

Swelling of Poly[Methacrylic Acid-co-poly(oxytetramethylene) Dimethacrylate]s

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SYNOPSIS

An equation of swelling equilibrium is derived for crosslinked copolymer including incomplete network structures, to be applied to the swelling data on copolymer of poly(oxytetramethylene) dimethacrylate (POTMDM) with methacrylic acid (MAA). Poly(MAA-co-POTMDM)s with various monomer contents, is prepared by copolymerization in *N,N*-dimethylformamide (DMF). The equation shows good applicability to the swelling behaviors of poly(MAA-co-POTMDM) for tetrahydrofuran (THF) and DMF systems. A difference in polymer-polymer interaction parameter between THF and DMF systems, derived from the results of curve fitting is explained in terms of dependence of polymer-solvent interaction parameter on crosslink density. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(oxytetramethylene) dimethacrylate (POTMDM) is a macromonomer with two chain ends containing a double bond. Therefore, copolymers of POTMDM with various monomers have polymer chains consisting only of comonomer units and only of oxytetramethylene units. Such copolymers are interesting because the influence of interactions between different polymer chains on their physical and physicochemical properties is expected, as in polymer alloys.¹⁻⁴ Before proceeding to study their physical and physicochemical properties, it is necessary to characterize such copolymers. Previously, we⁵ proposed an equation of swelling equilibrium for the copolymers. It was successfully applied to the swelling data on copolymers of POTMDM with methyl methacrylate (MMA).

Copolymers of POTMDM with methacrylic acid (MAA) have higher potential for practical application than do those with MMA because of hydrophilicity of poly(MAA-co-POTMDM). However, copolymerization of POTMDM with MAA in a homogeneous bulk system is difficult because of incompatibility of POTMDM with MAA.⁶ By solution copolymerization, it is possible to prepare homo-

geneous copolymers of POTMDM with MAA, though the copolymers have some crosslinks that do not contribute to formation of the network structure.

In the present study, we propose an equation of swelling equilibrium for copolymers of POTMDM with comonomers, including incomplete network structures, and apply it to poly(MAA-co-POTMDM) prepared by copolymerization in *N,N*-dimethylformamide (DMF).

EXPERIMENTAL

The synthesis of POTMDM is described in a previous study.⁵ All polymers used in the present work were prepared by copolymerization at 333 K for 24 h in a flame-sealed 20-mm diameter glass tube containing 60 wt % of DMF. The copolymers span the MAA/POTMDM composition range 1/5 to 20/1 (w/w). The copolymers were dried in an evacuated oven at room temperature until the weight became constant against time.

Swelling experiments were carried out by the procedure previously described.⁵ The degree of swelling was determined by measuring the weight of swollen sample. The swelling experiment was conducted until no further change in the weight of the sample was observed.

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RESULTS AND DISCUSSION

Extension of Partial Molal Free Energy of Swelling

Previously, we⁵ represented the partial molal free energy of swelling, ΔG_s , for polymer 1–polymer 2–solvent ternary system, according to the cycle proposed by Flory⁷ to calculate the swelling entropy for polymer–solvent binary system.

$$\Delta G_s = RT(\chi_{01}v_1^2 + \chi_{12}v_1v_2 + \chi_{02}v_2^2) + \ln(1 - v_p) + v_p - \left(\frac{2}{3}\right)\left(\frac{v_1}{Z_1} + \frac{v_2}{Z_2}\right) + v_p^{-2/3}\left(\frac{v_1r^2g^2}{Z_1} + \frac{v_2g^2}{Z_2}\right) \quad (1)$$

where χ_{01} and χ_{02} are the polymer–solvent interaction parameters for the binary systems of polymer 1–solvent and polymer 2–solvent, χ_{12} is the polymer 1–polymer 2 interaction parameter, Z_1 and Z_2 are approximately replaced by M_1/d_1V_0 and M_2/d_2V_0 , where d and M denote the density and the molecular weight of polymer, and V_0 is the molar volume of solvent. And v_1 and v_2 are the volume fractions of polymer 1 and polymer 2 and 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 n_0 , n_1 , and n_2 are the numbers of molecules of solvent, polymer 1, and polymer 2, respectively, and r is the expansion factor ratio of polymer 1 chain to polymer 2 chain, $v_p = v_1 + v_2$, and $g = (1 + w)/(1 + rw)$, where w is the weight ratio of polymer 1 to polymer 2. One of assumptions for derivation of Eq. (1) is that the polymer network is composed of all monomers (including macromonomers) fed in copolymerization, that is, has neither dangling nor loop ends. The dangling or loop ends are produced frequently in the solution copolymerization. Therefore, Eq. (1) should be extended to an equation applicable to the swelling behavior of incomplete polymer network, in order to use it for interpretation of the swelling data on poly(MAA-co-POTMDM). When the number of poly(oxytetramethylene) (POTM) chains with dangling or loop ends is expressed by qn_2 , the numbers of PMAA chains and of POTM chains, which contribute to formation of the network structure, are $(1 - q)n_1$ and $(1 - q)n_2$, respectively. Therefore, the volume fraction of polymer, observed in swelling experiment, $v_{p,ob}$, is given by

$$v_{p,ob} = \frac{(1 - q)v_p}{1 - qv_p} \quad (2)$$

Since the volume fraction of polymer in Eq. (1) is expressed by $v_{p,ob}$ in terms associated with inter-

linking process, and v_p in terms associated with dilution process, the relationship between $v_{p,ob}$ and w for poly(MAA-co-POTMDM) in swelling equilibrium is given by the following equation:

$$\chi_{01}v_1^2 + \chi_{12}v_1v_2 + \chi_{02}v_2^2 + \ln(1 - v_p) + v_p - \left(\frac{2}{3}\right)\left(\frac{v_1}{Z_1} + \frac{v_2}{Z_2}\right) + v_{p,ob}^{-2/3}\left(\frac{v_1r^2g^2}{Z_1} + \frac{v_2g^2}{Z_2}\right) = 0 \quad (3)$$

where v_1' and v_2' are replaced by $d_1v_{p,ob}/(d_1 + wd_2)$ and $wd_2v_{p,ob}/(d_1 + wd_2)$.

Determination of χ Values

The χ_{01} values were determined from the swelling data on copolymers of MAA with ethylenedimethacrylate (EDMA) (1 wt % of EDMA) prepared by copolymerization in DMF (60 wt %), according to the Flory-Rehner⁸ equation modified by use of Eq. (2):

$$\ln(1 - v_p) + v_p + \chi_{01}v_p^2 = -\left(\frac{d_1V_0}{M_1}\right)\left(v_{p,ob}^{1/3} - \frac{v_{p,ob}}{2}\right) v_{p,ob} = \frac{(1 - q)v_p}{1 - qv_p} \quad (4)$$

Table I shows the χ_{01} values determined from Eq. (4) with a given q value and an experimental value of the degree of swelling, $v_{p,ob}^{-1}$. Since poly(MAA-co-EDMA) hardly swells in THF, χ_{01} is considered to exceed 0.9 for the THF solution system.

Then, every q value from 1 to 0 is applicable. Usually, χ_{01} is expressed⁹ by

$$\chi_{01} = \chi_s + \frac{V_0(\delta_0 - \delta_1)^2}{RT} \quad (5)$$

Table I Determination of χ_{01}

Solvent	$V_{p,ob}$	q	χ_{01}
DMF	< 1.4	1–0	0.9 <
THF	6.8	0.1	0.37
	6.8	0.3	0.38
	6.8	0.5	0.39
	7.0	0.1	0.36
	7.0	0.3	0.37
	7.0	0.5	0.38

where δ_0 and δ_1 are the solubility parameters of solvent and polymer 1, and χ_s is the constant concerning entropy change in polymer motion. Since the largest value of $V_{0,THF}(\delta_{PMAA} - \delta_{THF})^2/RT$ is about 0.45 and the χ_s value is in the range from 0.3 to 0.5,⁶ we used χ_{01} equal to 0.9 for poly(MAA-co-POTMDM)-THF system.

The $v_{p,ob}^{-1}$ values in the range of 6.9 ± 0.1 were experimentally obtained for poly(MAA-co-EDMA) in DMF. By the use of several $v_{p,ob}^{-1}$ values in this range, the χ_{01} values in Table I were obtained. We used tentatively χ_{01} equal to 0.37 for poly(MAA-co-POTMDM)-DMF system because there are no considerable differences by use of χ_{01} equal to 0.36 or 0.39.

As the χ_{02} values, we used the data that had been obtained by the swelling experiment of POTMDM homopolymer in previous work (0.41 for THF, 0.59 for DMF).⁵

Swelling Behavior

Figure 1 shows the experimental plots of $v_{p,ob}^{-1}$ versus w for poly(MAA-co-POTMDM) in THF. The curves according to Eq. (3) are unstable in the neighborhood of $v_{p,ob}^{-1} = 1$ because of the appearance of negative values of $(1 - v_p)$ by the use of χ and d values within experimental error. Therefore, we tried fitting Eq. (3) with $v_{p,ob}^{-1}$ of 2 or above to the experimental plots. The experimental plots in Figure 1

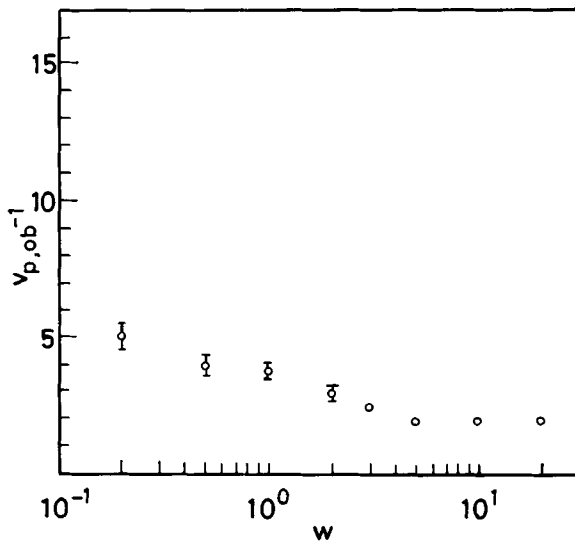


Figure 1 Experimental plots of $v_{p,ob}^{-1}$ versus w for poly(MAA-co-POTMDM) in THF. The plots depict the mean values and the standard deviation of triplicate data.

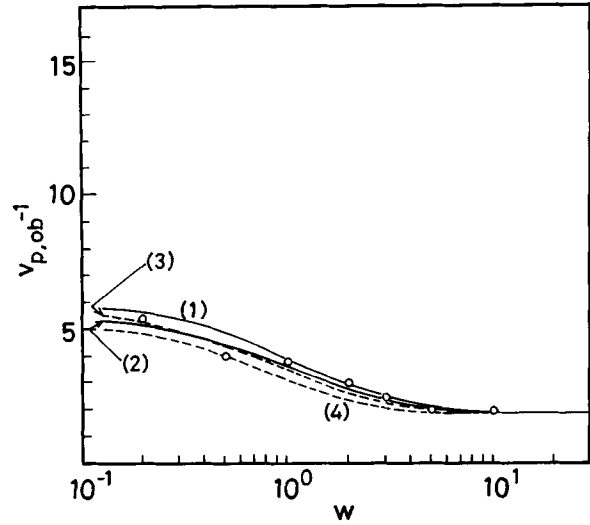


Figure 2 Curves according to Eq. (3) with $r = 0.17$ for poly(MAA-co-POTMDM) in THF: (1) $\chi_{12} = 0.30, q = 0.30$; (2) $\chi_{12} = 0.30, q = 0.20$; (3) $\chi_{12} = 0.60, q = 0.30$; (4) $\chi_{12} = 0.60, q = 0.20$. The plots depict the mean values of the experimental data.

show that for $w \geq 50, v_{p,ob}^{-1}$ gradually decreases to less than 2, and the curve according to Eq. (3) is almost dependent on r and χ_{01} . To satisfy these, an r value in the range from 0.17 to 0.19 is taken. Figures 2 and 3 show the mean values and the curves according to Eq. (3) with $r = 0.17$ and 0.19, respec-

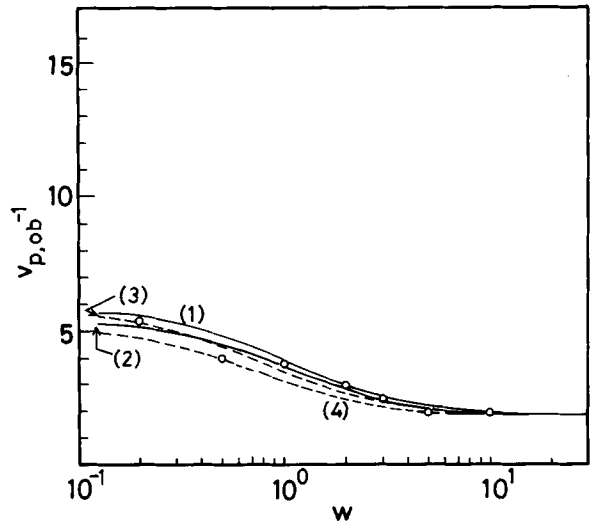


Figure 3 Curves according to Eq. (3) with $r = 0.19$ for poly(MAA-co-POTMDM) in THF: (1) $\chi_{12} = 0.30, q = 0.30$; (2) $\chi_{12} = 0.30, q = 0.20$; (3) $\chi_{12} = 0.60, q = 0.30$; (4) $\chi_{12} = 0.60, q = 0.20$. The plots depict the mean values of the experimental data.

tively. The χ_{12} and q values are arbitrarily given. $\chi_{12} = 0.3$ and $q = 0.2$, or $\chi_{12} = 0.6$ and $q = 0.3$ seem to be favorable for poly(MAA-co-POTMDM). These results suggest that we can find the χ_{12} value in the range of 0.3 to 0.6, satisfying the curve fitting for any q value in the range of 0.2 to 0.3.

Figure 4 shows plots of $v_{p,ob}^{-1}$ versus w for poly(MAA-co-POTMDM) in DMF. The $v_{p,ob}^{-1}$ value from Eq. (3) with $q = 0.3$ is overestimated. Figure 5 shows the curves according to Eq. (3) with $q = 0.2$. The most favorable χ_{12} value seems to be 0.5 (shown by a broken line). There is a considerable difference in q and χ_{12} values between THF and DMF systems, perhaps because of strong specific interactions in this system. Since the polymer-solvent interaction parameter is dependent on the density of crosslinks,¹⁰⁻¹² the χ_{02} value given by use of POTM homopolymer with high density of crosslinks is overestimated. Accordingly, χ_{12} for the THF system, in which pronounced swelling phenomenon appears at the larger POTMDM contents, is underestimated. This is an explanation for the difference.

The large difference in r between DMF and THF systems is interpreted in terms of solubility of polymer chains in THF and DMF: in THF, the expansion factor of POTM chain is larger than that of PMAA chain, and in DMF, the expansion factor of POTM chain is smaller than that of PMAA chain because the solubility parameter of POTMDM is close to that of THF and is far from that of DMF,

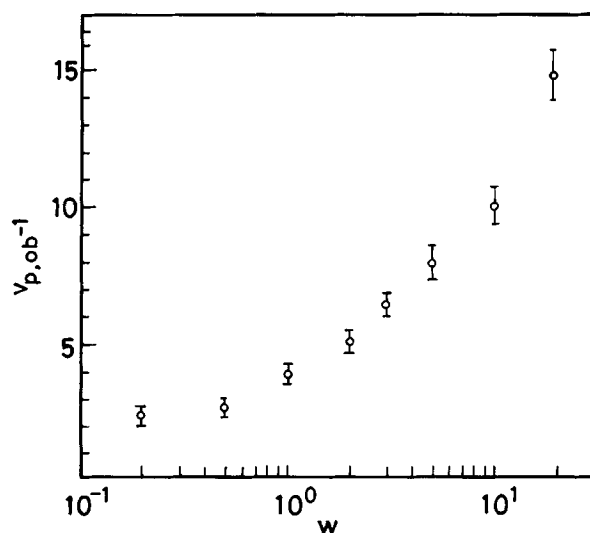


Figure 4 Experimental plots of $v_{p,ob}^{-1}$ vs. w for poly(MAA-co-POTMDM) in DMF. The plots depict the mean values and the standard deviation of triplicate data.

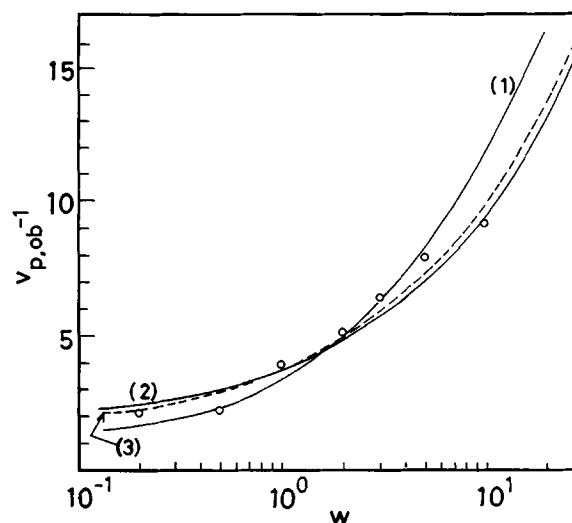


Figure 5 Curves according to Eq. (3) with $q = 0.2$ for poly(MAA-co-POTMDM) in DMF: (1) $\chi_{12} = 0.3$, $r = 3$; (2) $\chi_{12} = 0.6$, $r = 1.2$; (3) $\chi_{12} = 0.5$, $r = 1.4$. The plots depict the mean values of the experimental data.

and the solubility parameter of PMAA is close to that of DMF and is far from that of THF.

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