Water-soluble copolymers: 21. Copolymers of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride: Synthesis and characterization

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The copolymerization of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) has been studied in the range from 40 to 90% AM in the feed. The value of $r_1 r_2$ has been determined to be 0.19 for the AM–AMPDAC pair. The copolymer compositions have been determined from elemental analysis and ^{13}C n.m.r. The molecular weights of the copolymers were measured by low-angle laser light scattering, and ranged from $1.7-3.6 \times 10^6$. Furthermore, the molecular weights were found to be relatively unaffected by monomer feed ratios. The copolymer microstructures, including run numbers and sequence distributions, were calculated from the reactivity ratios. These model structures are utilized for assessment of structure/dilute solution property relationships reported in a subsequent paper in this series.

(Keywords: copolymerization; acrylamide copolymers; structure)

INTRODUCTION

The use of polyelectrolytes based on acrylamide is of increasing interest for a wide variety of industrial applications[1,2]. For example, cationic polymers have found uses in such areas as paper products, flocculation, film coatings and membranes[3,4].

The aim of our continuing research[5-8] is to prepare model water-soluble copolymers of acrylamide with large hydrodynamic dimensions in solution. The cationic comonomer, 2-acrylamido-2-methylpropanedimethyl-ammonium chloride (AMPDAC), was chosen in this study in order to assess the effects of a cationic moiety as the pendent group. Previously we reported the effects of analogous anionic monomers on aqueous solution behaviour[8]. We now report the synthesis and molecular characterization of charged copolymers of acrylamide (AM) with AMPDAC. The reactivity ratios were determined for the monomer pair, and the polymer microstructures calculated. Finally, molecular weight studies were performed using low-angle laser light scattering.

EXPERIMENTAL

Materials and monomer synthesis

2-Acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) was prepared by acidification of 2-acrylamido-2-methylpropanedimethylamine (AMPDA). Acryloyl chloride from Aldrich Chemical Co. and 1-dimethylamino-2-amino-2-methylpropane (DAMP) supplied by ANGUS Chemical Company were used without further purification. In a typical monomer synthesis, 0.5 mol DAMP was dissolved in 400 ml of tetrahydrofuran (THF) in a 1000 ml, 3-necked flask equipped with a mechanical stirrer. The reaction flask was then cooled to 5°C–10°C in an ice bath, followed by the dropwise addition of 0.5 mol acryloyl chloride with stirring. The temperature of the exothermic reaction was maintained at 10°C. A white precipitate formed which was filtered and determined to be AMPDAC. The crude yield of AMPDAC was found to be greater than 80%, and in some cases approached a quantitative level. For purification purposes, the crude AMPDAC was dissolved in deionized water and the pH adjusted to 12–13 by addition of NaOH. The aqueous solution was then extracted with methyl ethyl ketone and the uncharged 2-acrylamido-2-methylpropanedimethylamine (AMPDA) isolated by removal of the MEK. The crude AMPDA was recrystallized twice from a mixture of MEK and petroleum ether prior to use (m.p. 60°C–62°C). Anal. Calc. for $C_9H_{18}N_2O$: C, 63.53%; H, 10.59%; N, 16.47%. Found: C, 62.98%; H, 11.00%; N, 16.62%. I.r.: N–H, 3270 cm^{-1}; C=C–H, 2980 cm^{-1}; aliphatic C–H, 2880 cm^{-1}; C=O, 1660 cm^{-1} (s), 1550 cm^{-1} (m); tertiary amine, 1160 cm^{-1}.

Acrylamide (AM) from Aldrich Chemical Co. was recrystallized twice from reagent grade acetone and vacuum dried at room temperature prior to use (m.p. 83°C–84°C). Potassium persulphate from J. T. Baker Co. was recrystallized twice from deionized water prior to use.

Poly(2-acrylamido-2-methylpropanedimethylammonium chloride) and poly(acrylamide-co-2-acrylamido-2-methylpropanedimethylammonium chloride)

The homopolymer of 2-acrylamide-2-methylpropanedimethylammonium chloride (AMPDAC) and the copolymers of acrylamide (AM) with AMPDAC were prepared in aqueous solution at 30°C using 0.1 mol% potassium persulphate as the initiator. Each reaction was conducted in a 1000 ml, 3-necked flask equipped with a mechanical stirrer and nitrogen inlet

tube. A designated amount of 2-acrylamido-2-methylpropanedimethylamine (AMPDA) was dissolved in deionized water followed by the addition of an equimolar amount of HCl. A designated amount of acrylamide dissolved in deionized water was then added to the acidified AMPDA solution, and the pH of the entire mixture was adjusted to 5.0 ± 0.1. The pH adjustment was performed to insure that all of the amine monomer was in the hydrochloride salt form. Each reaction mixture was then deaerated with oxygen-free nitrogen for 20 min. The designated quantity of potassium persulphate initiator, dissolved in deionized water, was injected into the reaction vessel. The total monomer concentration in each reaction was held constant at 0.456 M. An aliquot was taken at low conversion to allow reactivity ratio studies to be performed, and the reaction terminated at 34–45% conversion due to increasing viscosity in the reaction vessel. The resulting reaction mixture was diluted with deionized water and the polymer precipitated by pouring the solution slowly into reagent grade acetone with gentle stirring. The polymers were further purified by reprecipitation into acetone followed by freeze-drying and then vacuum drying for 2 days. Conversions were determined gravimetrically. *Table 1* lists reaction parameters for the copolymerization of AM with AMPDAC and the homopolymerization of AMPDAC. I.r.: AMPDAC homopolymer, N–H (broad), 3300 cm^{-1}; C–H, 2940 cm^{-1}; C=O, 1690 cm^{-1} (s), 1550 cm^{-1} (m); ammonium chloride, 2700–2600 cm^{-1} (w), 1580 cm^{-1} (m). Typical copolymer: AMPDAC-40-2, N–H (broad), 3350 cm^{-1}; C–H, 2940 cm^{-1}; AM C=O, 1680 cm^{-1} (s), 1580 cm^{-1} (m); AMPDAC C=O, 1660 cm^{-1} (s), 1500 cm^{-1} (m); ammonium chloride, 2550 cm^{-1} (w).

Elemental analysis

Elemental analyses for carbon, hydrogen and nitrogen of the AM–AMPDAC copolymers were conducted by M–H–W Laboratories of Phoenix, AZ (*Table 1*). The copolymer compositions were calculated using C/N ratios due to the hygroscopic nature of the polymers. Elemental analyses were performed on low and high polymer conversion samples to assess the effects of compositional drift. The copolymer compositions at low

and high conversion were found to be in excellent agreement; thus, it can be concluded that the effects of compositional drift are minimal.

^{13}C Nuclear magnetic resonance spectroscopy

^{13}C n.m.r. spectra of the AM–AMPDAC copolymers and AMPDAC homopolymer were obtained at 22.5 MHz on a JEOL FX-90Q Spectrometer using 5–10 wt% aqueous (D$_2$O) polymer solutions in 10 mm tubes. The procedure for quantitatively determining copolymer compositions from ^{13}C n.m.r. has been discussed in detail elsewhere[9].

Low-angle laser light scattering

Low-angle laser light scattering measurements to determine molecular weights were performed with a Chromatix KMX-6 photometer. Refractive index increments were determined with a Chromatix KMX-16 laser differential refractometer. All measurements were conducted at 25°C in 0.514 M NaCl aqueous solutions at a pH of 6.5. Weight-average molecular weights and second virial coefficients derived from these data are shown in *Table 2* for the AM–AMPDAC copolymers and AMPDAC homopolymer.

RESULTS AND DISCUSSION

Reactivity ratio studies

The feed ratios of monomers and the resultant copolymer compositions as determined from elemental analyses (*Table 1*) were used to calculate reactivity ratios for the AM–AMPDAC pair. The Fineman–Ross method[10] and the Kelen–Tüdos method[11] were employed to determine the monomer reactivity ratios at low conversion. The Fineman–Ross method yielded reactivity ratios for acrylamide (M$_1$) and 2-acrylamido-2-methylpropanedimethylammonium chloride (M$_2$) of $r_1 = 0.90 \pm 0.02$ and $r_2 = 0.16 \pm 0.01$. Evaluation of the data according to the Kelen–Tüdos method produced values of 0.96 ± 0.02 and 0.20 ± 0.02 for r_1 and r_2, respectively. A comparison of the reactivity ratios obtained by the two low conversion methods is given in *Table 3*. The copolymer composition as a function of feed composition for the copolymerization of AM with

Table 1 Reaction parameters for the copolymerization of acrylamide (M$_1$) with 2-acrylamido-2-methylpropanedimethylammonium chloride (M$_2$) and homopolymerization of AMPDAC

Sample number	Feed ratio M$_1$:M$_2$	Reaction time (min)	Conversion (%)	Weight (% C)	Weight (% N)	M$_2$ in copolymer (mol%)[a]	M$_2$ in copolymer (mol%)[b]
AMPDAC-10-1	90:10	30	10.4	46.05	16.41	10.05 ± 0.17	9.55 ± 0.38
AMPDAC-10-2	90:10	180	40.9	46.42	16.57	9.82 ± 0.16	–
AMPDAC-25-1	75:25	30	6.1	46.89	15.63	20.00 ± 0.34	22.70 ± 2.26
AMPDAC-25-2	75:25	120	35.3	46.05	15.33	20.22 ± 0.35	–
AMPDAC-40-1	60:40	30	8.9	45.95	14.46	30.85 ± 0.56	32.69 ± 2.51
AMPDAC-40-2	60:40	105	39.9	45.65	14.29	31.98 ± 0.59	–
AMPDAC-60-1	40:60	30	12.8	46.96	13.83	47.16 ± 0.88	48.33 ± 2.02
AMPDAC-60-2	40:60	90	44.5	46.49	13.66	47.83 ± 0.91	–
AMPDAC	0:100	300	46.6	52.30[c]	13.56[c]	100	100
PAM-N	100:0	180	23.0	50.63[c]	19.69[c]	0	0

[a] From elemental analysis
[b] From ^{13}C n.m.r
[c] Theoretical value

Table 2 Molecular weight and second virial coefficient data for the copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) and homopolymer of AMPDAC

Sample number	Composition (mol%)[a]		$\bar{M}_w$ ($\times 10^{-6}$)	$\overline{DP}_w$ ($\times 10^{-4}$)	A_2 ($\times 10^3$) (ml mol g^{-2})
	AM	AMPDAC			
PAM-N	100	0	12.0	16.9	0.32
AMPDAC-10-2	90.2	9.8	1.7	2.0	1.2
AMPDAC-25-2	79.8	20.2	2.4	2.4	1.6
AMPDAC-40-2	68.0	32.0	2.2	1.9	1.4
AMPDAC-60-2	52.2	47.8	3.6	2.6	0.91
AMPDAC	0	100	1.2	0.58	1.0

[a] From elemental analysis

Table 3 Reactivity ratios for the copolymerization of acrylamide (M_1) with 2-acrylamido-2-methylpropanedimethylammonium chloride (M_2)
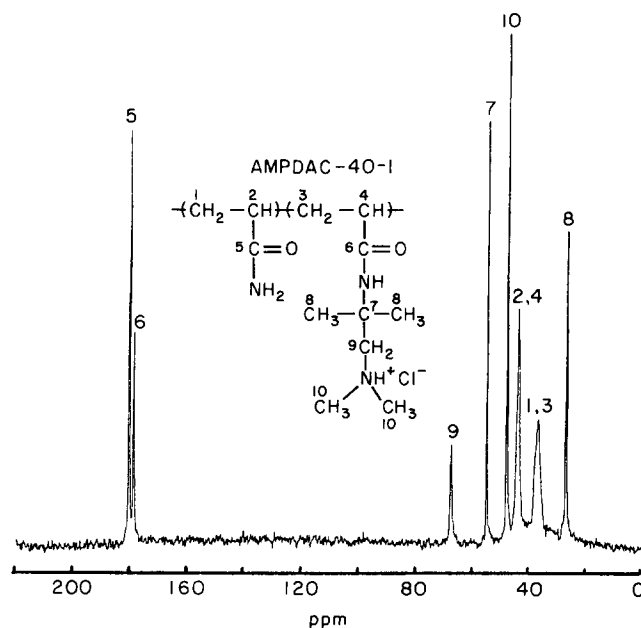
Method	r_1	r_2	$r_1 r_2$
Fineman–Ross	0.90 ± 0.02	0.16 ± 0.01	0.14
Kelen–Tüdos	0.96 ± 0.02	0.20 ± 0.02	0.19
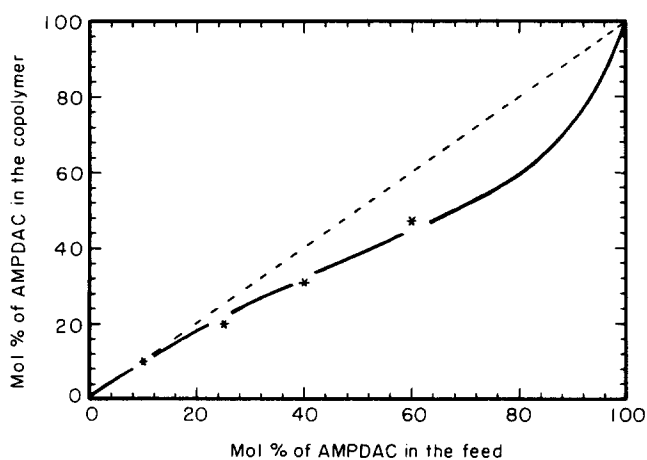
Figure 1 Copolymer composition as a function of feed composition for the copolymerization of AM with AMPDAC

Figure 2 Typical ^{13}C n.m.r. spectrum of a copolymer of AM with AMPDAC (AMPDAC-40-1)

AMPDAC is shown in *Figure 1*. The dashed line represents the ideally random copolymerization conditions. The solid line represents the copolymerization curve for the AM–AMPDAC system, and was generated from the copolymerization equation using the experimentally determined Kelen–Tüdos reactivity ratios. The experimental data points represented by (*) are in good agreement with those projected from the copolymerization equation. The AM–AMPDAC co-monomers (r_1 and r_2 both less than 1 and $r_1 r_2 = 0.19$) possess an alternating tendency in copolymerization. It can be seen from the copolymer composition plot (*Figure 1*) that the azeotropic copolymerization point occurs when there is approximately 5 mol% AMPDAC in the feed. At this point, the copolymer has the same composition as the monomer feed mixture, and a polymeric product of constant composition is formed throughout the copolymerization reaction.

Macromolecular structure

The structures of the AM–AMPDAC copolymers and AMPDAC homopolymer were verified by i.r., ^{13}C n.m.r. and elemental analysis. The procedure for quantitatively determining copolymer compositions using ^{13}C n.m.r. has been discussed in detail in a previous paper in this

series[9]. Briefly, the carbonyl peaks were used as a standard, and other AMPDAC peaks (peaks 7, 8, 9 in *Figure 2*) were integrated to give the mole percentage of AMPDAC in the copolymer. The copolymer compositions as determined by ^{13}C n.m.r. are shown in *Table 1*, and agree favourably with the compositions as determined from elemental analysis. A typical ^{13}C n.m.r. spectrum of a copolymer of AM with AMPDAC (AMPDAC-40-1) is shown in *Figure 2*. Typical copolymer peak assignments and spin-lattice relaxation times, T_1, are shown in *Table 4*.

Effect of feed composition

The effect of feed composition on molecular weight is shown in *Table 2* for the AM–AMPDAC polymers and, for comparative purposes, a homopolymer of acrylamide prepared under the same reaction conditions. The molecular weights (more particularly, the weight-average degrees of polymerization, $\overline{DP}_w$) were found to be relatively independent of monomer feed ratios. The weight-average molecular weights ranged from $1.7-3.6 \times 10^6$; however, the $\overline{DP}_w$ range was only $1.9-2.6 \times 10^4$. The second virial coefficients, A_2, of the AM–AMPDAC copolymers ranged from $0.9-1.6 \times 10^{-3}$ ml mole/g^2. The molecular weights of the copolymers were significantly lower than the molecular weight of the homopolyacrylamide sample (12.0×10^6). Lower degrees of polymerization are likely

due to increased cross-termination rates in copolymerization as compared to the very slow rate of termination observed for acrylamide[12,13]. An additional factor, although not studied in this work, could be increased chain transfer to the AMPDAC monomer.

Copolymer microstructure

The solution properties which the AM–AMPDAC copolymers exhibit are expected to be a function of the polymer microstructure. The calculation of the statistical distribution of monomer sequences, M_1-M_1, M_2-M_2 and M_1-M_2 may be performed utilizing the method of Igarashi[14]. Mean sequence lengths, μ_1 and μ_2, can be calculated utilizing equations (1) and (2)[15]:

$$\mu_1 = 1 + r_1[M_1]/[M_2] \tag{1}$$

$$\mu_2 = 1 + r_2[M_2]/[M_1] \tag{2}$$

where r_1 and r_2 are the reactivity ratios for AM and AMPDAC, respectively. *Table 5* lists the structural data for the copolymers of AM with AMPDAC.

The calculated mole per cent of AM–AMPDAC linkages in each copolymer was relatively high indicating an alternating tendency. The mean sequence length of acrylamide, μ_{AM}, varied from 9.6 at a 90.0/10.0 mole ratio of AM/AMPDAC in the copolymer to 1.6 at a 52.8/47.2 mole ratio. For those copolymer compositions, values of μ_{AMPDAC} were 1.0 and 1.3, respectively. The very low mean sequence length values of AMPDAC are an indication of the strong alternating tendency toward AM.

Table 6 lists additional structural data for the copolymers of AM with AMPDAC involving higher-order sequence distributions, i.e. triads and pentads, calculated using the method of Harwood and Ritchey[16]. The relatively high run numbers calculated for the copolymer series indicate that few long blocks of AM or AMPDAC units were produced due to their alternating tendency. P_{ABA} and P_{AABAA} are the probabilities of an AMPDAC-centred triad and pentad, respectively. N_{ABA} and N_{AABAA} are the expected numbers of AMPDAC-centred triads and pentads per 100 monomer units. The maximum frequency of AMPDAC-centred triads was found to occur at a copolymer composition of 40 mol % AMPDAC, while the maximum frequency of AMPDAC-centred pentads occurred at a copolymer composition containing approximately 21 mol % AMPDAC. The maximum triad and pentad values were obtained by calculating a broad spectrum of AM–AMPDAC copolymer compositions from the copolymerization equation using the experimentally derived Kelen–Tüdos reactivity ratios.

CONCLUSIONS

Copolymers of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride have been prepared in aqueous solution using potassium persulphate as the initiator. Elemental analysis and [13]C n.m.r. were used to determine the copolymer compositions; good agreement was obtained between the two methods. The reactivity ratios, $r_1 r_2 = 0.19$, have been determined from two low conversion methods, and indicate the tendency of these monomers toward alternation. [13]C n.m.r. peak assignments have been made, and spin-lattice relaxation time studies performed. The copolymer microstructures have been statistically predicted utilizing the methods of Igarashi[14] and Harwood and Ritchey[16]. Weight-average molecular weights in the range of $1.7-3.6 \times 10^6$ have been measured for the AM–AMPDAC copolymers. The weight-average degrees of polymerization, $\overline{DP}_w$, were only slightly affected by monomer feed ratios, and ranged from 1.9–2.6 × 10⁴. The knowledge of molecular weight, copolymer composition, and microstructure gained from the studies of these AM–AMPDAC copolymers is used for the development of structure/dilute solution property relationships in a subsequent paper of this series.

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Table 4 [13]C n.m.r. peak assignments and spin-lattice relaxation times for copolymers of acrylamide with 2-acrylamido-2-methylpropane-dimethylammonium chloride

Peak number	Chemical shift (ppm)	Spin-lattice relaxation times, T_1 (s)
1,3	37.9	0.04
2,4	45.2	0.07
5	182.2	1.2
6	180.6	1.0
7	56.0	1.0
8	27.9	0.15
9	68.8	0.06
10	48.9	0.4

Table 6 Calculated microstructural data for the AM–AMPDAC copolymers

Sample number	Run number	P_{ABA}	P_{AABAA}	N_{ABA}	N_{AABAA}
AMPDAC-10-1	18.8	0.96	0.77	9.2	7.4
AMPDAC-25-1	40.2	0.88	0.49	18.9	10.4
AMPDAC-40-1	56.0	0.78	0.27	24.7	8.6
AMPDAC-60-1	68.0	0.59	0.09	26.2	4.0

Table 5 Structural data for the copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC)

Sample number	Composition (mol %)[a]		'Blockiness' (mol %)[b]		Alternation (mol %)[b]	Mean sequence length	
	AM	AMPDAC	AM–AM	AMPDAC–AMPDAC	AM–AMPDAC	μ_{AM}	μ_{AMPDAC}
AMPDAC-10-1	89.95	10.05	80.1	0.2	19.7	9.6	1.0
AMPDAC-25-1	80.00	20.00	61.1	1.1	37.8	3.9	1.1
AMPDAC-40-1	69.15	30.85	41.8	3.5	54.7	2.4	1.1
AMPDAC-60-1	52.84	47.16	18.3	12.6	69.1	1.6	1.3

[a] From elemental analysis
[b] Statistically calculated using reactivity ratios

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