Macromolecules 1989, *22*, 1497–1499 1497

Communications to the Editor

Correlation between Solubility Parameter and Exclusion Limit on Polyacrylamide Terpolymer

Among packing materials for the separation and purification of various compounds by size exclusion, the advantages of polyacrylamide (PAAm) gels are the lower content of ionic groups and a lower amount of adsorption capacity for samples than other gels. For the Bio-Gel P types[1] which are generally used for these purposes, an increase in the exclision limits is brought about a narrowing of the fractionation ranges and an increase in the degree of gel softness. Dawkins and Gabbott[2,3] carried out more rapid separations (flow rate, 1 cm^3 min^{-1}) of water-soluble materials with spherical PAAm gels; these were prepared by inverse suspension polymerization. This gel has an exclusion limit of about 1×10^5 and a wider fractionation range than the Bio-Gel P types. The gel particles ($\simeq 10$ μm) are porous, rigid, and macroreticular (MR) type and have a swelling coefficient of about 1.15.

In many papers about PAAm gels, the gels were almost a bipolymer which consisted 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[4,5] the preparation of terpolymer gels composed of AAm, MBAA, and a third monomer by inverse suspension polymerization and characterized the MR type for these terpolymer gels by investigating them as packing materials. Acrylonitrile (AN) or methacrylamide (MAAm), which are more hydrophobic than AAm, were used as a third monomer. We obtained gels which have various exclusion limits by changing the composition of the third monomer in the monomer feed. Compared with the PAAm gels prepared by Dawkins and Gabbott, it is an advantage of the terpolymer gels prepared by us that they have high exclusion limits. But it is a disadvantage of these gels that they have a higher swelling coefficient, 1.41–1.47, than Dawkins's PAAm gel particles.

This paper presents the relationship between the magnitude of the solubility parameter of our terpolymer gels and their exclusion limits.

Experimental Section. The terpolymer gels used in this study have been already reported[4,5] with their characteristics when used as packing materials. Macroporous gel particles were produced in an inverse dispersion process by polymerizing AAm, MBAA, and the third monomer. Thus, the inverse suspension polymerizations of terpolymers were carried out under nitrogen in a 1-L cylindrical flask fitted with a turbine-type stirrer and a gas inlet and outlet tube. The reaction was performed by dispersing a aqueous ethanol solution (11.4 vol %) of three monomers in a normal paraffin hydrocarbon (d_4^{30} 0.749, bp 220–245 °C) containing a nonionic surfactant (sorbitan monostearate, Span60) with stirring. Ammonium peroxydisulfate as an initiator was introduced as an aqueous ethanol solution after mixing the two phases and the reaction flask was kept at 55 ± 2 °C for 2 h. These particles were filtered, washed by toluene, extracted with acetone to remove water, and dried under warm air at 50 ± 2 °C. Monomers were purified in the usual way. And other materials were used without further purification. The gel particles which were swelled in water were sieved to obtain 100–200 mesh (74–148 μm) sieve fractions. Then the sieved gel particles were packed into a glass column (500 × 8 mm i.d.) at atmospheric pressure. The chromatographic apparatus consisted of a pump, Model 396-31 (Milton Roy Co., FL), a injection valve, and differential refractometer, Shodex RI SE-11 (Showa Denko K.K., Tokyo, Japan). Degassed RO water and 0.001 mol/L NaCl(aq) were used as an eluent. The chromatographic behavior was carried out by the elution of water-soluble compounds, oligo(ethylene oxide)s and poly(ethylene oxide)s, at a pressure of 0–2 kg cm^{-2}, flow rate 82 cm h^{-1} (0.69 cm^3 min^{-1}). Details were described in previous papers. Table I shows compositions and properties of the terpolymer gels used in this study. Solubility parameters (δ) of gels were estimated by a swelling method.[6] Dry gel particles were placed into a graduated cylinder and their weight was measured. Then, at 25 ± 1 °C, they were swelled in various liquids[7] and their volumes on swelling equilibrium were measured. Other swelling agents used in this experiment were mixtures two liquids. The values of δ for liquid mixtures may be calculated as follows:[8]

$$\delta_{\text{mix}} = \frac{x_1 V_1 \delta_1 + x_2 V_2 \delta_2}{x_1 V_1 + x_2 V_2}$$

where x is the mole fraction and V is the molar volume of the components at 25.0 °C. The degree of swelling (Q) was defined as ratio of wet bed volume (cm^3) in a liquid to unit weight (g) of dry gel. Values of Q for various liquids were plotted against values of δ of used liquids. The value of δ of the gel was estimated as a maximum value in the obtained curve. Further, obtained values of δ of the gels were confirmed according to the method of Mangaraj.[9,10] In our measurements, the probable errors of obtained values of δ were 0.06 and below.

Results and Discussion. Table I shows compositions and properties of the terpolymer gels prepared. For these gels, we have already reported[4,5] the following results.

As shown in Table I, when using AN as a third monomer, at a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of obtained gel (AN–AAm–MBAA) increased from 1.6×10^4 to 1.4×10^6 with increase in the molar ratio of AN to AAm from 0 to 1.34. Table I shows that AN–AAm–MBAA gels have wider fractionation ranges than the Bio-Gel P types, which have similar exclusion limits to our gels. Similarly, when using MAAm as a third monomer at a fixed amount (10.0 g) of MBAA in the monomer feed, the exclusion limits of obtained gels (MAAm–AAm–MBAA) increased from 1.6×10^4 to 4.4×10^5 with increase in the molar ratio of MAAm to AAm from 0 to 0.834. MAAm–AAm–MBAA gels had wider fractionation ranges than the Bio-Gel P types, which had similar exclusion limits to our gels.

In general, there is aggregation and growth of microgels in the process of gel formation.[11,12] Therefore, the increase of the exclusion limit on addition of AN and MAAm is assumed to occur as follows. Addition of the third monomer decreases the magnitude of the solubility of polymers which constitute the microgels. Consequently, it furthers aggregation of the microgels rather than growth of them; in other words, phase separation is accelerated.

To estimate the magnitude of the solubility of each homopolymer (MBAA 5.0 mol %) of AAm, AN, and MAAm, δ, which is a measure of solubility of the polymer,

0024-9297/89/2222-1497$01.50/0

Table I
Composition and Properties of Gels[4,5]

gel	AAm,[a] g	MBAA,[b] g	3rd monomer, g	MBAA in monomer feed, mol %	molar ratio of 3rd monomer: AAm	exclusn limit M_w	fractnatn range M_w
1	30.0	10.0		13.3	0	1.6×10^4	58–1.6×10^4
2	27.5	10.0	AN,[c] 2.5	13.0	0.120	2.5×10^4	58–2.5×10^4
3	25.0	10.0	AN,[c] 5.0	12.7	0.270	6.9×10^4	58–6.9×10^4
4	20.0	10.0	AN,[c] 10.0	12.2	0.670	2.6×10^5	58–2.6×10^5
5	15.5	10.0	AN,[c] 15.0	11.6	1.34	1.4×10^6	58–1.4×10^6
6	27.5	10.0	MAAm,[d] 2.5	13.5	0.075	4.5×10^4	62–4.5×10^4
7	25.0	10.0	MAAm,[d] 5.0	13.6	0.168	7.2×10^4	62–7.2×10^4
8	20.0	10.0	MAAm,[d] 10.0	14.0	0.416	2.0×10^5	62–2.0×10^5
9	15.0	10.0	MAAm,[d] 15.0	14.4	0.834	4.4×10^5	62–4.4×10^5

[a] AAm: acrylamide. [b] MBAA: *N,N'*-methylenebis(acrylamide). [c] AN: acrylonitrile. [d] MAAm: methacrylamide.

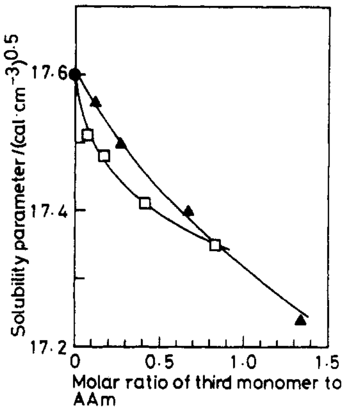

Figure 1. Correlation of solubility parameters of the gels with molar ratio of the third monomers to AAm on the gels: (●) AAm–MBAA gel; (▲) AN–AAm–MBAA gel; (□) MAAm–AAm–MBAA gel.

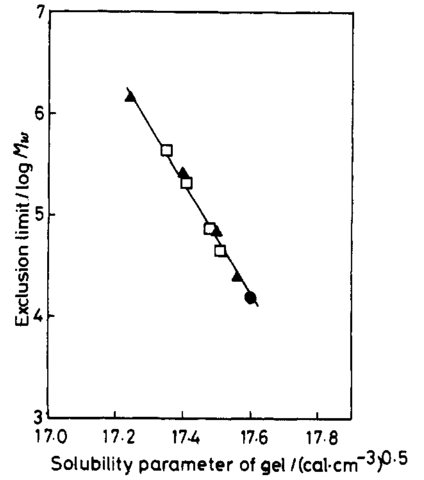

Figure 2. Correlation of exclusion limits with the solubility parameters of the gels: (●) AAm–MBAA gel; (▲) AN–AAm–MBAA gel; (□) MAAm–AAm–MBAA gel.

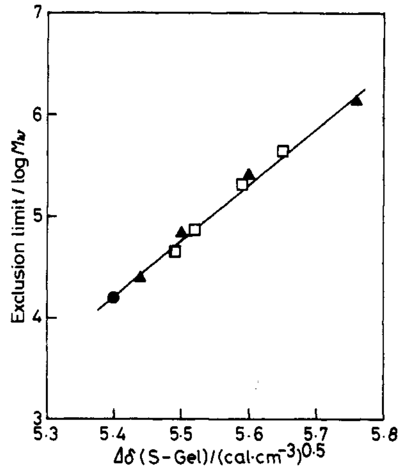

Figure 3. Correlation of the exclusion limits with the differences (Δδ) in the solubility parameters between the polymerization solvent (S) and the gels: (●) AAm–MBAA gel; (▲) AN–AAm–MBAA gel; (□) MAAm–AAm–MBAA gel.

was measured for each homopolymer. The value of δ of each homopolymer was 17.6, 13.5 and 17.0 (cal cm^{-3})$^{0.5}$. Moreover, as shown in Figure 1, the values of δ of AN-AAm-MBAA gels decreased from 17.60 to 17.24 with increasing molar ratio of AN to AAm from 0 to 1.34. Also, the values of δ of MAAm–AAm–MBAA gels decreased from 17.60 to 17.35 with increasing molar ratio of MAAm to AAm from 0 to 0.834. The value of δ of the polymerization solvent was 23.00 and higher than the value of δ of the AAm–MBAA gel. These results support the above assumption.

On the basis of the results[13] on the effect of solvents on pore structure, it is obvious that the structure of gel in aqueous ethanol solution (11.3 vol %) as a polymerization solvent is almost identical with the structure with water as an eluant. An elution experiment was carried out by using the gels which were almost held in the structure of gels in the polymerization. Figure 2 shows the correlation between the values of δ of the terpolymer gels and exclusion limits. The exclusion limits are so high that the values of δ of the gels are small, in other words, the magnitude of hydrophobicity is high. Then Figure 3 was obtained as a result of replacing the values of δ of gels on the abscissa of Figure 2 with the difference (Δδ) in the value of δ between the polymerization solvent and the gels and plotting over again. We found that the logarithm of the exclusion limits of gels had an approximately linear relationship with Δδ. Since this linear relationship applied to both the AN–AAm–MBAA gels and the MAAm–AAm–MBAA gels, the assumption described above can be accepted. Therefore, the causes of the formation of large macropores can be thought of as follows: the magnitude of δ of the polymer chains of the terpolymer gels is influenced by solubility of the third monomer, and aggregation of microgels is furthered as the values of δ of the terpolymer gels are lower than the value of δ of the AAm–MBAA gel.

In order to get solid gels of MR type, generally, one must use the method of accelerated aggregation of microgels by taking advantage of the difference in the value of δ between a gel and a polymerization solvent, by adding a solvent, which is good for monomer and poor for polymer, to a polymerization solvent. There is another method of accelerated aggregation of microgels, which involves taking advantage of the difference in the value of δ between a polymerization solvent and a gel which is allowed to change by addition of a third monomer. For the gels obtained with the second method, we found that the logarithm of the exclusion limits of gels had an approximately linear relationship with the difference in values of δ between the polymerization solvent and the terpolymer gels. And these results indicate that the magnitude of δ of the polymer chains of gels will control aggregation and growth of microgels in the process of gel formation.

At present we are considering whether the relationship described above can or cannot apply to both cases where the third monomer component of the terpolymer gels has about the same value of δ as AAm and has a lower value of δ than AAm. Later, we will report these results.

Conclusion. (1) The increase in molar ratio of the third monomer to acrylamide resulted in an increase in the exclusion limits of the terpolymer gels and a lowering in the values of the solubility parameters of these gels. (2) We found that the logarithm of the exclusion limits of these gels had an approximately linear relationship with the difference in the value of the solubility parameter between the polymerization solvent and the gels. (3) Obtained results indicate that the exclusion limits will be controlled by the adding of a third monomer which has a value of δ differing from that of AAm.

Acknowledgment. We thank Yasuji Ohtsuka and Haruma Kawaguchi for helpful discussions.

Registry No. (MBAA)(AN)(AAm) (copolymer), 29825-75-0; (MBAA)(MAAm)(AAm) (copolymer), 34364-91-5.

References and Notes

(1) Bio-Rad Laboratories, Richmond, CA.
(2) Dawkins, J. V.; Gabbott, N. P. *Polymer* **1981**, *22*, 291.
(3) Dawkins, J. V.; Gabbott, N. P.; Montenegro, M. C. *J. Chromatogr.* **1986**, *371*, 283.
(4) Suzuki, K.; Nakazato, K.; Takasaki, T. *Nippon Kagaku Kaishi* **1979**, 1327.
(5) Nakazato, K.; Suzuki, K. *Nippon Kagaku Kaishi* **1984**, 1914.
(6) Orofino, T. A.; Hopfenberg, H. B.; Stanett, V. *J. Macromol. Sci., Phys.* **1963**, *B3*, 711, 777.
(7) Hansen, C. M. *J. Paint Technol.* **1967**, *39*, 104.
(8) Burrell, H. *Encyclopedia of Polymer Science and Technology*; Interscience: New York, 1971; Vol. 12, p 618.
(9) Mangaraj, D. *Makromol. Chem.* **1963**, *65*, 29.
(10) Mangaraj, D.; Patra, S.; Rashid, S. *Makromol. Chem.* **1963**, *65*, 39.
(11) Earth, E. H.; Robinson, M. *J. Polym. Sci., Polym. Symp.* **1962**, *3*, 65. Wohnsiedler, H. P. *Ibid.* **1962**, *3*, 77.
(12) Horie, K.; Otagawa, A.; Muraoka, M.; Mita, I. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 445.
(13) Suzuki, K.; Nakazato, K.; Sugiyama, A.; Koike, J.; Hattori, K.; Nakahodo, A. *Nippon Kagaku Kaishi* **1977**, 1660.

Ken'ichi Nakazato* and Kiichi Suzuki
School of Hygienic Science, Kitasato University
1-15-1, Kitasato, Sagamihara-Shi
Kanagawa, 228, Japan

Received September 14, 1988;
Revised Manuscript Received December 27, 1988

Preparation and Characterization of Syndiotactic Poly(vinylcyclohexane)

Poly(vinylcyclohexane) (PVCH) is expected to be useful as an engineering plastic due to its high melting point. Head-to-tail PVCH has been synthesised frequently in the past.[1] Isotactic PVCH has been prepared either by polymerization of vinylcyclohexane with Ziegler–Natta catalysts or by hydrogenation of isotactic polystyrene (PS), whereas atactic PVCH was most conveniently prepared by hydrogenation of atactic PS.[2] However, syndiotactic PVCH has never been reported so far.

More recently, Ishihara et al. have succeeded in preparing syndiotactic PS by using a kind of Kaminsky-Sinn catalyst composed of certain titanium compounds and methylaluminoxane (MAO).[3] Zambelli et al. later reported that some zirconium compounds combined with MAO are also effective for the polymerization.[4,5]

It was the objective of the present work to prepare syndiotactic PVCH by hydrogenation of syndiotactic PS.

Experimental Section. Toluene, cyclohexane, and styrene were purified according to the usual procedures. Methylaluminoxane (MAO) was prepared from $Al(CH_3)_3$ and $CuSO_4{\cdot}5H_2O$ according to the literature[6] and reserved as stock solution in toluene (0.40 mmol/dm^3).

The Ni/SiO_2 catalyst was prepared from silica gel (350 m^2/g) with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$; After impregnation, the catalyst was dried at ambient temperature for 8 h, dried in vacuum for 3 h at 300 °C, and then calcinated at 300 °C under 300 Torr of H_2 for 5 h. Hydrogenation of PS was carried out in cyclohexane at 200 °C for 24 h under 50 kg/cm^2 of hydrogen by using the catalyst. Polymerization of styrene was carried out in a 0.1-dm^3 glass reactor equipped with a magnetic stirrer. $Zr(OBu)_4$, 0.1 mmol, 2.0 mmol of MAO (referred to $AlMe_3$; $Al/Zr = 20$), 86.9 mmol of styrene, and 24 cm^3 of toluene were placed in the reactor under nitrogen atom room temperature. Polymerization of styrene was conducted under vigorous stirring for 3 h at 80 °C (polymer yield, 964 mg). Atactic PS was obtained from Toso Co.

The ^{13}C NMR spectra of PS and hydrogenated PS were measured in chloroform-*d* at 60 °C with a JEOL JNH FX-100 spectrometer. The chemical shifts were refered to TMS and HMDS, added as internal standards for $\delta = 0.0$ ppm and $\delta = 2.0$ ppm.

The molecular mass distribution of the polymer was measured at 120 °C with a Shodex LCHT-3 GPC equipped with a Shodex AD 80 M/S column by using standard polystyrene gels obtained from waters chromatography division. *o*-Dichlorobenzene was used as solvent. M_n and M_w were determined by standard procedures from elution curves. The glass transition and decomposition temperatures of the polymer were measured by differential scanning calorimetry (DSC) and thermogravimetry (TG)–differential thermal analysis (DTA), respectively.

DSC and TG–DTA measurements were made under nitrogen atmosphere at a heating rate of 15 K/min.

Results and Discussion. The PS obtained with the $Zr(O\text{-}Bu)_4$–MAO catalyst was confirmed by ^{13}C NMR to be highly syndiotactic. Figure 1A,B shows the ^{13}C NMR spectra of the polymers prepared by hydrogenation of syndiotactic and atactic PS. For reference, the ^{13}C NMR spectrum of isotactic PVCH reported by Zambelli et al.[7] is shown in Figure 1C. The resonances of both atactic and isotactic PVCH were assigned according to the literature.[7]

The spectrum of the hydrogenated syndiotactic PS displays no resonances in the range 120–150 ppm attributed to the aromatic C, indicating that hydrogenation of the aromatic rings was complete.

Since the hydrogenation is not expected to affect the stereochemistry of the tertiary carbon atom of the polymer chain, the hydrogenated PS should have the same stereochemistry as the original PS.

Taking the assignments of atactic and isotactic PVCH into consideration, the resonances of the syndiotactic PVCH may be assigned as indicated in Figure 1A. The weight-average molecular mass (M_w) and polydispersity (M_w/M_n) were 13 000 and 3.0 for syndiotactic PS and 102 000 and 1.02 for atactic PS, respectively. The

0024-9297/89/2222-1499$01.50/0