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Polycation to polyanion by rapid alkaline hydrolysis

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Summary

Homopolymers and copolymers of [2-(acryloyloxy)ethyl]trialkylammonium chloride were synthesized, characterized, and hydrolysis of the ester functional group was studied as a function of pH. Hydrolysis was found to be rapid under basic conditions, converting the cationic [2-(acryloyloxy)ethyl]trialkylammonium chloride units into anionic acrylate salt monomer residue and choline chloride or its alkyl derivative, thereby transforming the polycation into a polyanion. The ester group under neutral or acidic pH is remarkably stable, although hydrolysis is catalyzed by carboxylate ions. Blends of these polymers with other polymers containing stable cationic groups remain in aqueous solution upon converting the functional groups from cationic to anionic by alkaline hydrolysis.

Introduction

Polymers and copolymers containing acryloyloxyethylammonium salts find a wide range of industrial use. Applications include cholesterol-lowering ion-exchange resins [1-4], flocculants for water treatment [5-7], breaking oil/water emulsions [8], binders for coated paper [9-11], priming and impregnating agents [12], antistatic coatings [13-15], etc. Certain synthetic methods, polymerization kinetics, solution properties of these polymers have been described [6, 16-22]. The hydrolytic stability of similar, cationic methacrylate copolymers improved in the presence of an acid buffer [23]. There is, however, little reference to the unique hydrolytic behavior of these monomer units, which is intriguing, and it could lead to new applications for these polymers.

Acryloyloxyethylammonium salt monomer units are likely to undergo facile hydrolysis under basic conditions producing an anionic acrylate salt monomer residue, due to the strongly electron withdrawing trialkylammonium functional group. This transformation could offer a convenient route towards introducing poly(acrylic acid) or its copolymers into polymer blends or film structures of cationic polymers without premature precipitation. Addition of poly(acrylic acid) to cationic polymers induces precipitation of the polymers. Even coating a film of poly(acrylic acid) or its copolymer over a cationic polymer produces a hazy film due to interfacial precipitation. Mixtures of cationic polymers on the other hand, are more likely to be stable, and adjacent layers of cationic polymers produce clear films. Blends of a cationic polymer with poly(acrylic acid) could be obtained by hydrolysis of these cationic side groups “in situ” after thorough mixing or in dry film form. Likewise, glossy two-layer cationic/anionic polymer film structure could be constructed by hydrolysis of the cationic functional groups after the films are formed.

Experimental

Materials and Synthesis

The monomers, hydroxypropyl methacrylate (HPMA), 2-(dimethylamino)ethyl acrylate (DMAEA), [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MAP), [2-(acryloyloxy)ethyl]trimethyl-ammonium methyl sulfate (ATAMS) from Aldrich, [2-(acryloyloxy)ethyl]trimethylammonium chloride (ATAC, trade name Adamquat MC 80) from Elf Atochem, N-acryloyltris(hydroxymethyl)aminomethane (Tris) from Acros, acrylic acid (AA) from Rohm and Haas, and the initiator, 2,2'-azobis(2-methylpropionamidine) (V-50) from Wako Chemicals, were used as received.

[2-(acryloyloxy)ethyl]benzyldimethylammonium chloride (ABC) was synthesized by dissolving equimolar amounts of 2-(dimethylamino)ethyl acrylate, 143 g (1 mole) and benzyl chloride, 126.5 g (1 mole) in 210 g of acetone. The mixture was agitated for 2 hours at room temperature, then allowed to crystallize. The crystals were broken up after 3 days, filtered and washed with a small amount of acetone and dried in vacuum to yield 254.6g (94.4% yield) of ABC. ^{1}H NMR: 3.1 ppm (6H: $C\underline{H}_3$-N-); 3.8 ppm (2H: $C\underline{H}_2$-O-); 4.6 ppm (2H: $C\underline{H}_2$-N-); 4.75 ppm (2H: Ph-$C\underline{H}_2$-N-); 6.0 ppm (1H: $C\underline{H}$=*(trans))*; 6.2 ppm (1H: =$C\underline{H}$-CO); 6.4 ppm (1H: $C\underline{H}$=*(cis))*; 7.5 ppm (3H: m,p-phenyl), 7.6 ppm (2H: o-phenyl).

Benzyl-2(hydroxy)ethyldimethylammonium chloride (BHEAC) was synthesized following the same procedure described above for ABC, with 92% yield. ^{1}H NMR: 3.0 ppm (6H: $C\underline{H}_3$-N-); 3.4 ppm (2H: $C\underline{H}_2$-O-); 3.9 ppm (2H: $C\underline{H}_2$-N-); 4.65 ppm (2H: Ph-$C\underline{H}_2$-N-); 5.7 ppm (1$\underline{H}$: -O$\underline{H}$); 7.5 ppm (3H: m,p-phenyl), 7.6 ppm (2H: o-phenyl)

Polymerization

Polymerization and copolymerization reactions were carried out in a round bottom flask with agitation (180 rpm) under nitrogen. The monomer (or mixture) was fed continuously to the aqueous solution of the initiator at the polymerization temperature (selected between 55 and 80 °C) within 0.5 to 4 hours. The polymerization mixture was heated for an additional 0.5-1 hour to complete the reaction. The residual monomer content, determined by HPLC, was below 500 ppm.

Characterization

A Hewlett Packard 1090 HPLC instrument equipped with a diode array detector and a YMC AQ ODS (150x46mm) column was used to determine residual monomer and hydrolyzed quaternary ammonium salt content (BHEAC). During a 10 minute gradient elution method the composition of the eluant, a 60/40 mixture of an aqueous 75 mmole/L triethylammoniumphophate buffer (pH=3.5) and methanol, was continuously changed to 100% methanol.

Choline chloride content was determined using Electrospray+ Mass Spectroscopy. An isocratic method with milliQ water/acetonitrile 80/20 mobile phase and 5 min collection time was used to collect mass range of 20 to 1000 daltons.

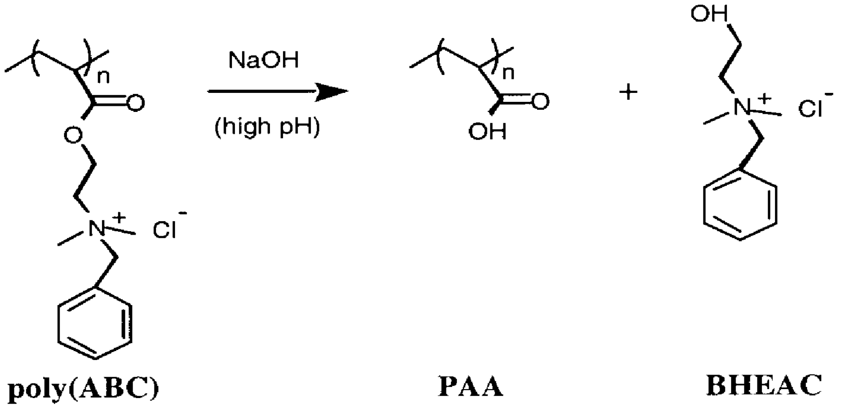
Molecular weights and molecular weight distributions were determined by aqueous GPC methods using a Waters 150C instrument equipped with PL AqOH 40 & 60

columns. An aqueous solution of 0.3M sodium nitrate containing 1.5% acetic acid was the eluant for the cationic homopolymers. Copolymers containing acrylic acid tended to adhere to the column. These were first hydrolyzed in 1N sodium hydroxide solution to convert them to poly(acrylic acid) for molecular weight measurement. The hydrolysis product, choline chloride, was removed by ion exchange chromatography (Dowex 50W-X4 cation exchange resin) prior to GPC measurement. An aqueous solution of 0.3M sodium nitrate was the eluant for the poly(acrylic acid) samples.
NMR spectra were recorded in D_2O solutions using a Varian 400 instrument.
Acid content of the homopolymers and copolymers was determined by titration with 0.1 N NaOH solution. The pH was followed by a Beckman Φ43 pH meter equipped with an Orion glass combination pH electrode.

Results and Discussion

Hydrolysis studies

Rapid hydrolysis of the ester functional group in poly(ABC), shown in Scheme 1 below, was followed by determining the hydrolysis product by HPLC.



Scheme 1. Hydrolysis of the ester functional group in poly(ABC)

According to the analysis of benzyl-2-(hydroxy)ethyldimethylammonium chloride (BHEAC), the ester groups underwent complete hydrolysis at pH 13.5 in about 10 minutes, shown in Figure 1.

In another series of experiments, the pH of the polymer solutions was adjusted by the addition of sodium hydroxide, and the decreasing pH of the solution was followed as a function of time. These experiments indicated similar, rapid rates of hydrolysis for polymers with functional groups containing either three methyl, or two methyl and one benzyl group on the nitrogen. (ATAC and ATAMS homopolymers, copolymers of AA with ATAC or ABC, and copolymer of ABC with HPMA were tested.) Due to the strong electron withdrawing group in the 2 position relative to the oxygen in the alcoholate (Hammet constant of trimethylammonium group is +0.88), hydroxyl ions readily replace the alcohol and hydrolyze the ester.

It was also of interest to determine the hydrolytic stability of the ester group at acidic pH. The acid content of polymers and copolymers of ATAC and ABC was determined by titration with 0.1N NaOH periodically over time. The hydrolysis of the

ATAC monomer unit produces choline chloride, also confirmed by mass spectroscopy. It is not detected, however, by the HPLC equipped with DAD, therefore, hydrolysis was routinely followed by titration.

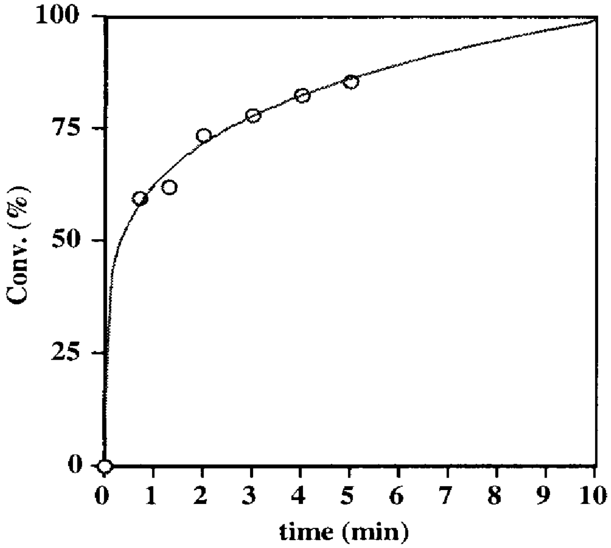


Figure 1. Hydrolysis of poly(ABC) in 1N NaOH solution, at pH=13.5

The ATAC monomer, the homopolymers and most copolymers showed remarkable hydrolytic stability in weakly acidic solutions. The acid content of the ABC and ATAC homopolymers was very low (0.3% and 1.5%, respectively) and remained practically constant (increasing by 0.5 % or less in about one year), summarized in Table 1. The acid content of the poly(ATAC) was initially higher, since the monomer contained a small amount of AA impurity, typically between 0.2 to 1 wt% (routinely determined by titration, since the lowest levels of AA content were close to the detection limit of the HPLC).

Table 1. Hydrolytic Stability of poly(ABC) and poly(ATAC) by Chromatography and Titration

Polymer	Age (days)	pH	BHEAC (%) (by HPLC)	AA (wt%) (by titration)
poly(ABC)	16	3.5	0.336	
	75	3.4	0.330	
	86	3.3	0.378	
	222	3.1		0.36
poly(ATAC)	39	2.9		1.34
	114	2.8		1.30
	156	2.8		1.35
	192	2.8		1.47
	241	2.7		1.64
	253	2.7		1.61
	368	2.7		1.85

The rate of hydrolysis of ABC copolymers containing no carboxylic acid, followed by titration, was very low as well, the analytical results are summarized in Table 2.

Table 2. Hydrolytic Stability of ABC Copolymers by Titration

Copolymer (comp. by wt)	pH	AA content (wt%)	AA content (mmole/g)	Age at titration (days)
ABC/HPMA 8/2	3.49	0.27	0.039	142
ABC/HPMA/MAP 8/1/1	3.62	0.18	0.025	40
	3.61	0.18	0.025	139
ABC/HPMA 9/1	3.41	0.13	0.018	19
	3.33	0.20	0.028	118
ABC/Tris 9/1	3.84	0.15	0.021	118

Copolymers of ABC with acrylic acid (29 to 48 mole % acrylic acid), however, have shown somewhat faster hydrolysis rate during storage at room temperature. Rather than the inherently lower pH of these polymer solutions, hydrolysis was most likely accelerated by the presence of carboxylic acid groups. Slow hydrolysis was followed both in the original polymer solutions without pH adjustment, and in aliquots taken immediately after the synthesis and adjusted to pH=4.0 by addition of sodium hydroxide solution. (Close to the pH of the ABC polymers containing no acrylic acid). The extent of hydrolysis in these pairs of polymer solutions, listed in Table 3, was found to be practically independent from pH in the range of pH=1.8-4.0.

Table 3. Hydrolytic Stability of ABC/AA Copolymers by Chromatography

Polymer Comp.	Age (days)	pH (not adj.)	BHEAC (wt %)	pH (adj. to 4.0)	BHEAC (wt %)
ABC/AA 9/1*	1	2.1	0.363	4.0	0.363
	2	2.1	0.378	4.0	0.400
	5	2.1	0.377	4.1	0.400
	11	2.1	0.422	4.1	0.302
	54	2.1	0.685	4.0	0.610
ABC/AA 8/2 **	1	1.8	0.318	4.0	0.318
	2	1.8	0.335	4.0	0.373
	5	1.8	0.355	4.0	0.368
	11	1.8	0.380	4.0	0.398
	54	1.8	0.667	4.0	0.711

*70.6/29.4(mole)
**51.7/48.3 (mole)

Refrigerated storage of the acrylic acid copolymers, however, successfully minimized hydrolysis to acceptable, low levels, similar to that experienced during storage of the homopolymers at room temperature. Copolymers of ATAC with AA stored with refrigeration displayed only minor change in composition, that is, negligible extent of hydrolysis, shown in Figure 2. Polymers containing no carboxylic acid functional group, such as the ATAC/Tris copolymer, also included in Figure 2, did not change in refrigerated storage.

Synthetic method

The homopolymers and copolymers were synthesized by semicontinuous aqueous solution polymerization, initiated by V50. Molecular weight is readily controlled by polymerization temperature and monomer feed rate; initiator concentration, as expected, has a much smaller effect. Typical molecular weight data with the corresponding reaction conditions are summarized in Table 4.

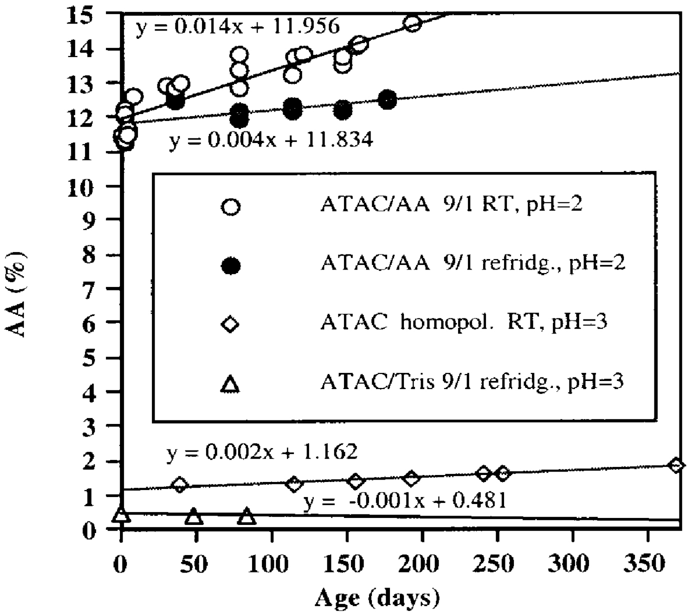
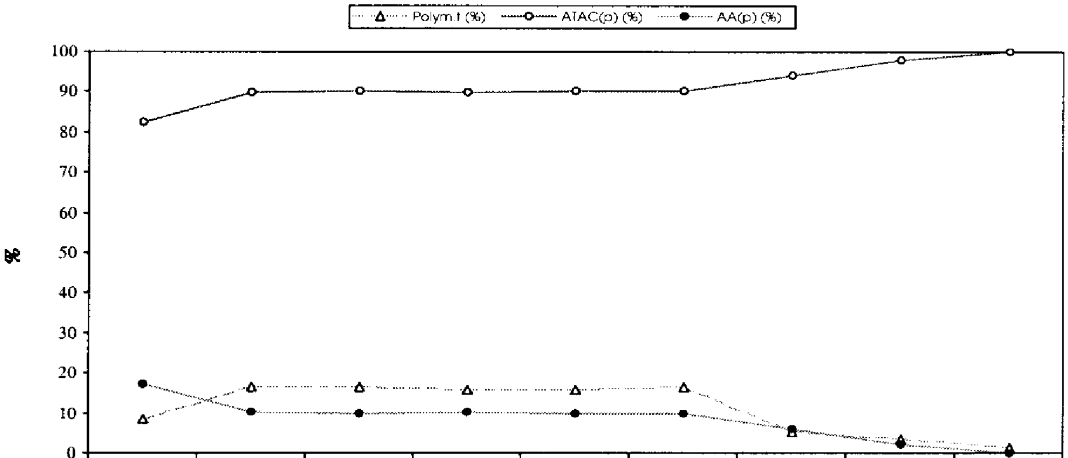


Figure 2. Hydrolytic Stability of ATAC Homopolymer and Copolymers

Table 4. Molecular Weight of Polymers by Semicontinuous Polymerization

Polymer	Polymn. temp. (°C)	Polymer cont.(wt%)	Mon. feed time (min)	Mn	Mw	PDI
polyABC	80	20.6	31	3,140	5,47	1.74
polyATAC	80	20.83	30	2,200	4,34	1.96
"	55	19.94	63	45,500	123,30	2.71
"	58	30.35	91	14,200	49,70	3.50
"	55	30.20	153	13,000	43,30	3.33
ATAC/AA 9/1	80	20.63	31	22,300	64,90	2.90

The semicontinuous method produces copolymers of quite uniform composition even at the fastest feed rates (20g/min, feed time: 30 min), illustrated by Figure 3. Copolymer composition averaged over periods of 5 minute reaction time is shown [ATAC (p) (%) and AA (p) (%), respectively], as well as the amount of polymer produced during each 5 minute time period [polym. t (%)]. These data are all calculated from the amounts of monomers added and the actual, instantaneous concentration of monomers. Monomer concentrations were determined by HPLC at 5 minute intervals up to 35 minutes, then at 45 minutes and at the end of the polymerization at 120 minutes (individual data not shown). Within experimental variation they were found to be constant from the time of the first sampling at 5 minutes till the end of the monomer feed at 30 minutes (average value of 2.1% for ATAC and 0.06% for AA). The composition of more than 81% of the copolymer, produced between 5 minutes and 30 minutes, was practically the same as the monomer feed composition. Copolymer produced during the first 5 minutes of the reaction (8.5%), and after the end of monomer feed, from 30 minutes to 120 minutes (10%) was slightly higher in AA or ATAC content, respectively.



	0 to 5	5 to 10	10 to 15	15 to 20	20 to 25	25 to 30	30 to 35	35 to 45	45 to 120
Polym.t (%)	8.48	16.57	16.49	15.75	15.88	16.63	5.28	3.44	1.26
ATAC(p) (%	82.5	89.7	90.1	89.9	90.1	90.3	93.9	98.0	100.0
AA(p) (%)	17.4	10.3	9.9	10.1	9.9	9.7	6.1	2	0

time period (min.)

Figure 3. Instantaneous ATAC/AA Copolymer Composition in Semicontinuous Polymerization

Blends and Films with Non-Hydrolyzing Cationic Polymers

Addition of poly(acrylic acid) solution to an aqueous solution of the cationic polymer poly[triethyl(vinylbenzyl)ammonium chloride] (PTEQ) causes the polymers to precipitate. When the same polymer is blended with the homopolymer of ATAC, which is then hydrolyzed “in situ” by the addition of base, no precipitation occurs, even as PTEQ is not hydrolyzed by the base and remains cationic.

ATAC homopolymers and ATAC/AA copolymers can be coated in multilayer film systems adjacent to a non-hydrolyzing cationic polymer layer. Upon processing the film with a highly alkaline solution, these polymers or copolymers are hydrolyzed to poly(acrylic acid), the stable cationic polymers remain cationic. Application of these polymers in the Polaroid instant film produces glossy images, free of haze, while similar film structures coated with poly(acrylic acid) are somewhat hazy [24].

Conclusions

Cationic polymers containing trialkylammonium chloride functional groups were readily synthesized by free radical homopolymerization and copolymerization of ABC and ATAC with other acrylate and methacrylate monomers, using a semicontinuous

aqueous method. The ester groups in these monomer units rapidly hydrolyze under basic pH, while at acidic pH the ester groups show remarkable hydrolytic stability.
"In situ" hydrolysis of these polymers by the addition of base in blends or multilayer film structures with stable cationic polymers may lead to new practical applications.

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