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Study of Polyacrylamide Terpolymer Gels. 2.[†] Correlation between Solubility Parameters and Exclusion Limits of Gels

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ABSTRACT: An aqueous ethanol solution of acrylamide, *N,N'*-methylenebis(acrylamide) as a cross-linking agent, and a third monomer was dispersed in a normal paraffin hydrocarbon, the three monomers were copolymerized to yield spherical porous terpolymer gels, and the effect of the composition of the third monomer in the monomer feed on the exclusion limits of the gels was investigated. Acrylonitrile, methacrylamide, *N,N*-dimethylacrylamide, *N*-[3-(dimethylamino)propyl]methacrylamide hydrochloride, and *N*-[3-(dimethylamino)propyl]acrylamide hydrochloride were used as the third monomers. The exclusion limits were determined from calibration graphs obtained by size-exclusion chromatography. Values for the solubility parameters of the gels were estimated by a swelling method. By changing the proportion of the third monomers in the monomer feed, the exclusion limits of gels could be varied from 8.7×10^2 to 1.4×10^6. We found that the logarithm of the exclusion limits of the gels had an linear relationship with the difference between the solubility parameters of the polymerization solvent and the terpolymer gels and that the magnitude of the solubility parameter of the polymer chain of the gels governed the aggregation and growth of the microgels during the process of gel formation.

Introduction

In many papers concerning polyacrylamide (PAAm) gels, the gels are almost bipolymers consisting of acrylamide (AAm) and *N,N'*-methylenebis(acrylamide) (MBAA) as a cross-linking agent.

With a view to obtaining gels that have macropores and a wide fractionation range, we studied[1,2] the preparation of terpolymer gels composed of AAm, MBAA, and a third monomer by inverse suspension polymerization. In a previous paper,[3,4] using acrylonitrile (AN) or methacrylamide (MAAm), which are more hydrophobic than AAm, as a third monomer, we obtained gels that have various exclusion limits by changing the composition of the third monomer in the monomer feed and characterized these terpolymer gels as the macroreticular (MR) type by investigating them as packing materials. We showed that there was a relationship between the solubility parameters and exclusion limits of PAAm terpolymers when the third monomer component had a lower solubility parameter value (δ) than AAm.

This paper claims that the relationship described above applies to the following cases: cases in which the third monomer component of the terpolymer gels has about the same δ value as AAm and cases in which the third monomer component of the terpolymer gels has a higher δ value than AAm.

Experimental Section

The terpolymer gel particles were produced by using an inverse dispersion process by polymerizing AAm, MBAA, and the third monomer. The inverse suspension polymerizations of terpolymers, the measurement of chromatographic behavior, and the estimation of the δ values of the gels were carried out in accordance with the procedures reported in our previous paper.[3]

In our measurements, the probable errors of the δ values obtained were 0.06 or less. Table I shows the δ values of the solvents[5] used and of the homopolymers[6] of the monomers used.

Specimens were coated with gold–palladium before viewing in a JFSM-30 scanning electron microscope (JEOL Ltd., Tokyo, Japan).

Table I
Solubility Parameters of the Solvents Used and of Homopolymers of the Monomers Used

materials	δ, (cal·cm^{-3})$^{1/2}$
solvent[a]	
1,4-dioxane	10.0
N-formylmorpholine	13.0
ethyl alcohol	13.0
ethylene glycol	16.3
formamide	17.8
glycerin	21.1
water	23.4
homopolymer[b,c]	
PAN[d]	13.5
PMAAm[e]	17.0
PAAm[f]	17.6
PDMAAm[g]	17.8
PDMAPMA·HCl[h]	21.1
PDMAPAA·HCl[i]	21.5

[a] The δ values of these solvents are based on values proposed by Hansen.[7] [b] Condition of polymerization: monomer concentration, 0.81 mol·dm^{-3}; concentration of *N,N'*-methylenebis(acrylamide) as a cross-linking agent, 5.0 mol %; initiator concentration, 1 mol % for monomer feed; diluent, H_2O. [c] Probable error was ±0.2. [d] PAN: polyacrylonitrile. [e] PMAAm: polymethacrylamide. [f] PAAm: polyacrylamide. [g] PDMAAm: poly(*N,N*-dimethylacrylamide). [h] PDMAPMA·HCl: poly[*N*-[3-(dimethylamino)propyl]methacrylamide] hydrochloride. [i] PDMAPAA·HCl: poly-[*N*-[3-(dimethylamino)propyl]acrylamide] hydrochloride.

Results and Discussion

We have already reported[3] the following results with respect to the AN–AAm–MBAA gels and the MAAm–AAm–MBAA gels.

When using AN or MAAm as third monomers having lower δ values than AAm, the exclusion limits of the gel (AN–AAm–MBAA or MAAm–AAm–MBAA) increases as the molar ratio of AN or MAAm to AAm increases. The δ values of the AN–AAm–MBAA and MAAm–AAm–MBAA gels decreased as the molar ratio of AN or MAAm to AAm increased. The δ value of the polymerization solvent was 23.00 and higher than the δ value of the AAm–MBAA gel, 16.7. The exclusion limits were so high that the δ values of the gels were small, and we found that

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[†] For Part 1, see ref 3.

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Table II
Compositions and Exclusion Limits of the Gels[a]

gel	AAm,[b] g	MBAA,[c] g	third monomer, g	MBAA in monomer feed, mol %	molar ratio of third monomer to AAm	exclusion limit M_w
1	30.0	10.0	0	13.3	0	1.6×10^4
2	29.7	10.0	DMAAm,[d] 0.42	13.3	0.010	1.3×10^4
3	29.1	10.0	DMAAm,[d] 1.29	13.3	0.032	1.1×10^4
4	28.5	10.0	DMAAm,[d] 2.09	13.3	0.052	1.1×10^4
5	27.1	10.0	DMAAm,[d] 4.16	13.3	0.110	1.0×10^4
6	24.0	10.0	DMAAm,[d] 8.37	13.3	0.249	1.1×10^4
7	29.7	10.0	DMAPMA·HCl,[e] 0.72	13.3	0.010	5.5×10^4
8	29.1	10.0	DMAPMA·HCl,[e] 2.21	13.3	0.032	1.6×10^4
9	28.5	10.0	DMAPMA·HCl,[e] 3.59	13.3	0.052	7.9×10^3
10	27.1	10.0	DMAPMA·HCl,[e] 7.15	13.3	0.110	7.9×10^3
11	24.0	10.0	DMAPMA·HCl,[e] 14.37	13.3	0.249	4.7×10^3
12	29.7	10.0	DMAPAA·HCl,[f] 0.66	13.3	0.010	1.4×10^4
13	29.1	10.0	DMAPAA·HCl,[f] 2.03	13.3	0.032	3.9×10^3
14	28.5	10.0	DMAPAA·HCl,[f] 3.30	13.3	0.052	3.8×10^3
15	27.1	10.0	DMAPAA·HCl,[f] 6.56	13.3	0.110	8.7×10^2

[a] Inverse suspension polymerization: diluent, mixture of EtOH and H_2O (EtOH 11.4 vol %) 167 mL; initiator concentration, 1 mol % for monomer feed. [b] AAm: acrylamide. [c] MBAA: *N,N*′-methylenebis(acrylamide). [d] DMAAm: *N,N*-dimethylacrylamide. [e] DMAPMA·HCl: *N*-[3-(dimethylamino)propyl]methacrylamide hydrochloride. [f] DMAPAA·HCl: *N*-[3-(dimethylamino)propyl]acrylamide hydrochloride.

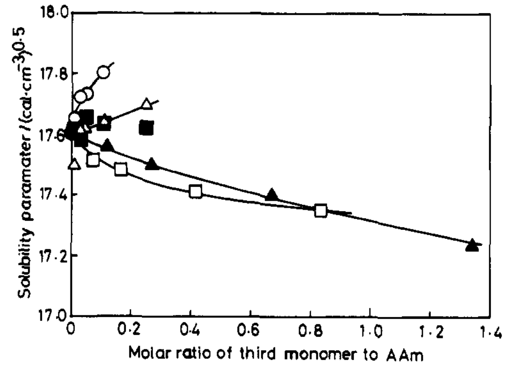

Figure 1. Correlation of solubility parameter of the gels with the molar ratio of third monomers to AAm on the gels: (▲) AN–AAm–MBAA gel; (□) MAAm–AAm–MBAA gel; (●) AAm–MBAA gel; (■) DMAAm–AAm–MBAA gel; (△) DMAPMA·HCl–AAm–MBAA gel; (○) DMAPAA·HCl–AAm–MBAA gel.

the logarithm of the exclusion limits of gels bore an approximately linear relationship to the difference between the δ values ($\Delta\delta$) of the polymerization solvent and the gels. The following conclusions can be drawn on the basis of these results.

In general, there is aggregation and growth of microgels in the process of gel formation.[8,9] The increase in the exclusion limit upon addition of AN or MAAm is therefore assumed to occur as follows. The addition of the third monomer altered the magnitude of the solubility of the polymers constituting the microgels. Consequently, it furthered the aggregation of the microgels rather than their growth; i.e., phase separation was accelerated. Also, the causes of the formation of large macropores could be thought of as follows. The magnitude of δ of the polymer chains of the terpolymer gels was influenced by the solibility of the third monomer, and the lower the δ values of the terpolymer gels are than the δ value of the AAm–MBAA gel, the more aggregation of the microgels was promoted.

If the model that was hypothesized above has general validity, the foregoing linear relationship should apply to a terpolymer gel when the δ value of a third monomer component is the same as or higher than the δ value of AAm. Hence, *N,N*-dimethylacrylamide (DMAAm), *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMA) hydrochloride, and *N*-[3-(dimethylamino)propyl]acrylamide (DMAPAA) hydrochloride were used as third monomers.

Table II shows the compositions and exclusion limits of the terpolymer gels prepared. When DMAAm was used as the third monomer with a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (DMAAm–AAm–MBAA) were in the range 1.0×10^4 to 1.6×10^4, unlike other terpolymer gels whose exclusion limits were influenced by the molar ratio of the third monomer to AAm. When DMAPAA·HCl was used as the third monomer with a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (DMAPAA·HCl–AAm–MBAA) decreased from 1.6×10^4 to 8.7×10^2 as the molar ratio of DMAPAA·HCl to AAm increased from 0 to 0.110. When DMAPMA·HCl was used as the third monomer with a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of the gels obtained (DMAPMA·HCl–AAm–MBAA) decreased from 5.5×10^4 to 4.7×10^3 as the molar ratio of DMAPMA·HCl to AAm increased from 0.010 to 0.249 but increased from 1.6×10^4 to 5.5×10^4 as the molar ratio of DMAPMA·HCl to AAm increased from 0 to 0.010.[10] Figure 1 shows the following. The δ values of the DMAAm–AAm–MBAA gels ranged from 17.58 to 17.65 and were independent of increases in the molar ratio of DMAAm to AAm. The δ values of DMAPAA·HCl–AAm–MBAA gels increased from 17.60 to 17.80 as the molar ratio of DMAPAA·HCl to AAm increased from 0 to 0.110. The δ values of DMAPMA·HCl–AAm–MBAA gels increased from 17.50 to 17.70 as the molar ratio of DMAPMA·HCl to AAm increased from 0.010 to 0.249 but decreased from 17.60 to 17.50 as the molar ratio of DMAPMA·HCl to AAm increased from 0 to 0.010. These results with respect to DMAPMA·HCl–AAm–MBAA gels were counter to the presumption that as the molar ratio increases, the exclusion limits decrease, and the δ values of the gels increase as the results showed in the case of DMAPAA·HCl–AAm–MBAA gels. We thought that this difference resulted from the presence of the α-methyl group of DMAPMA. This was supported by the finding of acceleration of phase separation by the α-methyl group in the MAAm–AAm–MBAA gels.[2] Based on the relationship between exclusion limits and molar ratio in the case of DMAPMA·HCl–AAm–MBAA gels, we hypothesized the following. There are factors that depress phase separation, i.e., electrostatic repulsion between the (dimethylamino)propyl groups, the hydrophilic nature of pendant groups, and steric hindrance by the bulkiness of pendant group, and factors

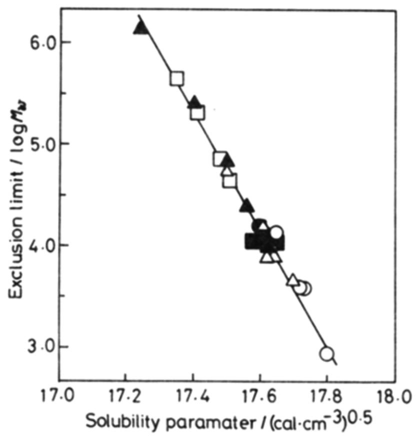

Figure 2. Correlation of exclusion limits with the solubility parameter of gels: (▲) AN–AAm–MBAA gel; (□) MAAm–AAm–MBAA gel; (●) AAm–MBAA gel; (■) DMAAm–AAm–MBAA gel; (△) DMAPMA; HCl–AAm–MBAA gel; (○) DMAPAA·HCl–AAm–MBAA gel.

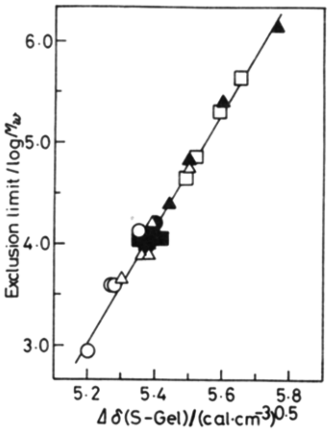

Figure 3. Correlation of exclusion limits with differences ($\Delta\delta$) in solubility parameter between the polymerization solvent (S) and the gels: (▲) AN–AAm–MBAA gel; (□) MAAm–AAm–MBAA gel; (●) AAm–MBAA gel; (■) DMAAm–AAm–MBAA gel; (△) DMAPMA·HCl–AAm–MBAA gel; (○) DMAPAA·HCl–AAm–MBAA gel.

that accelerate phase separation, i.e., the hydrophobic interaction between α-methyl groups. From a molar ratio of 0 to 0.010, the factors accelerating phase separation are stronger than the opposing factors.

Figure 2 shows the correlation between the δ values of the terpolymer gels and their exclusion limits. The exclusion limits of DMAPAA·HCl–AAm–MBAA gels and DMAPMA·HCl–AAm–MBAA gels were so high that the δ values of the gels were small. This correlation was same as reported in the previous paper. A plot of gel δ's versus logarithms of their exclusion limits yielded a straight line expressed by the following formula:

$$\log M_{\mathrm{w_{lim}}} = 102.44 - 5.58\delta \qquad (r = -0.988)$$

where $M_{\mathrm{w_{lim}}}$ is the molecular weight of the exclusion limit and r is the coefficient of correlation. Figure 3 also clearly shows that an approximately linear relationship exists between the logarithm of the exclusion limits of gels and $\Delta\delta$. This relationship applied in the three cases in which the third monomer component of the terpolymer gels had a lower δ value than AAm, a δ value about the same as that of AAm, and a higher δ value than AAm. The straight line obeyed the following formula:

$$\log M_{\mathrm{w_{lim}}} = 5.58\delta - 25.94 \qquad (r = 0.990)$$

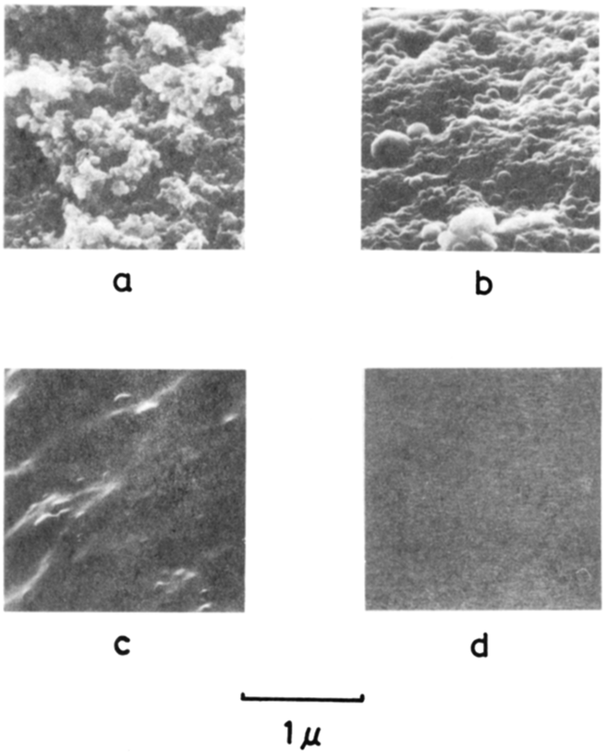

Figure 4. Scanning electron micrographs of the surface of the terpolymer gel particles.

Figure 4 shows some photographs typical of all the terpolymer gel particles obtained. Figure 4a is a photograph of MAAm–AAm–MBAA gel particles (molar ratio of MAAm to AAm: 0.834). Such surface morphology was observed in gel particles with larger $\Delta\delta$ values than the AAm–MBAA gel. The magnitude of unevenness of the surface of the gel particles was so high that the δ values of the gels were smaller than the δ values of the AAm–MBAA gel. This photograph shows that a gel particle consists of many microgels and that aggregation of these microgels occurs during the process of gel formation. The magnitude of the unevenness of the surface of the gel particles, which has a δ value close to that of the AAm–MBAA gel, was small as shown in Figure 4b. The magnitude of the unevenness of the AAm–MBAA gel was also small as shown in Figure 4c. Dawkins's PAAm gel particles,[11] whose swelling coefficient is smaller than that of the PAAm terpolymer gel particles used in this study and whose exclusion limit is about 1 × 10^5, have surface morphology similar to Figure 4a. Hence, we concluded that phase separation is accelerated as the $\Delta\delta$ value of the gels becomes greater. In addition, Figure 4d shows the surface morphology of all the terpolymer gel particles that had higher δ values than the AAm–MBAA gel. Their surfaces were smooth.

There is a method[3] of accelerated aggregation of microgels that takes advantage of the difference between the δ values of polymerization solvents and gels altered by the addition of a third monomer to preparations of gels to be used as packing materials. On the basis of the results described above, we found the following to be true of PAAm terpolymer gels obtained by this method. There was a linear relationship between $\Delta\delta$ and the logarithm of the exclusion limits of the gels, and this relationship applied to the three cases in which the third monomer component of the terpolymer gels had a lower δ value than AAm, about the same δ value as AAm, and a higher δ value than AAm. The preceding model was reasonable and the magnitude of δ of the polymer chain of the gels governed aggregation and the growth of microgels in the process of gel formation.

Conclusion

(1) We found that the logarithm of the exclusion limits of the polyacrylamide terpolymer gels bears a linear relationship to the difference between the value of the solubility parameter of the polymerization solvent and the gels and that the magnitude of δ of the polymer chains of PAAm terpolymer gels governs the aggregation and growth of microgels in the process of gel formation. (2) The surface morphology of terpolymer gels containing a third monomer that had a lower δ value than AAm revealed acceleration of phase separation as the molar ratio of the third monomer to AAm increased.

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(4) The δ values of the monomers used were estimated from the δ values of their homopolymers.
(5) The reason we chosed the solvents was that they did not react with the gels and homopolymers in period of measurement (about 2 months), no self-decomposition occurred, and with respect to hydrogen bonding tendencies of the solvents the contribution fraction $[f_h = [\delta_h/(\delta_d + \delta_p + \delta_h)] \times 100]$ of hydrogen bonding components to δ values of the solvents was between 30 and 50%, in which f_h is the fraction represented by δ_h divided by $(\delta_d + \delta_p + \delta_h)$, δ_d is the dispersion component of δ, δ_p is the polar component of δ, and δ_h is the hydrogen-bonding component of δ.
(6) With regard to the measurement of the δ values of homopolymers and gels containing DMAPMA·HCl or DMAPAA·HCl as a component, mixed solutions of glycerin and water were used as solvents having δ values between 21.1 and 23.4. While there seems to be preferential solvation in aqueous solvents, the extent of this solvation is unknown.
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Registry No. (AAm)(MBAA) (copolymer), 25034-58-6; (AAm)(MBAA)(DMAAm) (copolymer), 125109-64-0; (AAm)(MBAA)(DMAPMA·HCl) (copolymer), 125109-65-1; (AAm)(MBAA)(DMAPAA·HCl) (copolymer), 125109-66-2; (AN)(AAm)(MBAA) (copolymer), 29825-75-0; (AAm)(MAAm)(MBAA) (copolymer), 34364-91-5.

Direct Evidence for Transesterification and Randomization in a Mixture of Homopolyesters of Poly(HBA) and Poly(HNA) above 450 °C

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ABSTRACT: Preparation of blends of the homopolymers of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) has been investigated via compression molding at temperatures up to 460 °C and pressures up to 8 kpsi. It has been found that 1:1 mixtures of finely divided powders of the homopolymers when compression molded under these conditions can transesterify rapidly to form a 1:1 random copolyester. When mixtures of low $\bar{M}_n$ homopolymers (3-5 K) were molded, the conversion to the 1:1 random copolyester was nearly complete. However, for mixtures of high $\bar{M}_n$ homopolymer (>30K) only partial conversion to the random copolyester was observed in the brief time available for processing before degradation reactions ensue. Presumably, the limited conversion is due to the higher viscosity of the melt or the much lower concentration of end groups which act to limit transesterification.

Introduction

Recently, as part of a general study of the properties of liquid-crystalline aromatic polyesters, we decided to examine the formation of blends of homopolymers of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA). In earlier work in this laboratory, attempts to form blends of the various commercial copolyesters were complicated by the large differences in their melting temperatures, melt viscosities, and thermal stabilities. However, the recent observations[1,2] that the homopolymers of HBA and HNA display almost identical thermal transitions, including crystal to liquid-crystal transitions in the temperature range 400–450 °C, prompted us to examine the possibility of forming compatible blends of the two homopolymers at high temperature. Earlier work[3] on melt processing of the HBA homopolymer at 450 °C indicated a stability of several minutes before the onset of degradation and suggested potential for successfully processing mixtures of the two polyesters. We were particuarly interested to see if traditional plastic forming techniques could be used to pro-

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