Swelling of Poly(methyl methacrylate-*co*-poly(oxytetramethylene) dimethacrylate)s

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ABSTRACT: Swelling studies are given for copolymers of methyl methacrylate (MMA) with poly(oxytetramethylene) dimethacrylate (POTMDM). An equation applicable to the swelling equilibrium of cross-linked copolymer + solvent ternary systems is presented, which includes an assumption that the ratio between the different elastic expansion factors, α_1 and α_2, is constant at various compositions. This equation is applicable to the swelling behavior for poly(MMA-*co*-POTMDM) with various (M_1/M_2), though the negative χ_{12} values are estimated for the copolymer in moderately hydrogen-bonded solvents. These extraordinary χ_{12} values are explained in terms of a contribution of hydrogen bonding to the enthalpy.

Introduction

Copolymers of methyl methacrylate (MMA) with poly(oxytetramethylene) dimethacrylate (POTMDM) have either a MMA polymer (PMMA) chain or a poly(oxytetramethylene) (POTM) chain between cross-links, and, therefore, some of their physical and physicochemical properties are considered to be influenced by the MMA/POTM composition. Actually, even a POTMDM homopolymer exhibits a dependence of the relaxation process on the methacrylate/oxytetramethylene composition of the polymer.[1,2]

The Flory–Rehner equation[3,4] is used for interpreting consistently the swelling behavior of cross-linked polymer + solvent binary systems.[5-7] However, the Flory–Rehner equation with the number-average molecular weights of polymer chains of PMMA and POTM overestimates the degree of swelling of poly(MMA-*co*-POTMDM).

The expression for the cross-linked copolymer + solvent ternary systems should include two different polymer–solvent interaction parameters, χ_{01} and χ_{02}, and a polymer–polymer interaction parameter, χ_{12}, and two different expansion factors, α_1 and α_2, for PMMA and for POTM.

In the present work, our object is to derive and evaluate an equation applicable to the swelling equilibrium of poly(MMA-*co*-POTMDM) + solvent systems. The derivation of the swelling entropy is carried out according to a swelling cycle provided by Flory.[4] Here the most difficult problem is to differentiate the elastic expansion factors, α_1 and α_2 with respect to the number of solvent molecules, n_0. Assuming that α_1/α_2 is independent of n_0, we derive an equation of swelling equilibrium for poly(MMA-*co*-POTMDM) + solvent ternary systems.

The copolymers studied here span the MMA/POTM composition range 1/3 to 400/1 (w/w).

Experimental Section

Poly(oxytetramethylene) Dimethacrylate (POTMDM). The synthesis of POTMDM was performed by an usual esterification procedure[8] using poly(oxytetramethylene (POTM) with two hydroxy end groups and an excess of fresh methacryloyl chloride (10 times the stoichiometric amount). The reaction mixture was poured into warm water (about 330 K). The product was yielded after phasing out, washed with warm water several times, and dried at room temperature under vacuum. The fresh methacryloyl chloride was readily prepared, following a general procedure[9] starting with benzoyl chloride and methacrylic acid (both reagents were purchased from Wako Pure Chemicals USA, Ltd., Dallas, TX). By a courtesy of du Pont Japan Ltd., poly(oxytetramethylene) glycol (teratane 2900, $M_n \simeq 2900$) was provided to the present work.

Polymerization. All polymers used in the present work were prepared by bulk polymerization at 333 K for 24 h in a flame-sealed 20-mm ϕ glass tube. Benzoyl peroxide (Wako Pure Chemicals USA, Ltd.) recrystallized twice from ethanol was used as an initiator. We chose 10 MMA/POTMDM weight ratios in feed, in the range 1/3 to 400/1 (w/w), in order to obtain the copolymers with different MMA compositions. After Soxhlet extraction with acetone, the residual copolymer was dried under vacuum until its weight became constant. The PMMA content in copolymer was determined by weighing the polymer after the extraction, since the most abundant product extracted was linear PMMA. Methyl methacrylate (Wako Pure Chemicals USA, Ltd.) was used after distillation under reduced pressure.

A copolymer of MMA with 0.1 wt % of ethylene dimethacrylate (EDMA) was synthesized by a similar bulk polymerization, for determination of the polymer–solvent interaction parameter of PMMA.

Swelling Experiment. A ca. 20 mm ϕ × ca. 5 mm disk of polymer precisely weighed was immersed in a solvent at 298 K for 4 days. The swollen polymer was surface-dried and weighed in a closed vessel. The resulting volume fraction, v_p, of polymer in the swollen polymer was given as

$$v_p = [d_p d_0^{-1} (s_w - 1) + 1]^{-1}$$

where d_p and d_0 are the densities of polymer and solvent and s_w is the weight degree of swelling obtained as the ratio of weights between starting and swollen polymers. The d_p values were obtained by weighing polymer in atmosphere and in ethanol.

All solvents used in the swelling experiment were purchased from Wako Pure Chemicals USA, Ltd., and were purified by usual methods.[10]

Partial Molal Free Energy of Swelling

Entropy of Swelling. The entropy of swelling may be calculated by using the entropy changes associated with the following processes:[3,4] (1) interlinking of undiluted polymer chains (ΔS_1), (2) dilution of polymer chains with solvent molecules (ΔS_2), (3) interlinking of diluted polymer chains (ΔS_3), and (4) swelling of the polymer network (ΔS_s):

$$\Delta S_s = \Delta S_2 + \Delta S_3 - \Delta S_1 \tag{1}$$

The MMA/POTMDM copolymer is the assemblage of n_1 PMMA chains and n_2 POTM chains. The probability of formation of network, Ω_1, is given by

$$\Omega_1 = \omega_1\omega_2 \quad (2)$$

where ω_1 and ω_2 are the probabilities of formation of a chain end surrounded by two PMMA chains and by a PMMA chain and a POTM chain. The probability that a chain end in an element with a volume of $\Delta\tau$ will be surrounded by a polymer chain is equal to the product of the number of chains and $\Delta\tau/V$ where V is the volume of the whole swollen network. Therefore, ω_1 and ω_2 are given by (Appendix)

$$\omega_1^{1/2} = 3^{(n_2+1)}(\Delta\tau/V)^{(n_2+1)}(2n_1/3)!/[(n_2-1)/3]!$$

$$\omega_2 = \omega_{21}\omega_{22}$$

$$\omega_{21} = (\Delta\tau/V)^{n_2}(n_1-1)!/(n_2-1)!$$

$$\omega_{22} = 3^{n_2}(\Delta\tau/V)^{n_2}[(4n_2+1)/3-1]!/[(n_2+1)/3]!$$

Introducing the Stirling approximation and using the Boltzmann relation, we may express the entropy change through process 1 as

$$\Delta S_1 = (4/3)kn \ln (4n\Delta\tau/3Ve) + (2/3)kn \ln 2 \quad (3)$$

where $n = n_1 + n_2$ and $n_1 = 2n_2$ are used, and k is the Boltzmann constant and e is the Napier number.

The entropy of mixing through process 2 may be in accordance with the expression applied to a mixture of two polymers with different chain lengths and a solvent[11-13]

$$\Delta S_2 = -k(n_0 \ln v_0 + n_1 \ln v_1 + n_2 \ln v_2) \quad (4)$$

where n_0 is the number of solvent molecules and v_0, v_1, and v_2 are the volume fractions of solvent molecule 0, PMMA chain 1, and POTM chain 2.

Process 3 is accomplished by dilation of the most probable chain displacement length distribution by the factors α_1 for PMMA chain and α_2 for POTM chain, followed by joining of the dilated chains. Assuming that PMMA and POTM chains are independently dilated and according to the derivation[3,4,7] for binary systems, we give the elastic entropy, ΔS_{el}, for ternary systems as

$$\Delta S_{el} = kn_1(\ln \alpha_1^3 - (3/2)\alpha_1^2 + 3/2) + kn_2(\ln \alpha_2^3 - (3/2)\alpha_2^2 + 3/2) \quad (5)$$

The joining is accomplished in a fashion analogous to process 1. Then ΔS_3 is given by

$$\Delta S_3 = (4/3)kn \ln (4n\Delta\tau v_p/3Ve) + (2/3)kn \ln 2 + \Delta S_{el} \quad (6)$$

where v_p is the volume fraction of polymer; i.e., $v_p = v_1 + v_2$.

Finally, substituting these various expressions in eq 1, we obtain

$$\Delta S_s = -k(n_0 \ln v_0 + n_1 \ln v_1 + n_2 \ln v_2) + k(n_1 \ln \alpha_1^3 + n_2 \ln \alpha_2^3) - (3/2)k(n_1\alpha_1^2 + n_2\alpha_2^2 - n_1 - n_2) + (4/3)kn \ln v_p \quad (7)$$

In order to obtain the partial molal entropy of swelling with respect to solvent by using eq 7, v_1 and v_2 are replaced by $n_1Z_1/(n_0 + n_1Z_1 + n_2Z_2)$ and $n_2Z_2/(n_0 + n_1Z_1 + n_2Z_2)$, where Z_1 and Z_2 represent the ratios of the volume of a PMMA chain and a POTM chain to the volume of solvent, and Z_1 and Z_2 are approximately replaced by M_1/d_1V_0 and M_2/d_2V_0, where d_1 and d_2 are the densities of MMA homopolymer and POTM (practically POTMDM) homopolymer and V_0 is the molar volume of solvent. Now we need to express α_1 and α_2 as a function of n_0. For a swollen copolymer, the length, X, to the direction of the x-axis is given as the sum of X_1 and X_2, where X_1 and X_2 are the sums of the lengths to the direction of the x-axis for PMMA and POTM chains. The length, X', to the direction of the x-axis for the starting copolymer, is given as the sum of X_1/α_1 and X_2/α_2. Assuming that X' is proportionally distributed to X_1/α_1 and X_2/α_2 with respect to the numbers of bond vectors, we obtain

Table I
Values of δ_0[a] and χ_{01} for the Solvents Studied

solvent	$10^{-3}\delta_0/J^{1/2}\ m^{-3/2}$	χ_{01}
toluene	18.2	0.436
tetrahydrofuran (THF)	18.6	0.348
benzene	18.8	0.423
1,2-dichloroethane (DCE)	20.1	0.379
p-dioxane	20.5	0.393
N,N-dimethylacetamide (DMA)	22.1	0.385
N-methyl-2-pyrrolidone (NMP)	23.1	0.354
N,N-dimethylformamide (DMF)	24.8	0.448

[a] δ_0 in ref 23.

$$X_1/\alpha_1 = wX'/(w+1) \quad (8)$$

$$X_2/\alpha_2 = X'/(w+1) \quad (9)$$

where w is the ratio of the weight of PMMA chain to the weight of POTM chain and is equal to n_1M_1/n_2M_2. Since X/X' is equal to $v_p^{-1/3}$, we can obtain the relation

$$w\alpha_1/(w+1) + \alpha_2/(w+1) = v_p^{-1/3} \quad (10)$$

Furthermore, we may have another relation between α_1 and α_2 as

$$\alpha_1/\alpha_2 = r \quad (11)$$

where r is independent of n_0. By combination of eqs 10 and 11, α_1 and α_2 are replaced by $v_p^{-1/3}rg$ and $v_p^{-1/3}g$, where $g = (1+w)/(1+rw)$. Thus we differentiate eq 7 with respect to n_0 and thereby obtain the partial molal entropy of swelling:

$$\Delta\bar{S}_s = -R[\ln (1-v_p) + v_p - (2/3)(v_1/Z_1 + v_2/Z_2) + v_p^{-2/3}(v_1r^2g^2/Z_1 + v_2g^2/Z_2) \quad (12)$$

χ Function. There are various expressions of the thermodynamic interaction parameter χ for polymer + polymer + solvent ternary systems.[14-17] Some of them are very complicated and inadequate to interpret, our experimental results involving many parameters. Here we use the simple and certain expression[17]

$$\chi v_p^2 = \chi_{01}v_1^2 + \chi_{12}v_1v_2 + \chi_{02}v_2^2 \quad (13)$$

where χ_{01} and χ_{02} denote the χ functions for the binary systems of PMMA + solvent and POTM + solvent, and χ_{12} is the χ function between PMMA and POTM in the ternary system. Accordingly, the partial molal free energy of swelling is given by

$$\Delta\bar{G}_s = RT(\chi_{01}v_1^2 + \chi_{12}v_1v_2 + \chi_{02}v_2^2) - T\Delta\bar{S}_s \quad (14)$$

Thus in the swelling equilibrium of cross-linked copolymers

$$\chi_{01}v_1^2 + \chi_{12}v_1v_2 + \chi_{02}v_2^2 + \ln (1-v_p) + v_p - (2/3)(v_1/Z_1 + v_2/Z_2) + v_p^{-2/3}(v_1r^2g^2/Z_1 + v_2g^2/Z_2) = 0 \quad (15)$$

Results and Discussion

Determination of χ_{01}. The χ_{01} values for various solvents in Table I were determined from the swelling data

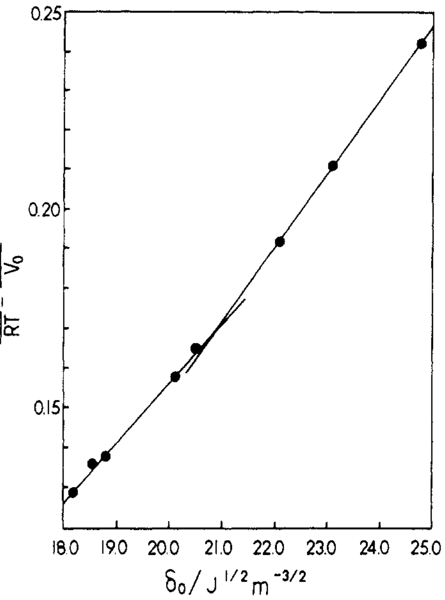

Figure 1. Bristow–Watson plot for poly(MMA-*co*-EDMA) with 0.1 wt % of EDMA. The straight lines were obtained by the least-squares method.

of poly(MMA-*co*-EDMA) with a small amount of EDMA (0.1 wt % of EDMA), according to the Flory–Rehner expression[3,4]

$$\ln(1 - v_p) + v_p + \chi_{01} v_p^2 = -(d_1 V_0 / M_1)(v_p^{1/3} - 2v_p/f) \quad (16)$$

where f is the functionality of cross-link (f = 4 for the poly(MMA-*co*-EDMA)), v_p is close to the volume fraction of PMMA, and M_1/M_{EDMA} is almost equal to a half of the MMA/EDMA weight ratio in the copolymer, where M_{EDMA} = 198. Using the χ_{01} values for various solvents in Table I, we made a plot of $\delta_0^2/RT - \chi_{01}/V_0$ versus δ_0, which had been proposed by Bristow and Watson,[7] in order to evaluate the solubility parameter according to the usual expression[18–20]

$$\chi_{0i} = \chi_{is} + V_0(\delta_0 - \delta_i)^2/RT \quad (17)$$

where δ_0 and δ_i are the solubility parameters of solvent and polymer i and χ_{is} is the constant concerning the coordination number and the chain length of polymer. The Bristow–Watson plot in Figure 1 seems to exhibit two slopes. Values of $\delta_1/J^{1/2}\,m^{-3/2}$ equal to 19.1 from the slope and 19.4 from the intercept of the plot for δ_0 from 18.0 to 21.0 $J^{1/2}\,m^{-3/2}$ and 22.9 from the slope and 23.1 from the intercept of the plot for $\delta_0 > 21.0\ J^{1/2}\,m^{-3/2}$ were obtained for poly(MMA-*co*-EDMA) with 0.1 wt % of EDMA. The δ_1 values are fairly close to δ_1 = 18.9 $J^{1/2}\,m^{-3/2}$ calculated from the structural formula by using the group molar attraction constants.[21–23]

Determination of *r*. By using eq 15 with a large w value (w = 200 or 300), where $\chi_{02}v_2^2$ and $\chi_{12}v_1v_2$ are negligible, we were determined the r values for various solvents, where v_1 and v_2 were replaced by $d_2wv_p/(d_1 + d_2w)$ and $d_1v_p/(d_1 + d_2w)$. The r values in Table II are in a narrow range of 0.20–0.35 and seem to be independent of the solubility parameter of the solvent.

Determination of χ_{02}. For the POTMDM homopolymer, w (=$2M_1/M_2$) is equal to 9.485 × 10^{-3}, where M_1 is given as the molecular weight of CH_2 and M_2 is the sum of the molecular weights of two C=O and POTM used in the present work, and therefore $\chi_{12}v_1v_2$ and $\chi_{01}v_1^2$ are negligible in eq 15. Thus we can obtain the χ_{02} values by application of eq 17 to the homopolymer.

Table II
Values of *r*, χ_{02}, and χ_{12} for the Solvents Studied

	r		χ_{02}		
solvent	w = 200	w = 300	r_{200}[a]	r_{300}[b]	χ^{12c}
toluene	0.25	0.32	1.045	1.040	2.16
THF	0.21	0.26	0.435	0.414	-1.41
benzene	0.27	0.31	0.890	0.886	2.84
DCE	0.27	0.29	0.985	0.983	0.95
p-dioxane	0.30	0.35	0.492	0.472	-0.53
DMA	0.27	0.30	0.407	0.392	-0.62
NMP	0.24	0.26	0.340	0.330	-2.50
DMF	0.20	0.24	0.598	0.590	-0.80

[a] χ_{02} obtained by use of r at w = 200. [b] χ_{02} obtained by use of r at w = 300. [c] χ_{12} obtained by use of r at w = 200.

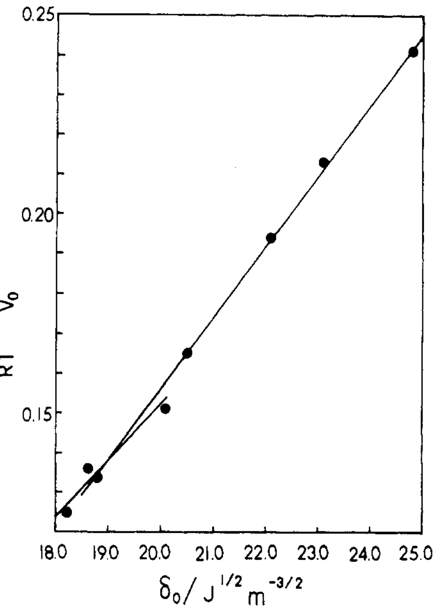

Figure 2. Bristow–Watson plot for poly(POTMDM). The straight lines were obtained by the least-squares method.

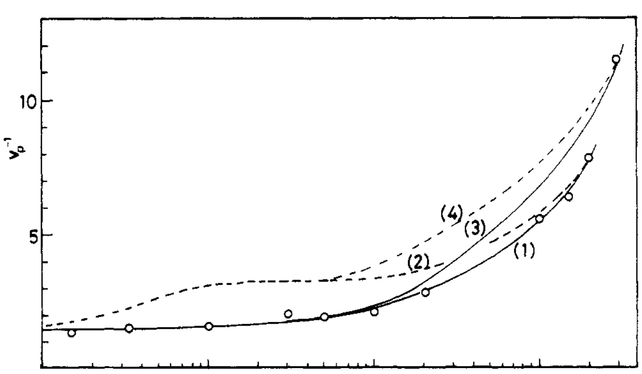

Figure 3. Representative relations between v_p^{-1} and w for the copolymers in toluene used as a poorly hydrogen-bonded solvent: (1) r = 0.25, χ_{01} = 0.436, χ_{02} = 1.045, and χ_{12} = 2.16; (2) r = 0.25, χ_{01} = 0.436, χ_{02} = 1.045, and χ_{12} = 0.00; (3) r = 0.32, χ_{01} = 0.436, χ_{02} = 1.045, and χ_{12} = 2.16; (4) r = 0.32, χ_{01} = 0.436, χ_{02} = 1.045, and χ_{12} = 0.00.

The Bristow–Watson plot depicted by using the χ_{02} values exhibits also two slopes, as shown in Figure 2. Values of $\delta_2/J^{1/2}\,m^{-3/2}$ are equal to 17.8 from the slope and 18.6 from the intercept of the plot for δ_0 from 18.0 to 21.0 $J^{1/2}\,m^{-3/2}$ and 21.5 from the slope and 21.8 from the intercept for $\delta_0 > 21.0\ J^{1/2}\,m^{-3/2}$. The former δ_2 are in accord with δ_2 equal to 17.8 $J^{1/2}\,m^{-3/2}$, calculated from the structural formula.

Determination of χ_{12}. Now we have experimentally known χ_{01}, χ_{02}, v_1, v_2, Z_1, Z_2, and r in eq 15, and therefore we can obtain the χ_{12} values by application of eq 15 to the copolymers with various w values. The χ_{12} values in Table II are the mean of the χ_{12} values at w = 1, 3, and 5. Depending on whether the χ_{12} value is positive or negative, the solvents are classified into two distinct groups A and B: A, toluene, benzene, and DCE; B, THF, dioxane, DMA, NMP, and DMF. The solvents of groups A and B are known as poorly hydrogen-bonded solvents and moderately hydrogen-bonded solvents,[23] respectively.

Figures 3 and 4 show representative relations between v_p^{-1} and w for the copolymers in toluene and DMA, respectively. Curve 1 in Figure 3 and curve 4 in Figure 4 are in good accord with observed relations between v_p^{-1} and w. Similar results were obtained for the copolymers in other solvents. The negative χ_{12} values for the copolymers in a moderately hydrogen-bonded solvent suggest the existence of association caused by a solvent–polymer hydrogen bond, since χ_{12} should be inherently positive and independent of the solubility parameter of solvents. Accordingly, for moderately hydrogen-bonded solvents, eq 15 is modified as

$$\chi_{01}v_1^2 + \chi_{12}v_1v_2 + \chi_{02}v_2^2 + \Delta\bar{H}_H/RT - \Delta\bar{S}_s/R = 0 \qquad (18)$$

where $\Delta\bar{H}_H$ is the partial molal enthalpy of hydrogen bonding and is negative. Roughly estimated, $\Delta\bar{H}_H$ values are in the range of 6–9 kJ mol^{-1}, which is close to the enthalpy of hydrogen bond formation in the literature.[24,25]

Appendix: Derivation of ΔS_1

We consider formation of a network in a way in which ω_1 and ω_2 are given as

$$\omega_1 = [2n_1(\Delta\tau/V)]^2[(2n_1 - 3)(\Delta\tau/V)]^2[(2n_1 - 6)(\Delta\tau/V)]^2...[n_2(\Delta\tau/V)]^2$$

$$\omega_2 = [(2n_2 - 1)(\Delta\tau/V)(2n_1 - 2)(\Delta\tau/V)][(2n_2 - 2)(\Delta\tau/V)(2n_1 - 5)(\Delta\tau/V)]... = \omega_{21}\omega_{22}$$

$$\omega_{21} = [(2n_2 - 1)(\Delta\tau/V)][(2n_2 - 2)(\Delta\tau/V)]...[n_2(\Delta\tau/V)]$$

$$\omega_{22} = [(2n_1 - 2)(\Delta\tau/V)][(2n_1 - 5)(\Delta\tau/V)]...[(n_2 + 1)(\Delta\tau/V)]$$

These equations are replaced by factorial expressions as follows:

$$\omega_1^{1/2} = 3^{(n_2+1)}(\Delta\tau/V)^{(n_2+1)}(2n_1/3)!/[(n_2 - 1)/3]!$$

$$\omega_{21} = (\Delta\tau/V)^{n_2}(n_1 - 1)!/(n_2 - 1)!$$

$$\omega_{22} = 3^{n_2}(\Delta\tau/V)^{n_2}[(4n_2 + 1)/3 - 1]!/[(n_2 + 1)/3]!$$

Using the Stirling approximation, we obtain the logarithms of ω_1, ω_{21}, and ω_{22} as

$$\ln \omega_1 = 2n_2 \ln (\Delta\tau/V) + (4n_1/3) \ln 2n_1 - (2n_2/3) \ln n_2 - 2n_2$$

$$\ln \omega_{21} = n_2 \ln (\Delta\tau/V) + n_1 \ln n_1 - n_2 \ln n_2 - n_2$$

$$\ln \omega_{22} = n_2 \ln (\Delta\tau/V) + (2n_1/3) \ln (2n_1) - (n_2/3) \ln n_2 - n_2$$

where $n_1 = 2n_2$ and $n_2 \gg 1$.

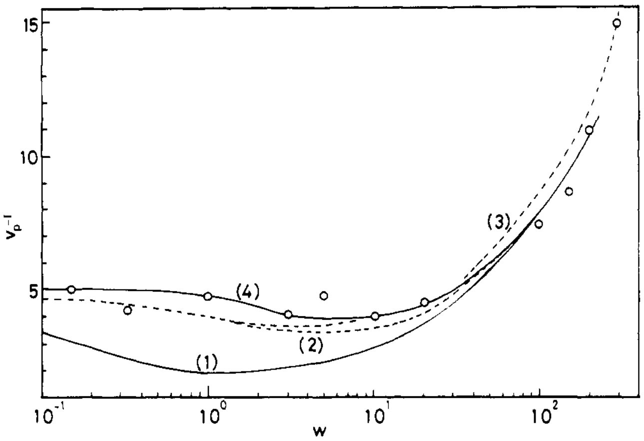

Figure 4. Representative relations between v_p^{-1} and w for the copolymers in DMA used as a moderately hydrogen-bonded solvent: (1) r = 0.27, χ_{01} = 0.385, χ_{02} = 0.407, and χ_{12} = 2.5; (2) r = 0.27, χ_{01} = 0.385, χ_{02} = 0.407, and χ_{12} = 0.0; (3) r = 0.30, χ_{01} = 0.385, χ_{02} = 0.407, and χ_{12} = 0.0; (4) r = 0.27, χ_{01} = 0.385, χ_{02} = 0.407, and χ_{12} = −0.62.

Accordingly, using the Boltzmann relation, we obtain the ΔS_1 expression, i.e., eq 3:

$$\Delta S_1 = k \ln (\omega_1\omega_2) = (4/3)kn \ln (4n\Delta\tau/3Ve) + (2/3)kn \ln 2$$

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Registry No. (MMA)(POTMDM) (copolymer), 52277-34-6; EDMA, 25777-71-3; THF, 109-99-9; DCE, 107-06-2; DMA, 127-19-5; NMP, 30207-69-3; DMF, 68-12-2; toluene, 108-88-3; benzene, 71-43-2; p-dioxane, 123-91-1.