Copolymerization of Acrylamide with Allyl-Acrylate Quaternary Ammonium Monomers

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Summary: A series of copolymers of N,N-morpholine-N-2-(ethoxycarbonyl)allyl allyl ammonium chloride, N,N-morpholine-N-2-(ethoxycarbonyl)allyl allyl ammonium bromide, N,N-piperidyl-N-2-(ethoxycarbonyl)allyl allyl ammonium chloride, N,N-morpholine-N-2-(t-butoxycarbonyl)allyl allyl ammonium bromide and diallyldimethylammonium chloride (DADMAC) with acrylamide (AAm) were prepared in water at 50-56 ^{0}C using 2,2'-azo-bis(2-amidinopropane)dihydrochloride (V-50). The ethyl ester monomers showed high cyclization efficiencies during copolymerizations. The tert-butyl ester derivatives showed high cross-linking tendencies. The molar fractions of allyl-acrylate monomers in the AAm: allyl-acrylate copolymers were higher than the one of DADMAC in the AAm:DADMAC copolymers. The intrinsic viscosities of the copolymers measured in 0.09 M NaCl ranged from 2.5 to 7.5 dL/g.

Introduction

Cationic water soluble polyelectrolytes are polymers of great significance due to their manifold applications. Cationic homopolymers and copolymers with acrylamide are used as retention aids in paper making, as flocculants in water treatment, as stabilizers for emulsion polymerization, in cosmetics, and in pharmaceuticals.[1-3] The copolymers of DADMAC with AAm have been the most common polymers for flocculation.[3] The synthesis of DADMAC and AAm is difficult by a large difference of the reactivity ratios which leads to conversion dependence of the copolymer composition.[4-11] Therefore, feeded polymerization with the addition of the more reactive monomer (AAm) was used for the synthesis of copolymers with various charge densities.[4]

In our previous work, a series of allyl-acrylate quaternary ammonium salt derivatives were synthesized and copolymerized with DADMAC.[12] Relative reactivities of the allyl-acrylate monomers in photopolymerizations were compared with the relative reactivity of DADMAC. Allyl-acrylate monomers were much more reactive than DADMAC. Therefore, copolymerization of these monomers with acrylamide is expected to give polymers with more uniform charge distributions than copolymers of DADMAC with acrylamide. In this article, we report the synthesis and solution properties of cyclocopolymers of allyl-acrylate quaternary ammonium salts and AAm.

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Experimental

2,2'-azo-bis(2-amidinopropane)dihydrochloride (V-50) is a product of Polysciences. DADMAC was obtained from Aldrich as a 65 wt% aqueous solution. Monomer and polymer characterization was carried out by ^{1}H and ^{13}C NMR spectroscopy (Varian 200), Fourier transform infrared (FTIR) spectroscopy (Mattson 5000), and a thermogravimetric analysis apparatus from TA Instruments. Intrinsic viscosities were measured in 0.09 M NaCl with a Cannon-Ubbelohde viscometer at 36 +/- 0.2 ^{0}C. Copolymer compositions were obtained by colloidal titration using 0.000115 M potassium poly(vinyl sulfate) (PVSK) solution as the titrant and toluidine blue as indicator.[13] The PVSK solution was standardized with polyDADMAC solution. Allyl-acrylate monomers were prepared according to previously reported procedures.[12] Conditions for obtaining the representative monomer N,N-piperidyl-N-2-(ethoxycarbonyl)allyl allyl ammonium chloride are given next.

Monomer synthesis: To a mixture of ethyl α-chloromethylacrylate (2.97 g, 0.02 m) in diethylether (60 mL) in an ice bath, N,N-piperidyl-N-allyl amine (2.5 g, 0.02 m) was added, and the mixture was stirred at 0 ^{0}C for 1 h. The precipitated product was filtered and further purified by dissolution in methanol and precipitation into diethylether to give a white solid, yield 70%, mp: 78-79 ^{0}C.

General Solution Polymerization Procedure: The copolymerizations were carried out in 25-mL septum-sealed glass tubes. For the synthesis of copolymer **2a**-AAm (10:90 mol %), **2a** (0.32 g, 0.001 m) and AAm (0.639 g, 0.009 m) were dissolved in 5 mL of water. V-50 (0.00135 g) was added and the tubes were subjected to four freeze-evacuate-thaw procedures. The tubes were than placed in an oil bath at 52-54 ^{0}C. The copolymer was precipitated into ethanol and dried under vacuum.

Results

The monomer synthesis involved the preparation of N,N-dialkyl-N-allyl amine followed by its reaction with ethyl α-chloromethyl acrylate, ethyl α-bromomethyl acrylate and tert-butyl α-bromomethyl acrylate.[12] The ^{13}C-NMR spectrum of the one of the monomers is shown in Figure 1. The copolymers of allyl-acrylate quaternary ammonium monomers and DADMAC with acrylamide were synthesized by free radical polymerization in water at 50-56 ^{0}C using V-50 as the initiator (Figure 2). The total

monomer and initiator concentrations were held constant at 2 M and $1x10^{-3}$ M (Table 1). For comparison AAm was homopolymerized under the same conditions. The copolymers, purified by precipitation in ethanol or acetone, were soluble in methanol and water but insoluble in tetrahydrofuran, acetone and ethanol. The ethyl ester monomers showed high cyclization efficiencies. ^{1}H-NMR spectra of the copolymers showed no residual double bonds which appear between 5.5 and 6.5 ppm in the monomer spectra. ^{1}H-NMR spectrum of one of the copolymers (AAm:**3**) is shown in Figure 3. The methylene protons of the piperidine ring, methyl protons of the ester, backbone protons of acrylamide and salt monomers appear between 1.0 and 3.0 ppm. Methylene protons attached to nitrogen and oxygen appear between 3.0 and 5.0 ppm.

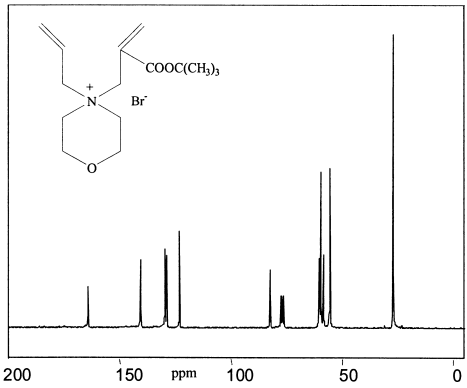

Figure 1. ^{13}C-NMR spectrum of monomer **4**.

The FTIR spectrum of one of the copolymers (Figure 4) exhibited two intense peaks at 1716 and 1668 cm^{-1} due to ester and amide carbonyl groups. The copolymerization of the tert-butyl ester monomers gave crosslinked polymers. In our previous work, it was found that the tert-butyl ester monomers were more reactive than the ethyl ester monomers. The high reactivity of the tert-butyl monomers probably leaves uncyclized units in the copolymers which lead to the formation of crosslinks. Water-soluble copolymers could not be obtained by decreasing the molar fraction of the tert-butyl ester monomer.

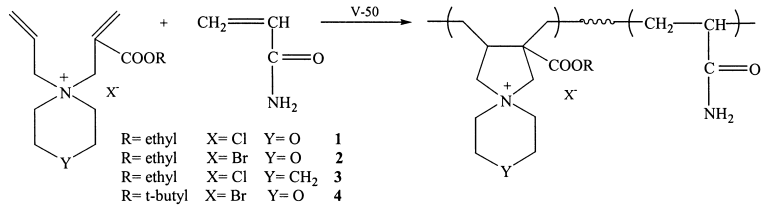

Figure 2. General synthetic scheme for the copolymers.

Table 1. Polymer characterization results.

Sample	Feed ratio	Temp. (^{0}C)	Reaction time (min)	Conversion (%)	Polymer composition	Intrinsic Visc.
AAm	100	52-54	90	90	-	8.9
AAm:DADMAC	95:5	52-54	90	75	99.98:0.02	7.4
AAm:DADMAC	90:10	52-54	90	57	99.98:0.02	-
AAm:**1**	90:10	52-56	95	-	96.4:3.6	-
AAm:**1**	70:30	52-56	95	14	69.2:30.8	7.1
AAm:**2**	90:10	52-54	90	37	92.4:7.6	7.5
AAm:**2**	70:30	52-54	90	15	-	3.2
AAm:**2**	50:50	53-55	226	29	66:34	-
AAm:**3**	90:10	52-56	80	17	86:14	2.5
AAm:**3**	70:30	52-56	80	50	72:28	3.0
AAm:**4**	98:2	52-56	95	Crosslinked	-	-
AAm:**4**	90:10	52-56	120	Crosslinked	-	-
AAm:**4**	70:30	52-54	90	Crosslinked	-	-

The content of DADMAC in the copolymers was much lower than the amount of DADMAC in the feed (Table 1). The molar fractions of DADMAC were calculated to be 0.02 % for the 5 and 10 % feed compositions of DADMAC. However, the feed ratios of the allyl-acrylate monomers and the copolymer compositions were not very different, a characteristic of random copolymers. These results also confirmed that the reactivity of DADMAC was much lower than the reactivities of the allyl-acrylate monomers. Copolymerization of AAm with the allyl-acrylate monomers give polymers with a more uniform charge distribution than the copolymers of DADMAC with AAm. The solutions of the copolymers in water showed a typical polyelectrolyte behavior, a strong increase in reduced viscosity at decreasing polymer concentrations. Intrinsic viscosities of the polymers measured in 0.09 M NaCl ranged from 2.5 to 8.9 dL/g and decreased by increasing the allyl-acrylate monomer contents. Chain transfer of the growing polymer radical to the allyl-acrylate monomer limited the molecular weights of

the copolymers. The high viscosity values were obtained for copolymers of DADMAC with AAm, consistent with the low incorporation of DADMAC.

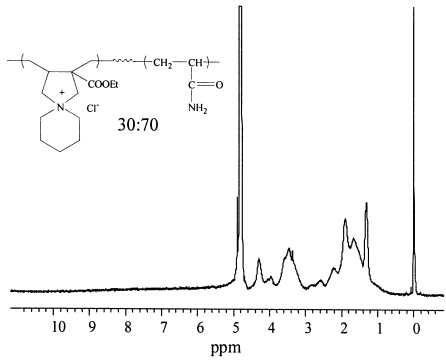

Figure 3. ^{1}H-NMR spectrum of AAm:**3** (70:30) copolymer.

Thermogravimetric analysis of the copolymers showed weight losses due to evaporation of water at about 100 ^{0}C, hydrolysis of ester groups starting at about 200 ^{0}C (Figure 5). The polyAAm and DADMAC copolymers were more stable than allyl-acrylate copolymers.

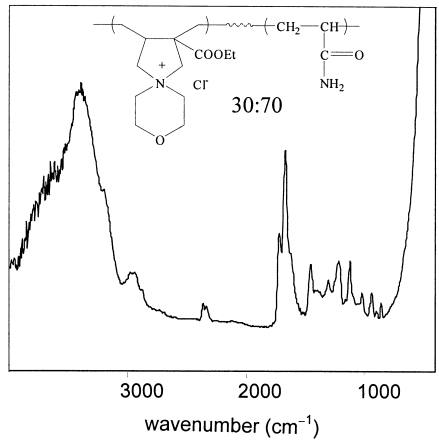

Figure 4. FT-IR spectrum of one of the copolymers.

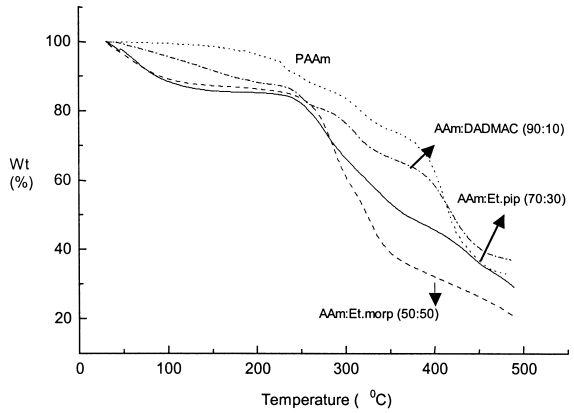

Figure 5. Thermogravimetric analysis curves of the copolymers.

Conclusions

Copolymerization of allyl-acrylate salts with acrylamide leads to polymers with higher charge densities than copolymers of DADMAC with acrylamide. By copolymerizing different allyl-acrylate monomers with acrylamide it is possible to produce water-soluble, high-molecular weight polymer structures with desirable aqueous solution properties.

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