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Dependence of swelling degree on solvent composition of two-component copolymer networks in mixed solvents

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The two-component copolymer networks, polystyrene/poly(tetrahydrofuran) and poly(methyl methacrylate)/poly(tetrahydrofuran), were synthesized and their swelling behaviour was investigated in three kinds of mixed solvents, which were chosen so as to contrast with one another in respect of solubility of the component polymers. These copolymer networks exhibited three types of solvent composition dependence of the swelling degree, corresponding to the three kinds of mixed solvents: existence of a maximum, a monotonic change, and a significant change having an inflection point, in the same manner as the polystyrene/poly(dimethylsiloxane) copolymer networks reported by us previously. These three types of swelling behaviour were analysed thermodynamically on the basis of swelling equations. For this purpose, the Flory–Huggins χ parameters were also determined from osmotic pressures for some polymer/solvent systems. The Flory–Rehner swelling equation, extended to copolymer networks by Kojima *et al.*, reproduced qualitatively the former two types of swelling behaviour. For the last type, the Flory–Huggins χ parameters were obtained from the experimental swelling degrees, from which it was suggested that an inflection point in the curve of swelling degree *versus* solvent composition appeared in the vicinity of the θ state.

(Keywords: copolymer network; swelling degree; mixed solvent)

INTRODUCTION

Recently, we have reported[1,2] the synthesis of two-component copolymer networks by a new method[1–5]. The two-component copolymer network does not comprise two kinds of polymer networks, like an interpenetrating polymer network (IPN), but is a single network having two components, as shown in *Figure 1*. The copolymer network is expected to exhibit unique swelling behaviour in mixed solvents because of various combinations of interactions between the different components in the swollen network.

In previous work[1] on polystyrene/poly(dimethylsiloxane) (PS/PDMS) copolymer networks, we found three different types of dependence of the swelling degree on the composition of the mixed solvents. In the present work it has been observed that polystyrene/poly(tetrahydrofuran) (PS/PTHF) and poly(methyl methacrylate)/poly(tetrahydrofuran) (PMMA/PTHF) copolymer networks also exhibit the same swelling behaviour in mixed solvents. In this paper we will present the swelling behaviour in mixed solvents for these copolymer networks and analyse it thermodynamically on the basis of the swelling equation provided by Flory and Rehner[6,7], and extended to two-component copolymer networks by Kojima *et al.*[8]. For this purpose, the Flory–Huggins χ parameters for some polymer/solvent systems were also determined from osmotic pressures.

EXPERIMENTAL

Syntheses of two-component copolymer networks

The copolymer networks, PS/PTHF and PMMA/PTHF, were prepared by crosslinking PS and PMMA, respectively, with telechelic PTHF by the method reported previously[1–5].

Telechelic PTHF with 1-methylpyrrolidinium salt was prepared by living polymerization of tetrahydrofuran (THF) initiated with trifluoromethanesulfonic anhydride and terminated with 1-methylpyrrolidine (*Scheme 1*)[2–5].

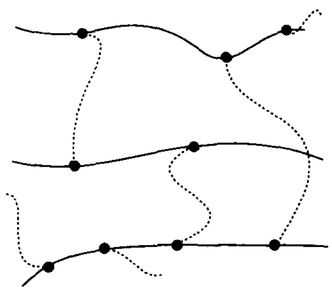

Figure 1 Schematic structure of a two-component copolymer network

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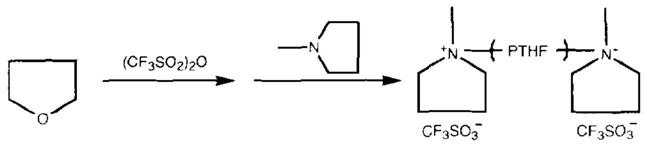
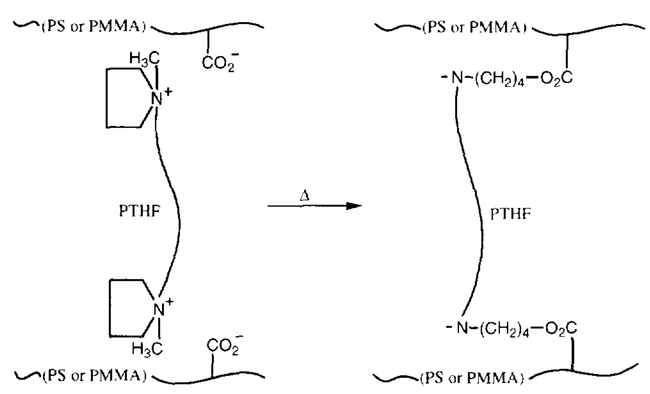


Scheme 1



Scheme 2

The product was purified by repeated precipitation from THF/cold water system, followed by freeze-drying from benzene solution. The molecular weight of PTHF was determined by gel permeation chromatography (g.p.c.) relative to polystyrene standards with the conversion factor of 0.556. The end groups of 1-methylpyrrolidinium salt were confirmed by ^1H n.m.r. spectra.

Polystyrene containing 5.26 mol% of acrylic acid was prepared by radical copolymerization of styrene and acrylic acid initiated with azobisisobutyronitrile in bulk at 60°C. The molecular weight was determined by g.p.c. measurements. The content of acrylic acid in the resulting poly(styrene-*co*-acrylic acid) was determined by titration; a 0.5% copolymer solution in THF was titrated with 0.02 N NaOH aqueous solution using phenolphthalein as an indicator. Acrylic acid units in the copolymer were converted to sodium acrylate units with sodium phenoxide according to the procedure described before[1].

PMMA containing 4.97 mol% of methacrylic acid was obtained by partial hydrolysis of PMMA; a commercial PMMA (18.8 g) with $\bar{M}_n = 75\,000$ was dissolved in the mixed solvent consisting of acetic acid (150.0 g), distilled water (37.5 g) and *p*-toluenesulfonic acid (11.25 g), and the solution was refluxed for 100 h. The reaction product was precipitated by pouring the solution into excess methanol. The product was purified by repeated precipitation from acetone/methanol and finally freeze-dried from benzene solution. The content of methacrylic acid in the copolymer was determined by titration of its solution in acetone with 0.05 N NaOH aqueous solution. Methacrylic acid was converted to sodium methacrylate with sodium phenoxide.

The crosslinking reaction was performed by the method of ionic crosslinking followed by conversion to covalent bonding[1-5]. The anion-exchange reaction of PTHF with 1-methylpyrrolidinium salt with poly(styrene-*co*-sodium acrylate) or poly(methyl methacrylate-*co*-sodium methacrylate) was carried out to give an ionically connected polymer network; both component polymers were dissolved in THF to give a total polymer concentration of 5 wt%, and then the solution was added dropwise into excess water cooled to below 5°C. In the PMMA/PTHF system, a THF/methanol mixed solvent was used instead of pure THF. The precipitate, which is a copolymer network crosslinked ionically, was recovered by filtration and subjected to heat treatment for 24 h at 100°C under vacuum, to be converted to the copolymer network crosslinked with covalent bonds (*Scheme 2*)[1-5]. This conversion was confirmed by i.r. measurements. The unreacted polymers were removed by Soxhlet extraction with THF. The composition of the copolymer network was determined by elemental analysis. As a result, the crosslinking reaction was found to proceed almost completely.

Measurements

^1H n.m.r. spectra were recorded by means of Jeol GX-270 apparatus in $CDCl_3$, at 40°C. I.r. spectra were taken on a Hitachi 260-10 i.r. spectrophotometer or Shimadzu FT-IR 8100 spectrometer. G.p.c. measurements were carried out using a Tohso model CCPH high liquid chromatograph equipped with a column of TSK G3000HXL or G4000HXL.

Degrees of swelling of the copolymer networks were determined by measuring the weights of the dry network and of the wet network immersed in the solvent at 25°C. Expression of the swelling degrees was converted from a weight ratio to a volume ratio using the densities of the polymers and solvents at 25°C.

The Flory–Huggins χ parameters for the polymer/solvent systems were determined from osmotic pressures measured with a high-pressure osmometer[9] at 25°C. The molecular weights of PS, PMMA, PDMS and PTHF used in the osmotic pressure measurements were $\bar{M}_v = 60\,000$, $\bar{M}_n = 75\,000$, $\bar{M}_v = 80\,000$ and $\bar{M}_w = 72\,000$, respectively.

RESULTS

The characteristics of the copolymer networks used in this work are shown in *Table 1*, together with those of PS/PDMS networks reported previously. In these networks, the molecular weight distribution between crosslinks for the PTHF and PDMS components is as narrow as ~1.1 because the PTHF and PDMS polymers were obtained by living polymerization; molecular weight distribution for the PS and PMMA components is less controlled. The crosslinking points along the PS and PMMA chains may be randomly distributed because those points given by acrylic acid and methacrylic acid monomer units were introduced by radical copolymerization and partial hyhdrolysis, respectively. Provided that the crosslinks are placed at the same interval along the PS or PMMA chain, the average degrees of polymerization between crosslinks can be estimated from the molecular weight of the crosslinkers, PTHF or PDMS, and the weight fractions of the component polymers. The degrees of polymerization between crosslinks thus determined are presented in *Table 1*.

Figure 2 shows the time dependence of degrees of swelling for the PMMA/PTHF-1 and PS/PTHF-1 networks in methyl ethyl ketone (MEK) at 25°C. PS/PTHF-1 reached an equilibrium state in about 300 min, and PMMA/PTHF-1 in about 2000 min. Hereafter the degree of swelling for all the samples was measured

Table 1 Two-component copolymer networks

Network	$M_n \times 10^{-3}$ PDMS or PTHF	$M_n \times 10^{-4}$ original PS or PMMA[a]	Weight fraction PDMS or PTHF	Degree of polymerization between crosslinks	
				PS or PMMA	PDMS or PTHF
PS/PDMS-1[b]	6.7	5.2	0.28	83	91
PS/PDMS-2[b]	6.7	3.0	0.24	102	91
PS/PTHF-1	23.0	10.6	0.81	25	317
PS/PTHF-2	3.6	10.6	0.24	53	50
PMMA/PTHF-1	11.0	7.5	0.50	56	150
PMMA/PTHF-2	3.6	7.5	0.43	24	5

[a] Polymers before crosslinking
[b] Reference 1

Table 2 Solubility of polymers in various solvents used in swelling measurements

Solvent	PS	PMMA	PDMS	PTHF
MEK	good	good	θ^a	θ^b
CH	θ^c		good	good
m-Xy		θ^d		
THF	good	good	good	good
Bz	good	good	good	good
MeOH	non	non	non	non

θ temperatures from ref. 13
[a] 20°C
[b] 25°C
[c] 34.5°C
[d] 24°C

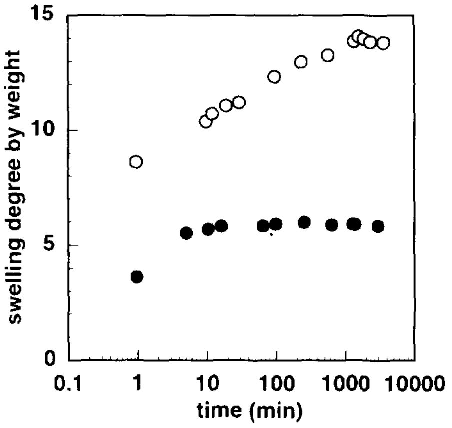


Figure 2 Time dependence of the swelling degree for the PMMA/PTHF-1 (○) and PS/PTHF-1 (●) networks in MEK at 25°C

for the network membrane kept in the solvent for 40 h. In that condition the swollen network may be in an equilibrium state.

The solvents used here were MEK, cyclohexane (CH), THF, benzene (Bz), *m*-xylene (*m*-Xy) and methanol (MeOH). Solubilities of the component polymers to these solvents are listed in *Table 2*, together with the solvents used for the PS/PDMS networks presented previously[1]. Three types of binary combinations of these solvents were used as mixed solvents for swelling measurements, so that the combinations would contrast with one another in respect of solubility of the component polymers: (1) combination of good and θ (i.e. poor) solvents which are reversed for two-component polymers; (2) combination of two good solvents for both component polymers; and (3) combination of a non-solvent and a good solvent for both component polymers. For the PS/PTHF and PS/PDMS networks, the MEK/CH mixed solvent corresponds to case (1), the Bz/THF mixed solvent to case (2), and the MeOH/THF mixed solvent to case (3). For the PMMA/PTHF network, the *m*-Xy/MEK mixed solvent corresponds to case (1), and the mixed solvents corresponding to cases (2) and (3) are the same as those for the PS/PTHF or PS/PDMS networks.

Figures 3–5 show the dependence of the swelling degree on the solvent composition of the three kinds of mixed solvents for the PS/PDMS, PS/PTHF and PMMA/PTHF networks, respectively. As shown in these figures, three different types of swelling behaviour were observed for three cases of mixed solvents, respectively. For all the copolymer networks in the mixed solvent corresponding to case (1), a maximum exists in the curve of the swelling degree *versus* solvent composition. In case (2), the swelling degree changed almost linearly with the solvent composition. In case (3), the swelling degree changed significantly with the solvent composition as if a swelling transition occurred.

DISCUSSION

We will duscuss the three kinds of swelling behaviour for cases (1)–(3) by applying the swelling equations.

Kojima *et al.*[8] proposed the following equation for swelling of the copolymer network with three-functional crosslinks by extending the Flory–Rehner expression[6,7]:

$$\chi_{ef} v_p^2 + \ln(1 - v_p) + v_p = (2/3)(v_1/Z_1 + v_2/Z_2) - v_p^{-2/3}(v_1 r^2 g^2/Z_1 + v_2 g^2/Z_2) \quad (1)$$

where χ_{ef} is the effective interaction parameter between the copolymer and solvent, v_p is the volume fraction of the copolymer, v_1 and v_2 are the volume fractions of the component polymers 1 and 2, i.e. $v_p = v_1 + v_2$, Z_1 and Z_2 are the ratios of the volume of the respective polymers to that of the solvent, r is given by the ratio of the elastic expansion factors α_1 and α_2, i.e. α_1/α_2, and g is the parameter given by

$$g = (w + 1)/(rw + 1) \quad (2)$$

where w was put as $2(Z_1/Z_2)^{1/2}$ by modifying the original expression (see Appendix 1).

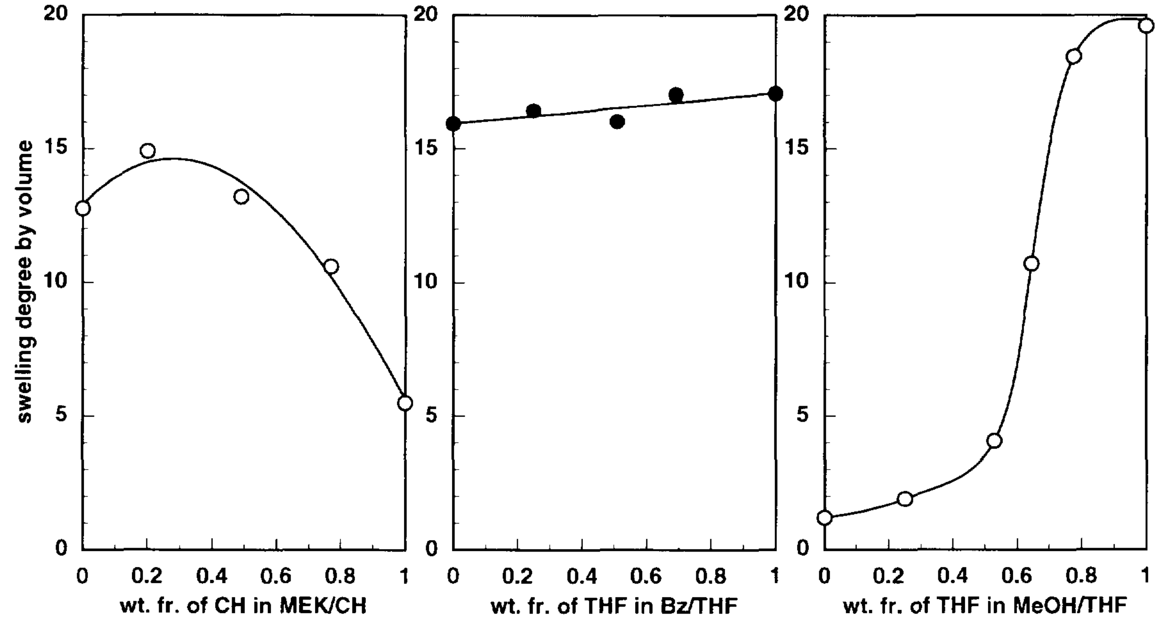


Figure 3 Dependence of the swelling degree on the solvent composition for the PS/PDMS-1 (○) and -2 (●) networks in three types of mixed solvents at 25 C. The swelling degrees expressed by weight ratio in the previous work[1] were converted to volume ratio

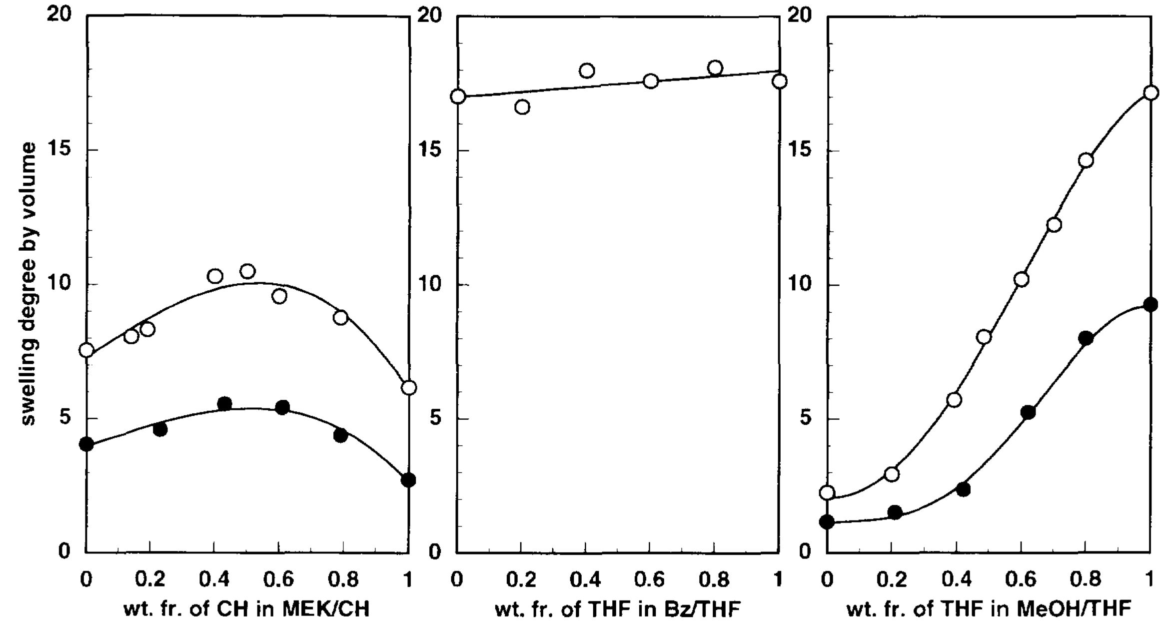


Figure 4 Depcncence of the swelling degree on the solvent composition for the PS/PTHF-1 (○) and -2 (●) networks in three types of mixed solvents at 25 C

Evaluating the swelling degree Q, i.e. v_p^{-1}, by the use of equation (1), we need the parameters χ_{ef}, v_i, α_i and w as well as Z_i which can be determined from the molecular weight and density of polymer i ($i = 1, 2$). The expansion factor α_i was calculated from the Flory–Rehner equation for the homopolymer network by use of the χ value for the corresponding system.

In the present work, the effective interaction parameter χ_{ef} between the copolymer and mixed solvent was evaluated on the assumption that the segments were mixed randomly in the swollen network because microphase separation was not considered to occur in the present swelling degrees, which corresponded to about 10% polymer solutions. Then, the parameter χ_{ef} may be expressed by the following equation[10] for the mixture of the copolymer ($P1_xP2_{1-x}$) and the mixed solvent ($S1_y/S2_{1-y}$):

$$\chi_{ef} = xy\chi_{P1/S1} + x(1-y)\chi_{P1/P2} + (1-x)y\chi_{P2/S1} + (1-x)(1-y)\chi_{P2/S2} - x(1-x)\chi_{P1/P2} - y(1-y)\chi_{S1/S2} \tag{3}$$

where $\chi_{i/j}$ is the intersegmental interaction parameter between the segments i and j, and x and y are the copolymer composition and the solvent composition, respectively, expressed with volume fractions.

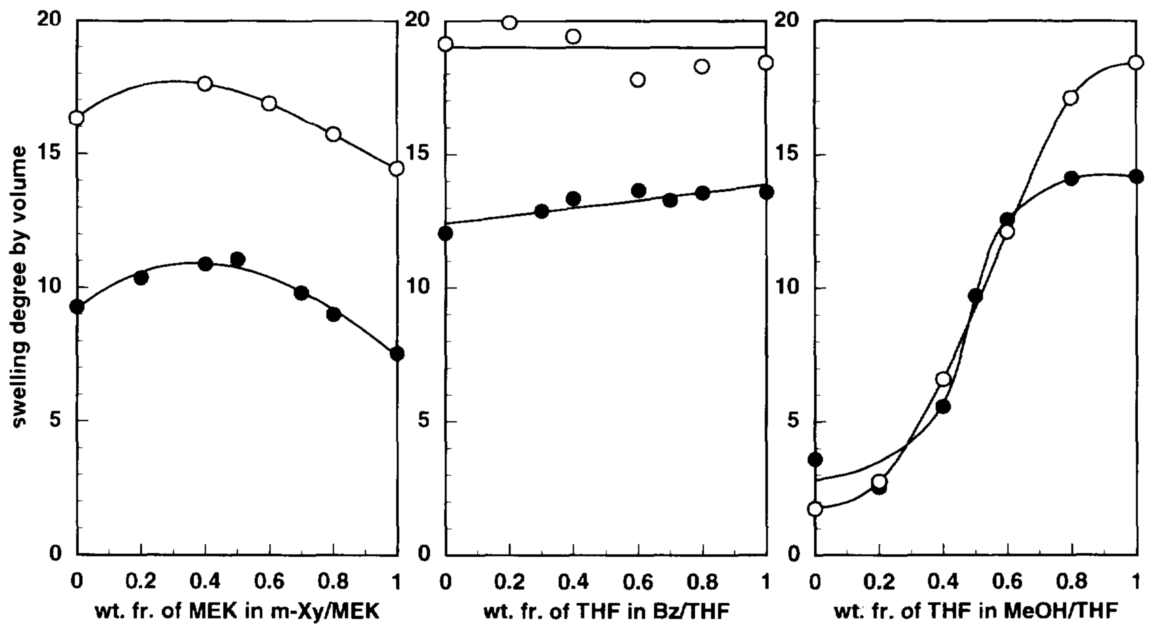


Figure 5 Dependence of the swelling degree on the solvent composition for the PMMA/PTHF-1 (○) and -2 (●) networks in three types of mixed solvents at 25 C

Table 3 Values[a] of χ parameters used in calculations of swelling degree

	PS	PMMA	PDMS	PTHF
CH	0.500[b]		0.429[c]	0.447
MEK	0.476[d]	0.400[e]	0.500[b]	0.500[b]
m-Xy		0.500[b]		0.470[e]
Bz	0.449[f]	0.467[g]	0.481[c]	0.472[h]
THF	0.474	0.442	0.454	0.292
PS			0.00497[i]	0.0144[i]
PMMA				0.088[i]

[a] Values per molar volume or Flory's molar core volume of the corresponding solvent except the polymer–polymer interaction parameters. The values without footnotes were determined in this work; see Appendix 2

[b] The θ temperature was approximated to be 25 C. See *Table 2* for θ temperature

[c] Reference 14

[d] Reference 15

[e] Arbitrary value

[f] Determined from the second virial coefficient in ref. 16

[g] Determined from the second virial coefficient listed in ref. 17

[h] Reference 18

[i] Values divided by molar volume of the segment

Table 4 Solubility parameters[a] δ used in determination of solvent–solvent χ parameters

	MEK	CH	THF	Bz	*m*-Xy
δ (cal cm^{-3})$^{1/2}$	9.3	8.2	9.1	9.2	8.8

[a] Reference 19

Some intersegmental parameters $\chi_{i/j}$ between the component polymer and solvent were taken from the literature (see footnotes to *Table 3*) and others were obtained from the osmotic pressures measured in this work (see Appendix 2). The $\chi_{i/j}$ parameters between the component polymers i and j were evaluated so that the calculated swelling degree in the pure solvent could fit that found experimentally: the swelling degree for PS/PDMS-1 in CH, for PS/PTHF-1 in THF, and for PMMA/PTHF-2 in THF. These $\chi_{i/j}$ values are listed in *Table 3*. In calculations of the swelling degrees, the values of $\chi_{i/j}$ shown in *Table 3* were converted to the values per molar volume of the mixed solvent averaged with respect to the solvent composition. The values of $\chi_{i/j}$ between the solvents S1 and S2 were estimated from the solubility parameters δ_{S1} and δ_{S2} using

$$\chi_{S1/S2} = (\delta_{S1} - \delta_{S2})^2 V_o / RT \qquad (4)$$

where V_o is the molar volume of the solvent, averaged with respect to the solvent composition. The solubility parameters used are listed in *Table 4*.

Equation (1) with the parameters thus determined was applied to swelling of cases (1) and (2) but not to case (3) because it is hard to evaluate the $\chi_{i/j}$ parameters between the non-solvent and polymer. The swelling curves calculated for cases (1) and (2) are shown in *Figures 6* and *7*, respectively. The calculated curves can qualitatively reproduce the features of the respective swelling types: existence of a maximum and a monotonic change.

The shape of the swelling curve may obey the dependence of χ_{ef} on the solvent composition y. A maximum point in the swelling curve may correspond to a minimum in the χ_{ef} *versus* y curve. Since χ_{ef} is a quadratic function of y, as seen in equation (3), a minimum of χ_{ef} occurs at

$$y = [x(\chi_{P1/S2} - \chi_{P1/S1}) + (1-x)(\chi_{P2/S2} - \chi_{P2/S1}) + \chi_{S1/S2}]/2 \qquad (5)$$

and a maximum in the swelling curve appears in the condition

$$0 < [x(\chi_{P1/S2} - \chi_{P1/S1}) + (1-x)(\chi_{P2/S2} - \chi_{P2/S1}) + \chi_{S1/S2}]/2 < 1 \qquad (6)$$

Therefore, the appearance of the maximum in the swelling curve of case (1) does not depend only on the relation between the values of $\chi_{i/j}$ parameters but also on the composition x of the component polymers. The solvent composition giving a maximum swelling degree in the

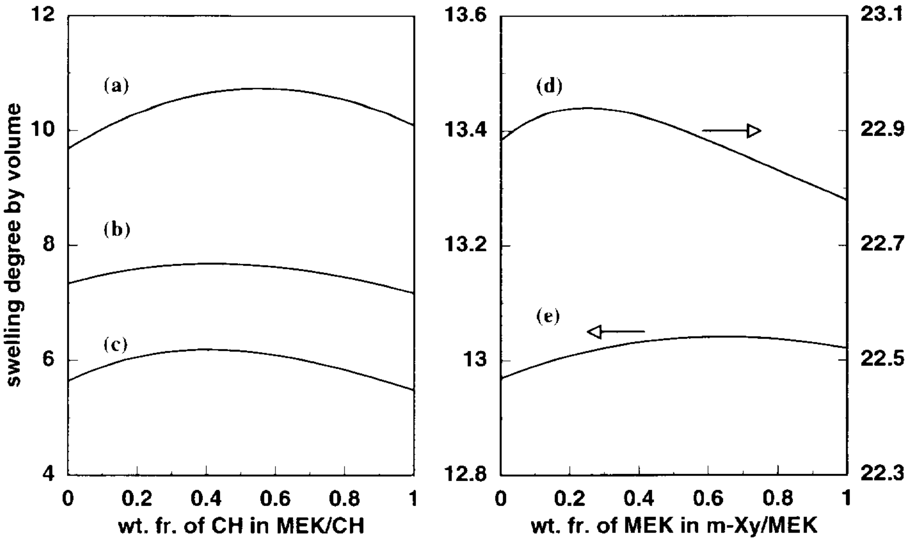


Figure 6 Calculated dependence of the swelling degree on the solvent composition for the systems corresponding to case (1): (a) PS/PTHF-1; (b) PS/PTHF-2; (c) PS/PDMS-1; (d) PMMA/PTHF-1; (e) PMMA/PTHF-2

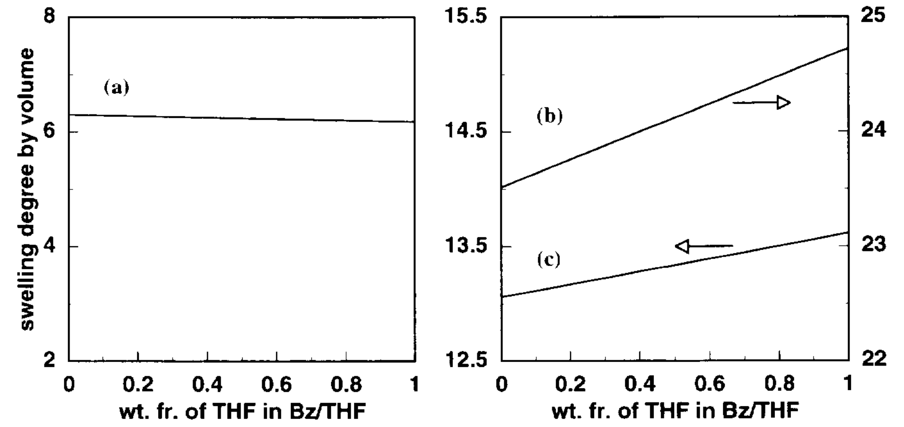


Figure 7 Calculated dependence of the swelling degree on the solvent composition for the systems corresponding to case (2): (a) PS/PDMS-2; (b) PMMA/PTHF-1; (c) PMMA/PTHF-2

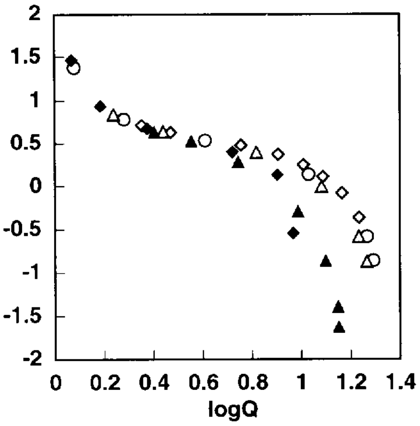


Figure 8 Interaction parameter χ *versus* logarithm of the swelling degree Q for various networks in the MeOH/THF mixed solvent: (○) PS/PDMS-1; (◇) PS/PTHF-1; (◆) PS/PTHF-2; (△) PMMA/PTHF-1; (▲) PMMA/PTHF-2. The χ values were obtained from the experimental swelling degrees using equation (7)

calculated swelling curves shown in *Figure 6* agrees qualitatively with that in the experimental swelling curves for case (1) shown in *Figures 3–5*. On the other hand, the swelling characteristic of case (2), i.e. a monotonic swelling curve, can be realized outside the condition (6). In particular, when both S1 and S2 are sufficiently good solvents for the component polymers P1 and P2, it may be considered that $\chi_{P1/S1} \approx \chi_{P1/S2}$ and $\chi_{P2/S1} \approx \chi_{P2/S2}$, which may lead to $\chi_{S1/S2} \approx 0$. Then, χ_{ef} depends almost linearly on y, as is obvious from equation (3). This may give a monotonic curve in the dependence of the swelling degree on the solvent composition.

In case (3), which has a significant change in the swelling curve, the χ_{ef} values were evaluated from the experimental swelling degrees using the following Flory–Rehner equation[6,7] for the three-functional polymer networks:

$$\chi_{ef} v_p^2 + \ln(1 - v_p) + v_p = -V_o(v_c/V_{po})(v_p^{-1/3} - 2v_p/3) \quad (7)$$

where v_c/V_{po} is the number of network chains per unit volume of dry network. The values of χ_{ef} obtained from the experimental swelling degrees in THF/MeOH mixed solvent are plotted against the logarithm of the swelling degree Q $(= v_p^{-1})$ in *Figure 8*. The curve of χ_{ef} *versus* log Q has an inflection point in the vicinity of $\chi_{ef} = 0.5$, and the swelling degree changes greatly with a slightly differing value of χ_{ef} around 0.5. This means that the swelling behaviour in the THF/MeOH mixed solvent is not a swelling transition but a continuous change occurring in the θ state, as discussed by Hsu and Cohen[11]. A higher order of magnitude of the crosslink density v_e/V_{po} will be required for the swelling transition to occur for the present non-ionic networks.

ACKNOWLEDGEMENTS

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APPENDIX 1

In the original paper by Kojima *et al.*[8], the length to the direction of an axis (for example, the x-axis) for the unswollen copolymer network was assumed to be the sum of the lengths proportional to the numbers of bond vectors of the component polymers, i.e. approximately proportional to the weights of the component polymers. Thus, w was put as the ratio of the weights of the component polymers, i.e. $w = n_1M_1/n_2M_2$, where n_i and M_i are the number and the molecular weight, respectively, of the component chain i ($i = 1, 2$) between crosslinks. In this paper, on the other hand, we assumed that the length to the x-axis for the unswollen copolymer network was distributed proportionally with respect to $n_iZ_i^{1/2}$ on the basis of the Gaussian chain of the component polymer. This assumption gives $w = n_1Z_1^{1/2}/n_2Z_2^{1/2}$, which leads to $2(Z_1/Z_2)^{1/2}$ for the three-functional network.

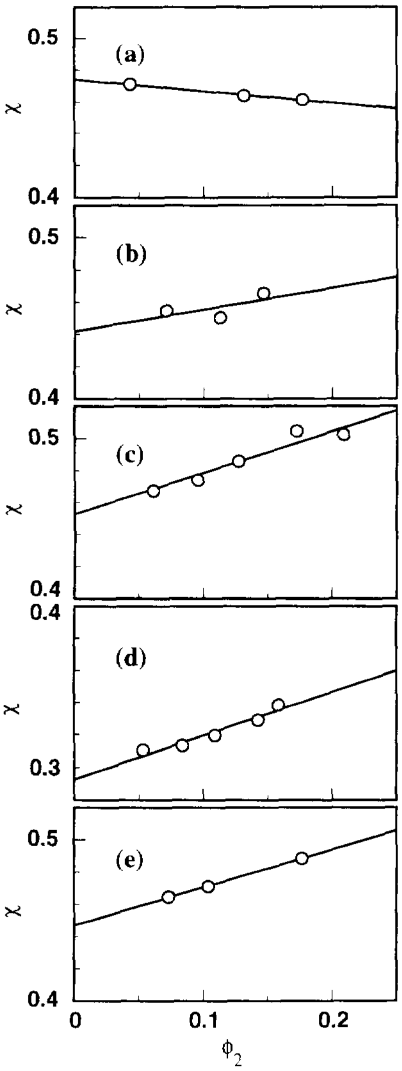

Figure A-1 Dependence of the χ parameter on the core volume fraction obtained from osmotic pressures for systems (a) THF/PS, (b) THF/PMMA, (c) THF/PDMS, (d) THF/PTHF and (e) CH/PTHF at 25°C

APPENDIX 2

The χ parameters determined in this work were obtained from osmotic pressures measured with a high-pressure osmometer. *Figure A-1* shows the dependences of the χ parameter on the core volume fraction ϕ_2 of the polymer at 25°C. The core volume fraction defined by Flory[12] can be written as:

$$\phi_2 = w_2v^*_{sp,2}/(w_1v^*_{sp,1} + w_2v^*_{sp,2}) \tag{A-1}$$

where w_i and $v^*_{sp,i}$ are the weight fraction and the specific core volume of component i ($i = 1, 2$), respectively. v^*_{sp} can be experimentally obtained from the thermal expansion coefficient α and the specific volume v_{sp} using

$$\tilde{v}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \tag{A-2}$$

$$\tilde{v} = v_{sp}/v^*_{sp} \tag{A-3}$$

The results obtained from the experimental χ values by the least squares method are as follows:

THF/PS	$\chi = 0.474 - 0.073\phi_2$
THF/PMMA	$\chi = 0.442 + 0.135\phi_2$
THF/PDMS	$\chi = 0.454 + 0.258\phi_2$
THF/PTHF	$\chi = 0.292 + 0.269\phi_2$
CH/PTHF	$\chi = 0.447 + 0.235\phi_2$

The values extrapolated to $\phi_2 = 0$ are shown in *Table 3*, and in the calculations of swelling degrees those values were converted to the values per molar volume of the corresponding mixed solvents, as described in the text.