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Synthesis and Characterization of Amphiphilic Copolymer Acrylic Acid-co-*p*-Chloromethylstyrene

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The free radical copolymerization of acrylic acid (M_1) with *p*-chloromethylstyrene (M_2) in dioxane and in the presence of α,α'-azobisisobutyronitrile (AIBN) at 65°C is reported. Copolymer compositions of six copolymer samples obtained from feed ratios of $M_1{:}M_2 = 95.2{:}4.8$ to 21.4:78.6 were determined by ^{1}H-NMR. The reactivity ratios of AA/*p*-CMS copolymerization system calculated by the F-R method were $r_1 = 0.50 \pm 0.06$ and $r_2 = 1.52 \pm 0.15$, almost the same as $r_1 = 0.43 \pm 0.21$ and $r_2 = 1.31 \pm 0.14$ by the extended K-T method. On the basis of the reactivity ratios of two monomers, the sequence length distribution in the AA/p-CMS copolymers was obtained. For $f_2 = 4.77\%$, the monomer unit of p-CMS is individually separated in the chain of AA; for $f_2 = 35.53\%$, the alternating tendency prevails and a large number of mono-sequences are formed. The number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights were determined by gel permeation chromatography. The effect on molecular weights of feed composition is also discussed. In the presence of constant initiator concentration, the gradual increase in the ratio of $M_2{:}M_1$ (from14.7:85.3 to 78.6:21.4) was accompanied by a decrease in molecular weights ($\overline{M}_n$ from 11907 to 3961).

Keywords: Acrylic acid, *p*-chloromethylstyrene, amphiphilic polymer, reactivity ratios, segment length distribution

1 Introduction

Copolymerization of a hydrophobic monomer with a hydrophilic monomer can result in an amphiphilic polymer, the specific nature of which can be controlled via polymerization parameters (1). The dual hydrophilic/hydrophobic nature provides these materials with unique solubilization characteristics and modifies physical properties of the bulk polymer (2). Water-soluble amphiphilic polymers are of particular interest as a chemical system due to the presence of microdomains that may impart unusual reactivity to a given chemical system (1).The tendency of the hydrophobic parts to aggregate into micelles in water and also the surface active properties exhibited by such amphiphilic polymers are two features that have been thoroughly investigated and exploited in miscellaneous applications (3), including the replacement of high molecular weight viscosifiers (4), the dispersion of pigments and oils, the stabilization of proteins (5), and drug delivery (6, 7).

As a consequence, in the past few years, there has been increasing interest in the synthesis of amphiphilic polymers. A particularly interesting amphiphilic polymer is the copolymer of acrylic acid and other hydrophobic monomers. In these hydrophobic monomers, *p*-chloromethylstyrene is a functional styrene with a reactive pendent benzyl group susceptible to Lewis acid-assisted cation formation, nucleophilic substitution, etc. (8). The copolymers containing $-\mathrm{ChCH_2Cl}$ group serve as versatile intermediates in polymer chemistry, as their chlorine groups are easily displaced by nucleophiles (9, 10) to produce anion-exchange polymers (11) and electron beam negative resists (12–14). In this paper, we prepared an amphiphilic copolymer—acrylic acid-co-*p*-chloromethylstyrene with a variety of compositions. The compositions of the copolymers are analyzed by ^{1}H-NMR. The reactivity ratio was determined by Fineman-Rosss method and the Kelen-Tudos method. On the basis of the reactivity ratios of two monomers, the sequence length distribution in the AA/*p*-CMS copolymers was obtained. The molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and the polydispersity indices ($\overline{M}_w/\overline{M}_n$) of the copolymers were also presented. To our knowledge, the preparation and characterization of this acrylic acid and p-chloromethylstyrene random copolymer have never been studied and reported before.

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Table 1. Reaction parameters for the copolymerization of acrylic acid (m_1) with p-chloromethylstyrene (M_2)

Sample	*Reaction time, h*	*Conversion, Wt %*	f_2 *(mol %)*	F_2 *(mol %)*	*GPC*	
					$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
AA/*p*-CMS-5	2.5	5.12	4.77	8.51		
AA/*p*-CMS-15	1	6.51	14.71	32.51	3961	1.98
AA/*p*-CMS-35	1	5.91	35.53	41.82	8225	2.63
AA/*p*-CMS-50	1.5	4.02	52.03	65.70	8771	2.35
AA/*p*-CMS-65	2.0	10.58	65.02	72.38	10895	2.45
AA/*p*-CMS-80	2.0	6.54	78.62	85.71	11907	2.08

2 Experimental

2.1 Materials

p-Chloromethylstyrene (*p*-CMS) from Aldrich Chemical Co. was purified by passing through a column of activated basic alumina to remove inhibitor, stored over CaH_2, and then vacuum distilled before use. Acrylic acid (AA) from Tianjin Chemical Co. was distilled under reduced pressure to remove stabilizer before use. Dioxane from Tianjin Chemical Co. was distilled according to the usual techniques. The initiator, α,α'-azobisisobutyronitrile (AIBN) from Tianjin Chemical Co. was crystallized from chloroform. Acetone from Laizhou Chemical Co. was reagent grade products. Distilled water was used throughout.

2.2 Poly(acrylic acid-co-p-chloromethylstyrene)

The copolymers of acrylic acid and *p*-chloromethylstyrene were prepared in dioxane at 65°C using 0.6 wt% AIBN as the initiator. The feed ratio of AA and *p*-CMS was varied from 95.2:4.8 to 21.4:78.6 (mole ratios). Each reaction was conducted in a 100 mL, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube. Designated amounts of *p*-CMS and AA were dissolved in 35 ml dioxane. The reaction mixture was then deaerated with oxygen-free nitrogen for 30 min and placed in a water bath at 65°C. After the reaction mixture had equilibrated, 0.0224 g of AIBN dissolved in 5 ml of dioxane was injected into the stirring solution. The total monomer concentration was held constant below 10 wt% in each reaction. After a designated time (1–2.5 h), the resulting polymer was precipitated into acetone. The polymers were redissolved and reprecipitated, washed, and vacuum dried for ^{1}H-NMR analysis. Conversions were determined gravimetrically.

2.3 Characterization

^{1}H-NMR spectra were measured on a VarianGemini-500 NMR spectrometer using dimethyl sulfoxide-D6 as the solvent. Chemical shifts are reported in parts per million (ppm). A Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopy analysis. The $\overline{M}_n$, and $\overline{M}_w/\overline{M}_n$ values of polymers were measured using a Waters GPC (gel permeation chromatography) equipped with a 510 differential refractometer and a Viscotek T50 differential viscometer by flowing copolymer-dissolved THF at a flow rate of 1.0 ml/min.

3 Results and Discussion

3.1 Compositional and Structure Studies

The AA/*p*-CMS series of copolymers were synthesized by varying the ratio of AA and *p*-CMS from 95.2:4.8 to 21.4:78.6 (mole ratio) in the feed. Reaction parameters and compositions of the resulting copolymers determined by ^{1}H-NMR are given in Table 1. The number appended to the AA/ *p*-CMS refers to the amount of *p*-CMS in the feed. The IR spectrum of the polymer is reported in Figure 1. The broad band observed around 3319 and peak at 1702 cm^{-1} are characteristic peaks of the O—H and C=O stretching from the carboxyl group, respectively. A band at 1620 cm^{-1} is due to the benzene skeleton vibration from *p*-CMS. However, the IR spectrum alone does not give all the information concerning composition. The complete ^{1}H-NMR spectrum (Figure 2) assignment was straightforward: methylene protons H (a) at 1.2–1.8 ppm; methine proton H, (b) at 2.0–2.3 ppm; chloromethyl protons H,

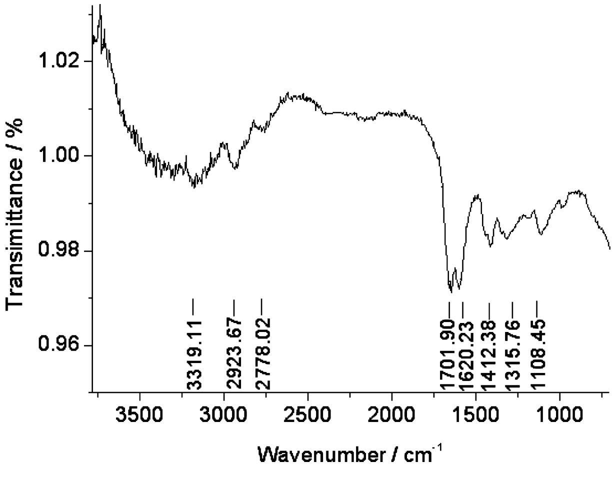

Fig. 1. FT-IR spectrum of the AA/*p*-CMS copolymer.

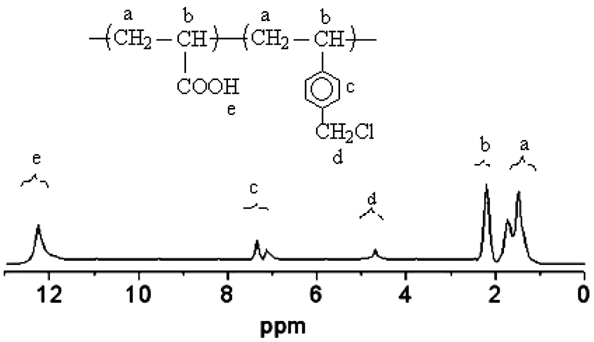

Fig. 2. Expansions of the 500-MHz ^{1}H-NMR spectra of AA/*p*-CMS copolymer (feed ratio = 95.2 : 4.8) recorded at 5.12% conversion using dimethyl sulfoxide-D6 as the solvent.

(d) at 4.6 ppm; phenyl protons H, (c) at 6.8–7.4 ppm; acrylic protons H, (e) at 12.2 ppm.

3.2 Reactivity Ratio Studies

Reactivity ratios for the AA/*p*-CMS series were determined from the feed ratios of the monomers and the resultant copolymer compositions obtained by ^{1}H-NMR spectrum. A quantity of polymer was dissolved in a volume of dimethyl sulfoxide-D6, containing TMS as the chemical shift standard, the spectrum obtained and integrated, and the composition determined by using $X_C = (S_B/4)/(S_A/2)$ where X_C is the mole fraction of *p*-CMS in the copolymer, S_B is the integrated area of the aromatic protons, and S_A is the integrated area of the methylene protons. In Figure 3, a copolymer composition plot of mol%*p*-CMS found in the copolymer vs, mol% *p*-CMS in the feed is shown.

The Fineman-Ross (15) method and the Kelen-Tudos (16) method were employed to determine the monomer reactivity ratios at low conversion. Fineman-Ross is a double method. On one hand, it is possible to plot $f_1\,(2F_1 - 1)/(1 - f_1)F_1$ vs. $f_1^2\,(1 - F_1)/(1 - f_1)^2F_1$, and then r_1 is the slope of the straight line and $-r_2$ the intercept (FR1); on the other hand, if $(2F_1 - 1)(1 - f_1)/(1 - F_1)\,f_1$ is plotted vs. $(1 - f_1)^2F_1/(1 - F_1)f_1^2$, the slope is $-r_2$ and the intercept r_1 (FR2) as shown in Figure 4. The obtained values of r_1 and r_2 using FR1 and FR2 are different in general. The FR1 method would be more accurate for determining r_1 and the FR2 method for calculating r_2 (17). The confidence intervals are calculated according to the usual statistical least-squares method for linear regression (18). Kelen and Tudos (K-T) use a change of variables to obtain a better distribution of the points over the range of variation of the abscissa. Let G and F represent the ordinate and abscissa, respectively, in the FR1 method; the Kelen-Tudos variables are then defined as $\eta = \frac{G}{\alpha+F}$ $\xi = \frac{F}{\alpha+F}$ where α is an undetermined constant. The value $\alpha = (F_M\,F_m)^{1/2}$ (where F_M and F_m are the highest and the lowest values of F, respectively) leads to a better distribution of the experimental points in the range of variation of ξ, which is 0 ($F = 0$) to 1 ($F = \infty$) (Figure 5). Thus, r_1 is the value of η when $\xi = 1$, and the intercept of the straight line $\eta = f(\xi)$ gives $-r_2/\alpha$. The straight line is calculated according to the least-squares technique, as well as the confidence intervals.

The Fineman-Ross method yielded values of $r_1 = 0.50 \pm 0.06$ and $r_2 = 1.52 \pm 0.15$ while the Kelen-Tudos method generated values of $r_1 = 0.43 \pm 0.21$ and $r_2 = 1.31 \pm 0.14$ (Table 2). These data reveal that *p*-CMS is more active than AA no matter for $\sim M_1\cdot$ and $\sim M_2\cdot$ (chain end free radical). *p*-CMS in copolymer is always larger than *p*-CMS in feed and the curve is always above the diagonal. Similar behavior ($r_2 > r_1$) has been

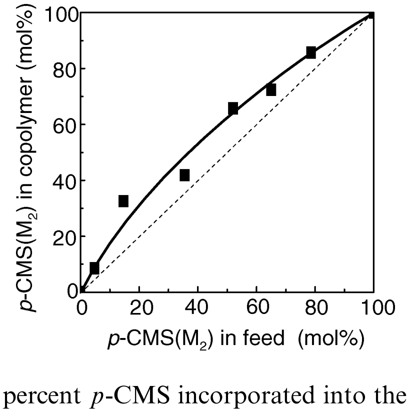

Fig. 3. Mole percent *p*-CMS incorporated into the AA/*p*-CMS copolymers as a function of the comonomer feed ratio. The dashed line represents ideal random incorporation.

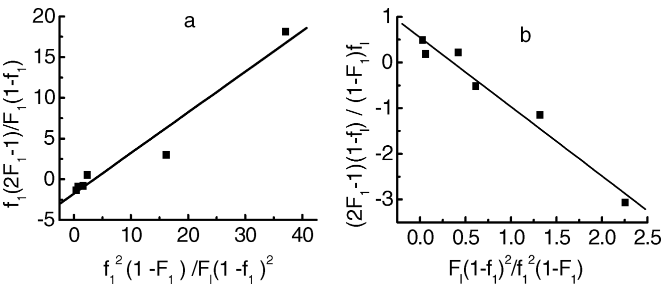

Fig. 4. (a) Fineman-Ross (FR1) plot; (b) Fineman-Ross (FR2) plot.

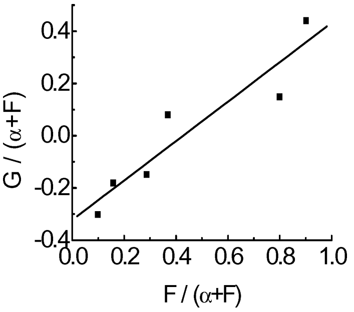

Fig. 5. Kelen-Tudos plot.

Table 2. Calculated Values of r_1 (AA) and r_2 (*p*-CMS)

Method	$r_1 \pm \delta r_1$	$r_2 \pm \delta r_2$	$r_1r_2 \pm \delta(r_1r_2)^a$
Fineman-Ross (FR1)	0.50 ± 0.06	1.78 ± 0.96	0.89 ± 0.59
Fineman-Ross (FR2)	0.55 ± 0.16	1.52 ± 0.15	0.84 ± 0.33
Kelen-Tudos (KT)	0.43 ± 0.21	1.31 ± 0.14	0.56 ± 0.34

$^a\delta(r_1r_2) = r_1\delta r_2 + r_2\delta r_1$.

observed by Yong-ming Zhang et al. (19) for copolymers of *p*-CMS(M_2) with various monomers including styrene, methyl methacrylate, butyl methacrylate, acrylonitrile and vinyl acetate. This tendency is probably related to the electron-with-drawing effect of chloromethyl and conjugated effect of the benzyl group in *p*-CMS. So, *p*-CMS is prone to produce steady radicals as compared with AA.

3.3 Sequence Length Distribution

By using the probability method, the ratio of different length of $(M_1)_x$ and $(M_2)_x$ segments in macromolecule chain can be calculated, which is named as segment length distribution. $(PM_1)_x$ and $(PM_2)_x$ are a segment sequence number distribution function that express the probability of $(M_1)_x$ and $(M_2)_x$ segments in copolymers, respectively.

On the basis of the reactivity ratios of two monomers, the sequence length distribution of the AA/p-CMS copolymers was obtained (Figure 6). For $f_2 = 4.77\%$, the probability of the *p*-CMS sequence of 1 unit in the copolymer chain is 93.8% which shows that the monomer unit of *p*-CMS is individually separated in the chain of AA. For $f_2 = 35.53\%$, the probability which forms both $(M_1)_1$ and $(M_2)_1$ segments accounts for more than 50%. The alternating tendency prevails and a large number of mono-sequences are formed. In the case of $f_2 = 78.62\%$, the probability of the AA sequence of 1 unit in the copolymer chain is 86.0%, the monomer unit of AA is mostly separated by the sequence of *p*-CMS.

3.4 Molecular Weights

The number-average $\overline{M}_n$ molecular weights and the polydispersity indices $\overline{M}_w/\overline{M}_n$ of the copolymers are given in Table 1. *p*-CMS (M_2) in the corresponding feed mixtures and the resulting copolymers are also given in the same table. The most interesting result is that the gradual increase in the mole fraction of M_2 in the copolymers is accompanied by an increase in molecular weights. A plot of $\overline{M}_n$ against the mole fraction of M_2 in the polymer is shown in Figure 7 and appears to be progressively curved as M_2 increases.

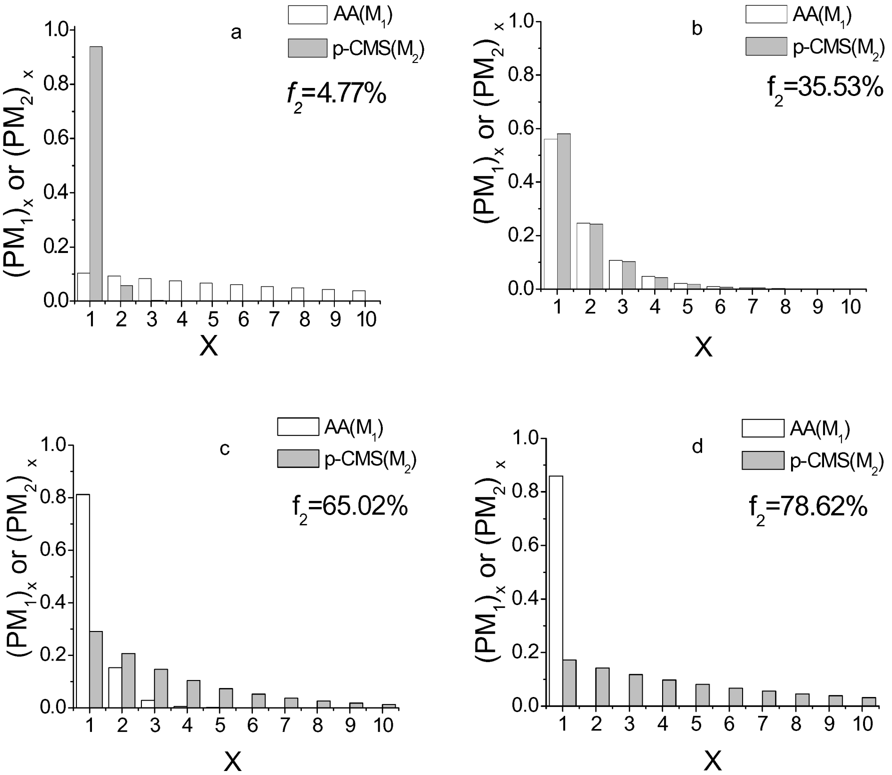

Fig. 6. Sequence length distribution of AA/*p*-CMS copolymers $f_2 = 4.77\%$. (a) 35.53%, (b), 65.02%, (c) and 78.62%, (d); *x* is the number of sequence length of AA and *p*-CMS unit; $(PM_1)_x$ and $(PM_2)_x$ is the probability of AA and *p*-CMS unit in AA/*p*-CMS copolymers, respectively.

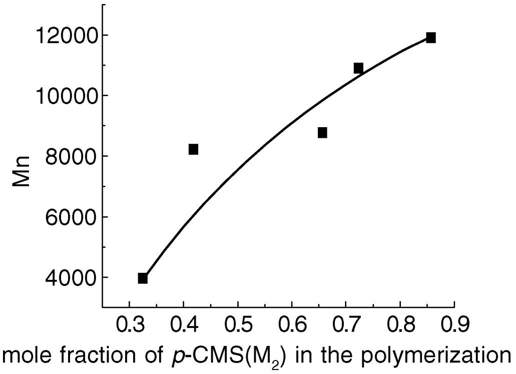

Fig. 7. Dependence of $\overline{M}_n$ on the mole fraction of p-CMS (M_2) in the polymerization.

It is known that in the homopolymerization of p-CMS, the polymeric radicals undergo termination mainly by recombination (20). Poly(acrylic acid) radicals are expected to terminate predominantly by disproportionation, as is the case for many (meth)acrylates (21). The value of $\overline{M}_n$ in copolymerization is also known to depend on the chain termination mechanisms in the same way as it does in the respective homopolymerizations. The $\overline{M}_n$ for various copolymers of M_1 and M_2 reported here (Table 1) clearly suggest that there is an increasing tendency for combination of the polymer radicals involved in copolymerization to occur as the mole fraction of p-CMS in the monomer feed increases.

4 Conclusions

Copolymer of acrylic acid with p-chloromethylstyrene was prepared by free radical polymerization. ^{1}H-NMR was used to determine the copolymer compositions by integration of the protons peaks. The reactivity ratios were determined by two methods and indicate that p-CMS in copolymer is always larger than p-CMS in feed and the curve is always above the diagonal. The sequence length distribution of the AA/p-CMS copolymers was obtained from the reactivity ratios of two monomers. The molecular weights were determined by gel permeation chromatography. There is an increasing tendency for combination of the polymer radicals involved in copolymerization to occur as the mole fraction of p-CMS in the monomer feed increases.

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