

Copolymerization of 2-acrylamido-2-methylpropane sulfonic acid with 2-hydropropyl methacrylate

Zhen Tong*, Yuhua Yi, Xinxing Liu

Research Institute of Materials Science, South China University of Technology, Guangzhou 510641, China

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Summary

Copolymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS, monomer 1) with 2-hydropropyl methacrylate (monomer 2) was conducted in pure water at 80°C. The reactivity ratios estimated from the compositional data of the copolymers at low conversion are $r_1=0.04\pm 0.04$ and $r_2=6.30\pm 0.48$, and values of Q_1 and e_1 are 0.16 and 1.37, respectively. Copolymer microstructure predicted by statistical calculation shows mean sequence length of M_1 shorter than 2. These results can be attributed to the strong repulsion between the ionized chain radical and charged monomer of AMPS.

Introduction

Recently, we have studied some swelling and dynamic mechanical properties of hydrogels copolymerized with 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as the ionized monomer and a water-soluble monomer *N,N*-dimethylacrylamide. The observed behavior is different from those on weakly dissociative polyelectrolyte gels(1-3). In order to reveal the swelling properties of strong electrolyte networks not only in aqueous solutions but also in organic solvents, we chose 2-hydropropyl methacrylate (HPM) as the comonomer for its homopolymer is insoluble in water but soluble in some polar solvents. It is desirable to make a gel sample with homogeneous microstructure and composition. However, the copolymer drift may occur at high conversions since the process of copolymerization for synthesizing a gel sample is usually carried through to the end and the reactivity ratios r_1 and r_2 generally do not equal to unit, resulting the monomer feed ratios skewed during the process. Therefore, the azeotropic copolymerization would be greatly expected. McCormick's group has synthesized a series of water-soluble copolymers containing AMPS and reported its reactivity ratio with other monomers(4-6). Following their way, the reactivity ratios of copolymerization of AMPS and HPM comonomers and the mean sequence lengths of M_1 and M_2 in copolymers were experimentally determined.

* Corresponding author

Experimental

Materials

The monomers 2-Acrylamido-2-methylpropane sulfonic acid (AMPS, monomer 1), 2-hydropropyl methacrylate (HPM, monomer 2) and the initiator ammonium persulfate (APS) were all special grade reagents of Wako Chemicals Co., Japan, and used without further purification. The water used in the experiment was distilled and deionized till its resistivity higher than $10^6 \Omega\text{cm}$.

Copolymerization

Specified amounts of AMPS, HPM, and APS were dissolved in water in a round-bottom flask and sparged with nitrogen for 20 min. Then, the flask was immersed into a thermostated bath at 80°C to initiate the radical copolymerization under the nitrogen atmosphere. After a period, the reaction mixture was removed out into a dialysis bag made by Union Carbide Co. with molecular weight cutoffs of 12000-14000 and cooled with iced water. The mixture was dialyzed with pure water for about 7 days till the residual monomers in the external water was undetectable by ultraviolet spectrum. The solution in the dialysis bag was freeze-dried to constant weight and the conversion was determined gravimetrically. True copolymer was formed because that the precipitate of poly(HPM) did not appear during the dialysis in water, which would be the case if the polymer were the blend of poly(AMPS) and poly(HPM). The total monomer concentration was kept 0.45M/L in each synthesis solution and the initiator concentration was 0.2 mol% to all monomers.

Analysis of copolymer composition

The low conversion aliquots of the copolymer were chosen to estimate the monomer reactivity ratio. The weight percentage of element sulfur S% in each copolymer sample was determined with oxygen flask method and the results were used in calculating the mole fraction F_1 in our copolymers which were referred to as HMAS series.

Results and discussion

Copolymer composition

The mole fraction f_1 of AMPS in comonomer feed, reaction time, conversion, and compositional data of S% and F_1 for HMAS series of copolymers are illustrated in Table 1. The number appended to the acronym HMAS refers to the amount of AMPS in the feed. The relation between F_1 and f_1 is also presented graphically in Fig. 1. F_1 values are much lower than the azeotropic composition represented by the straight line where r_1 and r_2 are unity. This result indicates that the AMPS monomer is very difficult to be directly linked during copolymerization because of the strong electrostatic repulsion as expected.

Table 1. Reaction parameters and resulting compositions of HMAS copolymers

sample	f_1	reaction time /min	conversion wt%	S wt%	F_1
HMAS-0	0	90	87.6	---	0
HMAS-15	0.152	20	18.5	0.59	0.027
HMAS-30	0.304	20	7.2	1.25	0.58
HMAS-50	0.499	20	5.8	2.47	0.117
HMAS-65	0.651	25	7.9	4.93	0.246
HMAS-80	0.794	25	7.0	6.58	0.340
HMAS-90	0.898	50	4.4	7.64	0.404
HMAS-100	1.000	90	13.4	---	1.000

Reactivity ratio

Monomer feed compositional data as well as low conversion polymer compositional data (Table 1) derived from elemental analysis were used to calculate reactivity ratios of the HMAS copolymer series. Four methods of Mayo-Lewis (M-L) (7), Fineman-Ross (F-R) (8), Kelen-Tüdös (K-T) (9), and Yezrielev (YBR) (10) were employed for the calculation. All these methods are based on the terminal model, viz. the Mayo-Lewis equation (7):

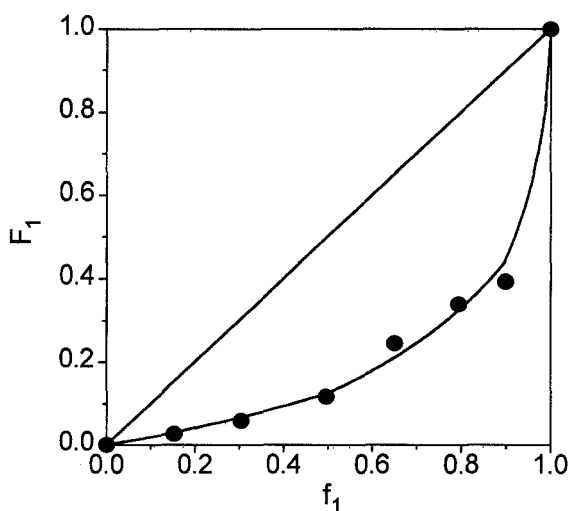


Fig. 1 Plots of F_1 vs. f_1 ; straight line: azeotropic copolymerization; curve: calculated composition curve

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] \left(r_1 [M_1] + [M_2] \right)}{[M_2] \left(r_2 [M_2] + [M_1] \right)} \quad (1)$$

where $[M_1]$ and $[M_2]$ are the molar concentration of the monomers AMPS and HPM, $d[M_1]$ and $d[M_2]$ the molar concentration of repeat units M_1 and M_2 in the copolymer. The initial feed composition f and the average copolymer composition at low conversion F are defined as

$$f = \frac{f_1}{(1 - f_1)} = \frac{[M_1]}{[M_2]} \quad (2)$$

$$F = \frac{F_1}{(1 - F_1)} = \frac{d[M_2]}{d[M_1]} \quad (3)$$

The following equations are used for the corresponding method:

i) M-L method:

$$r_1 = \frac{F}{f^2} r_2 + \frac{1}{f} (F - 1) \quad (4)$$

ii) F-R method:

$$\frac{(1 - F)}{f} = r_2 \frac{F}{f^2} - r_1 \quad (5)$$

iii) K-T method:

$$= r_1 \zeta - \frac{r_2}{\alpha} (1 - \zeta) \quad (6)$$

where

$$\eta = \frac{G}{(\alpha + H)} \quad \zeta = \frac{H}{(\alpha + H)} \quad (7)$$

$$\alpha = \sqrt{H_{\min} \times H_{\max}} \quad (8)$$

Here

$$G = \frac{f(F - 1)}{F} \quad H = \frac{f^2}{F} \quad (9)$$

iv) YBR method:

$$\frac{f}{F^{1/2}} r_1 - \frac{F^{1/2}}{f} r_2 + \left(\frac{1}{F^{1/2}} - F^{1/2} \right) = 0 \quad (10)$$

The plots according to the above equations are shown in Figs 2 through 4 except those from the YBR method. For this system the highest conversion is only 18.5% and the linearity of the data points can be found in Figs 3 and 4. Fig 2 presents the M-L plots on a r_1 vs. r_2 coordinate and the intersection point gives r_1 and r_2 values of 0.04 and 6.53, respectively. However, these values will include quite large and uncertain errors because of the long distance extrapolations. By the linear least-square mathematics the data in Figs 3, 4 are fit and eq 10 is solved and the resulting r_1 , r_2 values are listed in Table 2 with the

Table 2 Reactivity ratios and Q-e values of HMAS copolymerization

method	r_1	r_2	Q_1	e_1
M-L	0.04	6.53	0.15	1.40
F-R	0.06 ± 0.07	6.40 ± 0.18	0.15	1.18
K-T	-0.004 ± 0.05	5.98 ± 0.57	---	---
YBR	0.04 ± 0.04	6.30 ± 0.48	0.16	1.37

corresponding standard deviations. The reactivity ratios calculated with the later three methods are almost equal to each other, this means that all these reactivity data can be accepted. The solid curve in Fig 1 is formed by using eq 1 with the values of $r_1=0.04$ and $r_2=6.30$, which quantitatively describes the observed copolymer drift induced by the monomer feed.

It can be seen that r_1 is much smaller than r_2 . This is mainly due to the strong electrostatic repulsion between charged chain terminal of AMPS radical and ionized monomer AMPS in pure water and partially due to the fast propagation reaction of HPM radical and monomer, the latter reason can be judged by comparing the conversion data of HMAS-0 and HMAS-100 samples in Table 1 after the same reaction period of 90 minutes.

The Q_1 and e_1 values of AMPS can be estimated by equations derived from the Alfrey-Price scheme(11), taking values of $Q_2 = 0.79$ and $e_2 = 0.20$ for HPM(12). The results are shown in Table 2. The facts that e_1 and e_2 are positive and $e_1 \gg e_2$ suggest that two enormous groups attaching to the double bonds in the AMPS and HPM monomers would be electron attractive and the attracting ability in AMPS is stronger than that in HPM. While the fact that Q_1 is smaller than Q_2 means the ability of forming radical is weaker for AMPS monomer than that for HPM.

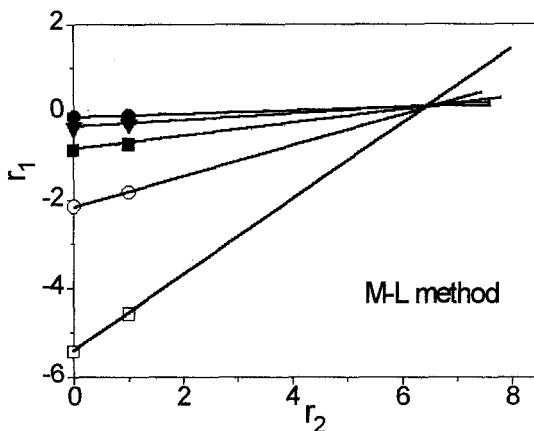


Fig. 2 Linear plots of the M-L method

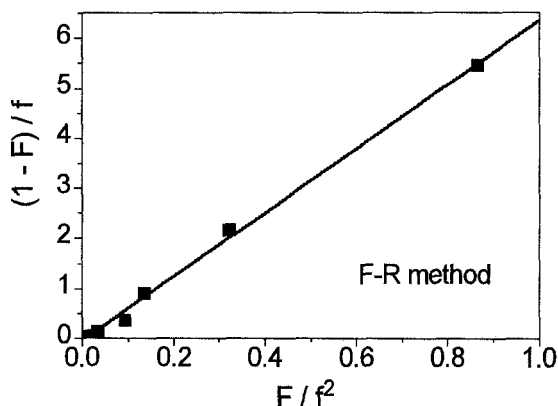


Fig. 3 Linear plots of the F-R method

Statistical microstructure

The calculation of the statistical distribution of monomer sequences M_1-M_1 , M_2-M_2 , and M_1-M_2 (respectively X, Y, and Z in mol%) was performed, according to Igarashi's equations (13) with the experimental reactivity ratios and copolymer compositions.

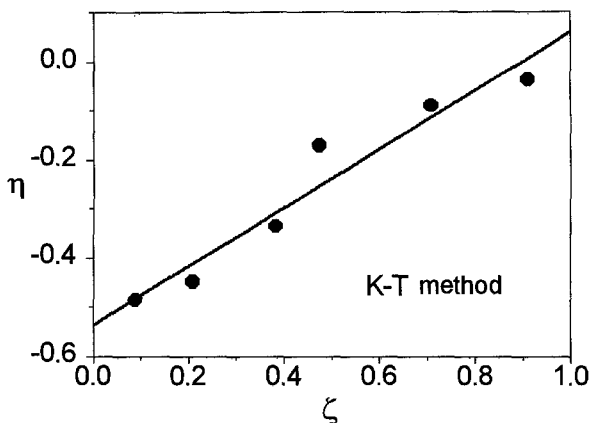


Fig. 4 Linear plots of the K-T method

$$X = F_1 - \frac{2F_1(1-F_1)}{1 + [(2F_1 - 1)^2 + 4r_1r_2F_1(1-F_1)]^{1/2}} \times 100\% \quad (11)$$

$$Y = (1-F_1) - \frac{2F_1(1-F_1)}{1 + [(2F_1 - 1)^2 + 4r_1r_2F_1(1-F_1)]^{1/2}} \times 100\% \quad (12)$$

$$Z = \frac{4F_1(1-F_1)}{1 + [(2F_1 - 1)^2 + 4r_1r_2F_1(1-F_1)]^{1/2}} \times 100\% \quad (13)$$

Mean sequence lengths L_1 and L_2 were calculated with the method of Pyun(14) using r_1 and r_2 values estimated with the YBR method. These statistical data are summarized in Table 3.

Table 3 HMAS series copolymer statistics

sample	F_1	blockiness		alternation	L_1	L_2
		M_1-M_1	M_2-M_2	M_1-M_2		
HMAS-15	0.027	0.02	94.64	5.34	1.00	35.72
HMAS-30	0.058	0.17	88.53	11.30	1.01	15.22
HMAS-50	0.117	0.37	76.97	22.65	1.04	7.31
HMAS-65	0.246	2.13	52.92	44.95	1.07	4.33
HMAS-80	0.340	5.07	36.94	57.99	1.14	2.61
HMAS-90	0.404	7.69	28.99	63.31	1.32	1.70

The maximum values in blockiness of M_1-M_1 and M_2-M_2 naturally occur for HMAS-90 and HMAS-15, respectively, while the alternation monotonically increases with the increase in AMPS concentration in the comonomer feed. Because of the electrostatic repulsion between the charged chain radical and monomers, the mean sequence length L_1 of AMPS is even smaller than 2 for all of our copolymer samples.

The above results indicate that it is impossible to prepare a strong polyelectrolyte gel with homogeneous composition simply by copolymerizing the monomers AMPS and HPM in water. Further efforts have to be made in choice of the reaction medium if these two monomers are selected.

Acknowledgment

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References

- 1 Tong Z, Liu X (1993) *Macromolecules* 26:4964
- 2 Tong Z, Liu X (1994) *Macromolecules* 27:844
- 3 Liu X, Tong Z, Hu O (1995) *Macromolecules* 28:in press
- 4 Hutchinson BH, McCormick CL (1986) *Polymer* 27:623
- 5 McCormick CL, Johnson CB (1988) *Macromolecules* 21:686
- 6 McCormick CL, Salazar L (1992) *Macromolecules* 25:1896
- 7 Mayo FR, Lewis FM (1944) *J Am Chem Soc* 66:1594
- 8 Fineman M, Ross S (1950) *J Polym Sci* 5:259
- 9 Kelen T, Tüdös F (1975) *J Macromol Sci-Chem* A9:1
- 10 Ying S, Yu F (1984) *Principles in copolymerization (in Chinese)*, Chem Indu, Beijing
- 11 Alfrey JrT, Price CC (1947) *J Polym Sci* 2:101
- 12 Chow CD (1975) *J Polym Sci* 13:309
- 13 Igarashi S(1963) *Polym Lett* 1:359
- 14 Pyun CW (1970) *J Polym Sci A-2* 8:1111