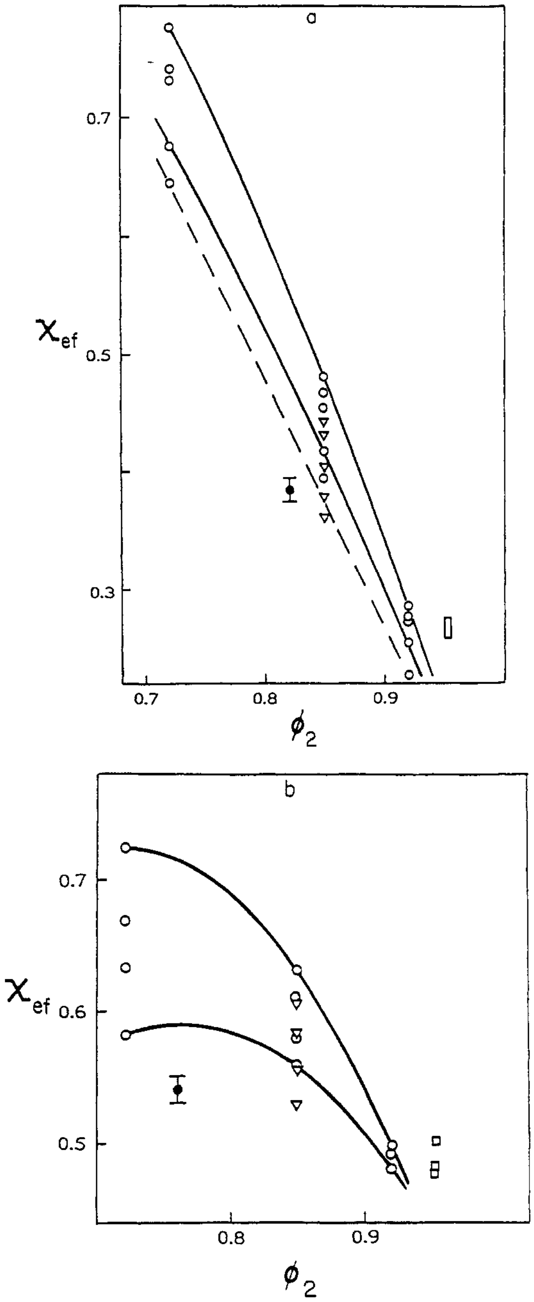

Figure 2. χ_{ef} as a function of the PG content ϕ_2 of the dry network. Networks PPG 425/DRF, PPG 1000/DRF, and PPG 2000/DRF (○); networks PPG 4000/DRF (□); PPG 1000/DRF, bimodal (▽). The lower measuring temperatures go with the higher χ_{ef} values. Effect of probable experimental errors indicated by Ɨ: (a) toluene, (b) methanol. —(– – –) straight-line relation. Calculation based on $A = 1$; $B = {}^2/_3$, BVU, toluene; trimeric methanol.

Selecting the g_{ef} values corresponding to $\sigma_1 = 6 \times 10^9$ cm^2/mol, we can construct $g_{ef}(\phi_2)$ curves to compare with $\chi_{ef}(\phi_2)$ in Figure 2. We see in Figure 3 that a similar result is obtained although the deviation from linearity for toluene is now just significant.

We believe it to be a significant finding that the introduction of the physical fact of disparity in size and numbers of nearest-neighbor contacts between the various molecular entities in the system brings such an obvious improvement in the description. The numbers of nearest-neighbor contacts can simply be translated into ratios of molecular surface areas with Staverman's approach. While further measurements with other, nonassociating solvents of different size are obviously called for, it is of interest to note that the conclusion is consistent with recent findings with polymer solutions[31] and polymer mixtures.[32]

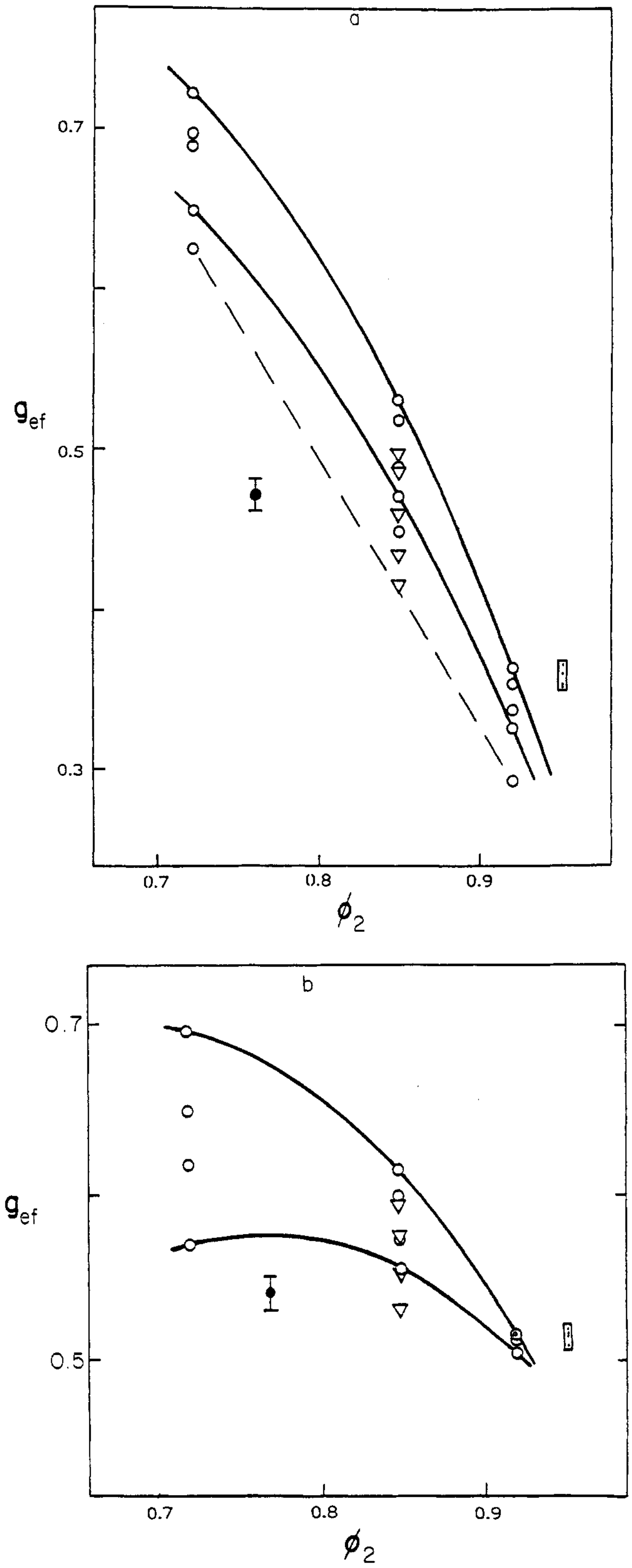

Figure 3. g_{ef} as a function of ϕ_2. See caption for Figure 2.

Swelling in Solvent Mixtures

The data demonstrate that the 2–3 interaction is important in determining the swelling behavior in a single solvent. Other specific interactions, such as those between two solvents, may be expected to reveal themselves also, e.g., as an excess swelling in a mixed solvent. Figure 4 shows that this is the case. The degree of swelling, q, does

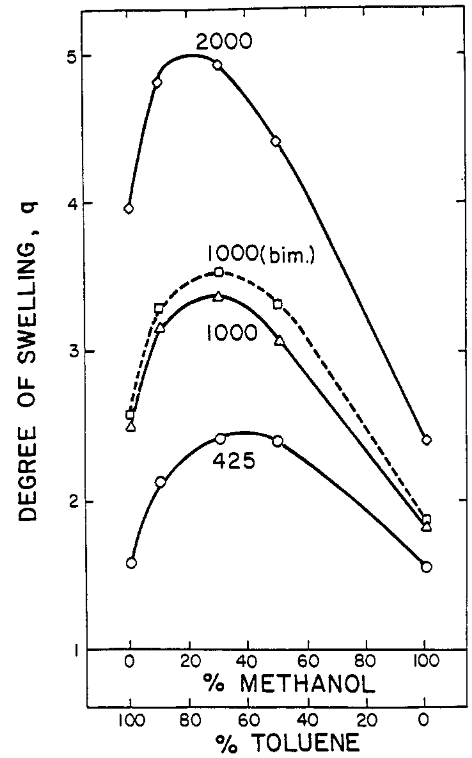

Figure 4. Degree of swelling vs. solvent composition in mixtures of methanol and toluene (experimental).

Table VI
Solubility Parameters δ and Effective χ Parameters from Group Contributions

polymer	χ (in toluene)	δ,[a] $(J/cm^3)^{1/2}$	χ (in methanol)
PPG 425/DRF	0.708	22.24	0.925
PPG 1000/DRF	0.179	20.25	1.485
PPG 2000/DRF	0.036	19.11	1.866
PPG 4000/DRF	0.0008	18.34	
PPG ($M = \infty$)	0.0108	17.7	2.395
DRF (urethane form)	8.175	31.9	0.081

[a] δ(toluene) = 18.2 $(J/cm^3)^{1/2}$; δ(methanol) = 29.7 $(J/cm^3)^{1/2}$.

not decrease monotonically with changing composition from good to less good solvent but exhibits a maximum, the position of which varies with the solvent composition. For lower DRF contents in the network the fraction of methanol at the maximum is lower.

If the mixing behavior of the system methanol–toluene could be modeled by the present treatment one could try to predict the equilibrium swelling of the network in the mixed solvent. While this approach is being studied we draw attention here to a possibly less accurate but useful approximation that does not depend on knowledge of the behavior of methanol–toluene and might for that reason offer a procedure of practical interest.

If the interaction parameters of a system are not known the solubility parameter approach may be used for their estimation. Solubility parameters, δ, can be calculated from cohesive energy densities, E_{coh}, and the volume contribution of atomic groups[33]

$$\delta^2 = (\sum E_{coh})/(\sum V_m) \tag{9}$$

and the χ parameter is given by

$$\chi_{12} = (\delta_1 - \delta_2)^2 V_1/RT \tag{10}$$

Calculated values of δ and χ for the PPG/DRF networks in toluene and methanol are given in Table VI.

The values of E_{coh} and V_m were taken from ref 33 and, δ for toluene and methanol was taken from ref 34. It has been found that a polymer will dissolve in a solvent if $|\delta_1 - \delta_2|$ is less than 4 $(J/cm^3)^{1/2}$. In the case of the two solvents, methanol and toluene, complete miscibility is observed at room temperature. The relatively large difference in δ parameter between PPG and DRF suggests that phase separation of PPG chains and DRF units would occur if they were not covalently bonded. Yet, it has been shown that the triisopropylurethane of DRF dissolves in PPG 4000 although the trimethylurethane of DRF does not. The latter compound, however, is a highly crystalline substance and kinetic factors may have impeded complete dissolution. The mixing of DRF and PPG might be due to specific interactions. DSC measurements did not show any melting or transitions of a separate DRF phase. All networks were very clear, and DRF–PG mixtures are also clear above the melting point of DRF (90 °C). No evidence for phase separation was found by small-angle X-ray diffraction.

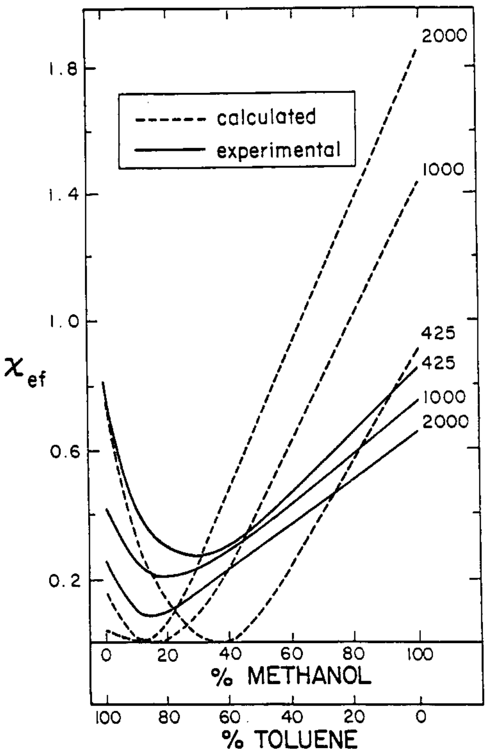

Figure 5. χ_{ef} vs. solvent composition: predicted (---), experimental (—).

It is an interesting point that the occurrence of the swelling maxima can be predicted if a solvent mixture is looked upon as a single solvent with an average solubility parameter: $\delta_{ef} = \phi_{tol}\delta_{tol} + \phi_{me}\delta_{me}$, where ϕ_{tol} and ϕ_{me} are the volume fractions of toluene and methanol and δ_{tol} and δ_{me} the corresponding solubility parameters. Figure 5 shows calculated and experimental swelling curves in terms of χ_{ef} vs. solvent composition. In view of the simplicity of the calculation the agreement can be considered quite satisfactory.

Discussion

It has been demonstrated that the modified three-parameter model eq 6 offers a rational basis for the analysis of the swelling of copolymer networks in single solvents. The number of parameters needed for the description may seem quite large, since there are two surface area ratios in addition to the three interaction parameters of the three-parameter model (eq 6 and 7). However, there is no need to obtain these extra parameters from a fit to the same data. They can be taken from literature (e.g., the

Table VII
Modified Three-Parameter Model: Effect of *A* and *B*[a]

			g_{23}	
σ_{1_M}	A^*	B^*	methanol	toluene
10.74	1	$^2/_3$	−0.2; −0.3; +0.1; −0.2	−3.5; −3.7; −1.2; −2.6; −3.4
7			−2.5; −2.6; −1.6; −2.0	
6[b]			−3.2; −3.3; −2.2; −2.6	
10.74	$^1/_3$	0	+1.6; +1.3; +1.3; +1.0	+0.5; +0.3; +1.3; +0.6; +0.3
9[b]			+0.4; +0.1; +0.4; +0.1	
8			−0.4; −0.6; −0.2; −0.5	
10.74	1.3	0.9	−0.8; −0.9; −0.3; −0.8	5.3; −5.5; −2.9; −4.1; −5.0
7			−2.9; −3.0; −2.0; −2.4	
4.5[b]			−4.8; −5.0; −3.5; −4.0	

[a] BVU: toluene; methanol: trimer. [b] Value of σ_{1_M} for which agreement for g_{23} between ethanol and toluene is obtained.

Table VIII
Modified Three-Parameter Model[a]

			g_{23}	
σ_{1_M}	A	B	methanol	toluene
12	1	$^2/_3$	−4.3; −4.4; −2.9; −3.4	−2.3; −2.7; +0.3; −1.3; 2.1
15			−2.9; −3.0; −1.8; −2.3	
17			−2.1; −2.2; −1.2; −1.7	
12	$A(\phi)$	$B(\phi)$	−2.3; −2.4; −1.6; −1.8	+1.1; +0.6; +2.7; +1.3; +0.8
15			−0.5; −0.6; −0.2; −0.4	
18			+1.1; +0.9; +1.0; +0.8	

[a] BVU: toluene; methanol: trimer; $\sigma_2 = 8.05$; $\sigma_3 = 6.64$; $\sigma_{1_T} = 7.45$.

Table IX
Modified Three-Parameter Model:
***ν* and *ϕ* Dependence of *A* and *B*[a]**

			g_{23}	
σ_{1_M}	A^*	B^*	methanol	toluene
10.74[b]	var[c]	0	+1.9; +1.5; +1.4; +1.1	+1.9; +1.6; +2.4; +1.8; +1.5
6			−2.1; −2.3; −1.6; −2.0	
10.74	$A(\phi)$	$B(\phi)$	+1.4; +1.1; +1.3; +1.0	+1.0; +0.8; +1.9; +1.1; +0.8
10[b]			+0.9; +0.6; +0.9; +0.6	
6			−2.2; −2.4; −1.5; −1.8	

[a] BVU: toluene; methanol: trimer. [b] Value of σ_{1_M} for which agreement for g_{23} between methanol and toluene is obtained. [c] var means different A^* values for networks PPG425/DRF ($^1/_3$), PPG1000/DRF ($^1/_4$), and PPG2000/DRF ($^1/_5$).

estimations of molecular surface areas by Bondi[26]). The improvement over the three-parameter model is obvious but can only be obtained if the association of methanol is accounted for. Therefore, further support for the interpretation presented here is desirable, e.g., by swelling measurements in other solvents, either associating or not and differing in molecular surface area. It is also clear that swelling data in at least two solvents are necessary to expose fully the shortcomings of the two-parameter and three-parameter models.

The theory of rubber elasticity, which supplies one part of the equilibrium swelling equation, contains two front factors *A* and *B*, the values of which and their dependence on the degree of swelling are still very much under discussion. The present analysis does not discriminate between the various suggestions, but this is partly due to the remaining uncertainty with respect to the concentration of elastically active network chains and the attainable surface area of the associated alcohol molecules. It is conceivable that swelling measurements on well-defined networks in a number of nonassociating solvents, differing widely in molecular surface area, might offer possibilities here, but they would have to be very accurate (see Table VII), and the evaluation should be supported by independent measurements of the enthalpic part of g_{23}. Ethers and urethane solvents might provide suitable candidates.

It might be objected that the modified three-parameter model as used here makes the rigid lattice into a physically unreal abstraction. The assignment of different numbers of nearest-neighbor contacts to the various sites seems to be in contradiction to the concept of the lattice representation of a liquid. However, the expression for the chemical potential of the solvent, used in this study, does not follow from rigid lattice considerations alone. Free volume or "equation of state" treatments yield exactly the same expression (first three terms in eq 8). The lattice can be understood to represent a mathematical aid in enumerating possible contacts and conformations[35] and the procedure finds justification in the adequacy of the descriptions it provides. Moreover, the Bondi volumes of the various entities in the system studied here are of the same magnitude (including the trimer of methanol), except for the PG repeat unit.

Still, one might prefer a "calibration" of the surface areas to the BVU, as i.e., Huggins[36] and Flory[37] have suggested. One way of doing this consists of converting the surface areas of the various species into the values they would have had if their molecular volumes were equal to that of toluene. Table VIII shows that agreement on g_{23} can again be achieved, but the surface area of the methanol trimer must not be assumed to be larger than proportionality suggests. However, we believe that the model should not be taken too literally and are satisfied with the useful trends it supplies. Table IX, finally, gives further examples for the influence of network imperfection and a swelling-ratio dependence of *A* and *B*. The better approximations seem to remove the need to treat the surface area of trimeric methanol as an adjustable parameter.

Treating the PPG/DRF networks as statistical copolymers might seem an unsuitable approach. We refer to the strictly regular mixture treatment of the solvent, PPG unit, and DRF group species in our systems, the structure of which resembles block copolymers more than statistical ones. We have no other justification than the quality of the description of the data, except perhaps Roe and Zin's finding that statistical and block copolymers based on the same two monomers do not necessarily show significant differences in thermodynamic properties as long as the system remains isotropic.[38]

So far the emphasis has been on the three networks PPG 425/DRF, PPG 1000/DRF, and PPG 2000/DRF. The $g_{ef}(T)$ relations for these three and the other two swollen networks show an interesting feature (Figure 6). It is seen that the usual relationship[39]

$$g_{ef} = g_S + g_H/T \tag{11}$$

appears to be reasonably well obeyed. The enthalpic term

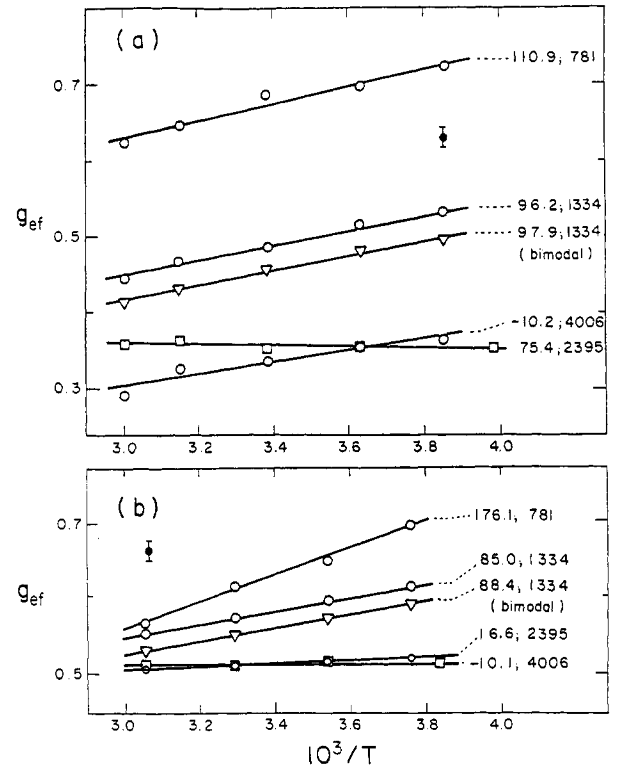

Figure 6. Swelling in single solvents, g_{ef} vs. $1/T$. Values of g_H (eq 10), determined by least-squares analysis, and M_c are indicated. Effect of probable experimental errors indicated by I: (a) toluene, (b) methanol. Calculation based on $A = 1$; $B = {}^2/_3$, BVU, toluene; trimeric methanol.

g_H varies between samples 1–3 and 5, which probably reflects a systematic dependence on ϕ_2, the latter being somewhat stronger with methanol. It is of particular interest to note the correspondence for *both* solvents between the unimodal and bimodal networks with identical M_c. The enthalpic terms (g_H) are essentially identical but they differ in the entropic conribution g_s to g_{ef}. It is not obvious why this should be so. The enthalpic term may be assumed independent of the chain geometry (linear, long-chain branched, cross-linked) but depends—within the strictly regular approximation—on ϕ_2 which has the same value in networks 2 and 5. The same situation is encountered with other A/B combinations. Little is known about the entropic consequences of the chain length distribution between cross-links, which, if we use the modified Flory–Rehner equation, might show up in g_S. The little information available at present deals with stress–strain behavior only[40–42] and predicts no influence at all from elastic sources.[42] The mixing term in the swelling equation can hardly be considered responsible for the significant differences in g_S and we have to leave the problem open for the moment. The same holds for network 4, which shows a differing $g_{ef}(T)$ behavior in both solvents for which we cannot offer an explanation though we suspect that a relatively large number of dangling chains are present that they might partially invalidate the analysis.

Conclusion

The objective of the study, separation of the χ parameters in χ_{ef}, or the g terms in g_{ef}, has been achieved up to a point only. The experimental accuracy limits the discussion to rough values of χ_{23} or g_{23} only, but they are good enough to reject two of the three interaction models considered. The results stress (a) the importance of accounting for disparities in numbers of nearest neighbors in the analysis of swelling data, (b) the necessity of comparing such data in different solvents, (c) the need for more decisive information on the front factors A and B, and (d) the importance of attempting to prepare perfect networks, particularly when the emphasis is on the evaluation of interaction parameters.

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Appendix. Modified Three-Parameter Model

We have three different molecules and repeat units in the system in which the polymeric constituent is considered not cross-linked for the moment: solvent, PG units, and $OCNC_6H_4O$ groups with coordination numbers (average numbers of nearest neighbors) z_1, z_2, and z_3, respectively. The usual strictly regular calculation of the various numbers of contact pairs P_{ij}[24,43] yields $P_{ij} = N_i\theta_j$ for $i \neq j$ and for pairs of identical species $P_{ii} = N_i\theta_i/2$, where $N_i = z_i n_i m_i$, $\theta_j = N_j/\sum_1^3 N_i$ (n_i representing the number of moles of species i, each occupying m_i moles of BVUs). We may write

$$\sum_1^3 N_i = N_\phi z_1 Q$$

where $N_\phi = \sum n_i m_i$, $Q = \phi_1 + s_{21}\alpha\phi = \phi_1 + \beta\phi = 1 + (\beta - 1)\phi$, $\alpha = \phi_2 + s_{32}\phi_3$, $s_{32} = z_3/z_2$, $\phi_1 = n_1 m_1/N_\phi$, $\phi = nm/N_\phi$, n is the number of moles of polymer molecules occupying M BVUs each, $\beta = s_{21}\alpha$, and $s_{21} = z_2/z_1$.

Making up the changes ΔP_{ij} the numbers of pairs ij undergo upon mixing, and multiplying each of them by the relevant contribution to the internal energy per contact, w_{ij}, we derive the internal energy change upon mixing, ΔU

$$\Delta U/N_\phi RT = (N_1\theta_2/N_\phi)(\Delta w_{12}/RT) + (N_1\theta_3/N_\phi)(\Delta w_{13}/RT) + [N_2(\theta_3 - \theta_3^0)/N_\phi](\Delta w_{23}/RT) \quad \text{(A1)}$$

where $\theta_3^0 = N_3/(N_2 + N_3)$ is the surface fraction of 3 in the dry network. Changing to volume fractions ϕ_1 and ϕ, we obtain

$$\Delta U/N_\phi RT = (\phi_1\phi/Q)(\phi_2 g_{12} + \phi_3 g_{13} - \phi_2\phi_3 g_{23}/\alpha) = (\phi_1\phi/Q)g_{ef} \quad \text{(A2)}$$

where $g_{ij} = z_j\Delta w_{ij}/RT$. The second expression in brackets defines g_{ef} in the modified three-parameter model (eq 5). (Note that $n_2 m_2 = N_\phi\phi_2\phi$ and $n_3 m_3 = N_\phi\phi_3\phi$.)

The Gibbs free energy, ΔG_{mix}, of mixing n_1 moles of solvent with n moles of copolymer is obtained adding combinatorial contributions[8–10]

$$\Delta G_{mix}/RT = n_1 \ln \phi_1 + n \ln \phi + n_1 m_1 \phi g_{ef}/Q \quad \text{(A3)}$$

Following Flory and Rehner[1] we combine eq A3 with their expression (1) for the elastic contribution ΔG_{el} (setting $\lambda_x = \lambda_y = \lambda_z = \lambda$) and subsequently take the first derivative with respect to n_1. We set $m = \infty$ in the resulting equation and obtain

$$\ln (1 - \phi) + \phi + m_1\chi_{ef}\phi^2 + \nu_e m_1 V_b(A\phi^{1/3} - B\phi) = 0 \quad \text{(A4)}$$

which is eq 8 with $\chi_{ef} = g_{ef}\beta/Q^2$. If we set $\nu_e = \rho/M_c$ we assume all chains in the network to be elastically active. Corrections may be introduce via A^* and B^* (see text).

We follow Staverman[24] and set the ratios of coordination numbers s_{21} and s_{32} equal to the ratios of molecular surface areas σ, attainable for the other molecules and units:

$$s_{ij} = \sigma_i/\sigma_j \qquad \text{(A5)}$$

Estimations for σ_k have been obtained from Bondi's work.[26]

Values for g_{ef} calculated from equilibrium swelling data depend on the choice of V_b (monomeric or trimeric methanol, or toluene) as well as on the model used for front factors A and B. In modern views on rubber elasticity one encounters the possibility for A and B to depend on the swelling ratio.[44] The relations are complex and implicit and we have checked on the effect such dependencies will have on the interaction parameters using as a first approximation

$$A = A_1 + A_2\phi; \qquad B = B_1 + B_2\phi \qquad \text{(A6)}$$

and setting $A = {}^1/_3$, $B = 0$ at $\phi = 0$, and $A = 1$, $B = {}^2/_3$ at $\phi = 1$. Equation A4 has to be amended and changes into

$$\ln (1 - \phi) + \phi + m_1\chi_{ef}\phi^2 + \nu_e m_1 V_b\{A_1\phi^{1/3} - B_1\phi + A_2\phi(3\phi - \phi^{1/3})/2 - B_2\phi^2(1 + \ln \phi)\} = 0 \qquad \text{(A7)}$$

Registry No. (Desmodur RF)(PPG) (copolymer), 88546-51-4.

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Light Scattering Studies of Ionomer Solutions

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ABSTRACT: The molecular parameters responsible for the solution properties of poly(styrenesulfonate) ionomers in both a polar and a relatively nonpolar solvent have been studied. The second virial coefficients, apparent molecular weights, and diffusion coefficients have been measured by a combination of static and quasi-elastic light scattering techniques. Solution viscosities have also been measured. From this combination of scattering and rheological information, a more detailed description emerges of ionomer solution behavior over a range of solvent polarities, polymeric molecular weights and ionic contents, and concentrations.

Introduction

Rheological properties of flexible long-chain polymers can be dramatically altered by introducing a very small fraction of ionic groups along the hydrocarbon backbone. A frequently observed manifestation of this ionic effect is the significant change in the melt-flow behavior of bulk ion-containing polymers.[1,2] Polymers containing up to 10 mol % of such groups are commonly called ionomers. Recently, solution viscosity studies have revealed several unusual properties in dilute and semidilute ionomer solutions.[3-9] This behavior must have its origins in the conformations of the individual chains and the interactions induced by the presence of the salt groups. The conformation of a single ionomer chain in solution is determined by a complicated balance of forces. These forces can include charge repulsion and screening, van der Waals in-

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