

Synthesis and characterization of quaternized poly-alkyl α -chloroacetoxymethacrylates

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Summary

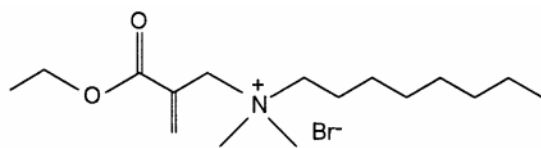
The homopolymers of ethyl α -chloroacetoxymethacrylate (ECAM) and t-butyl α -chloroacetoxymethacrylate (TBCAM) were quaternized homogeneously with trimethylamine (TMA) and N,N-dimethyldodecylamine in N,N-dimethylformamide (DMF). The $^1\text{H-NMR}$ measurements were used for the determination of the degree of quaternization (DQ) values. The DQ value of poly-ECAM quaternized with TMA at room temperature after 1 h was found to be 84 %, while the DQ value for poly-ECAM quaternized with N,N-dimethyldodecylamine was 37 %. Reactivity of poly-TBCAM was lower than that of poly-ECAM. The lower DQ value of TMA quaternized poly-TBCAM (19 %) is caused by steric hindrance in the vicinity of $-\text{CH}_2\text{Cl}$ group due to bulky t-butyl group. Increasing reaction time, polymer concentration and temperature above a certain value for each polymer, resulted in crosslinked polymers. Solubility of the quaternized polymers is controlled by the substituents. Thermogravimetric analysis showed distinct differences in thermal stabilities which is controlled by the quaternary amine groups and ester substituents.

Introduction

Cationic water soluble polyelectrolytes are polymers of increasing significance due to their applications in water purification and waste water treatment, papermaking, mining and the petroleum industry (1,2). Cationic polyelectrolytes with various charge densities have been synthesized either by copolymerization of charged and uncharged monomers or by modification of known polymers (3-9). In our continuing studies of α -substituted methyl acrylate derivatives, we previously reported synthesis of new quaternary ammonium amphiphilic methacrylates bearing a polymerizable group either at the ionic head (head type) or at the tail of the aliphatic chain (tail-end type) (Figure 1) (10). Although all the tail-end type monomers exhibited high radical polymerizability in water, the head type monomers were not polymerizable due to steric effects.

We describe here a different approach to the synthesis of quaternary ammonium methacrylate polymers some with the head type geometry by modification of the homopolymers of ECAM and TBCAM. In our previous work, chloroacetate derivatives of ethyl α -hydroxymethylacrylate (ECAM) and t-butyl α -hydroxymethylacrylate (TBCAM) were synthesized and polymerized to give unexpectedly high molecular weight polymers (number average values of 1.15 million and 328,000, respectively) (11). ECAM and TBCAM monomers and their polymers were expected to offer potential for synthesis of a wide variety of derivatives, but all attempted nucleophilic reactions of ECAM and TBCAM monomers gave Michael-

type substitution products with loss of the α -chloroacetyl substituent. In this article, we describe successful quaternization of the poly-ECAM and poly-TBCAM by tertiary amines to give new cationic polymers with various charge densities.



head type monomer

Figure 1. General formula for synthesized amphiphilic methacrylates

Experimental

All solvents and reagents were used as obtained. Monomer and polymer characterization was obtained by ^1H - and ^{13}C NMR spectroscopy (Bruker AC-200), FT-IR spectroscopy (Mattson 5000), differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) using TA Instruments 2920 and 2960 modules, respectively. Both modules were controlled by a Thermal Analyst 2100. Ethyl α -chloroacetoxymethacrylate (ECAM) and t-butyl α -chloroacetoxymethacrylate (TBCAM) were prepared using previously reported procedures (11).

Quaternization

Quaternization of poly-ECAM with TMA was carried out in different solvents at different polymer concentrations; e.g., in N,N-dimethylformamide (DMF) (10 w/v %), ether (3 w/v %), acetonitrile (13 w/v %) and THF (21 w/v %). TMA gas was bubbled through solutions of the polymer at room temperature for 15 minutes and the reaction mixture was kept under an inert atmosphere for an hour. Quaternized polymers which precipitated from ether, acetonitrile and THF solutions were washed with ether several times. Quaternization of the polymer proceeded homogeneously in DMF and the resulting polymer was isolated by precipitation into ether. The product was dried in a vacuum oven over phosphorous pentoxide at room temperature for 12 h.

Quaternization of poly-TBCAM with TMA was carried out homogeneously in DMF at 33 w/v % polymer concentration at room temperature for an hour. The resulting very viscous polymer solution was diluted with methanol and precipitated into ether.

Quaternizations of poly-ECAM and poly-TBCAM with N,N-dimethyldodecylamine were carried out homogeneously in DMF at 12-17 w/v % polymer concentration with a molar ratio of the tertiary amine to the polymer of five and four. Reactions were done at room temperature and at 60 °C for 2-10 h. The products were precipitated into ether, then dried in a vacuum oven over phosphorous pentoxide for 12 h.

Result and Discussion

Monomer synthesis involved reaction of ethyl α -hydroxymethylacrylate (EHMA) and t-butyl α -hydroxymethylacrylate (TBHMA) with excess chloroacetyl chloride using TEA as catalyst and base (11). Monomers were polymerized in bulk at 65-69 °C using AIBN. The number average molecular weights of poly-ECAM and poly-TBCAM were found to be 350000 and 90000, respectively. Initial reactions of poly-ECAM and poly-TBCAM with trimethyl amine were carried out by bubbling TMA gas into 10 to 33 w/v % polymer solutions with different solvents (Figure 2). When reactions were done in acetone, acetonitrile, THF or ether at room temperature, quaternized polymers precipitated from solution in 10 to 60 minutes, whereas polymers stayed in solution when DMF was used as solvent.

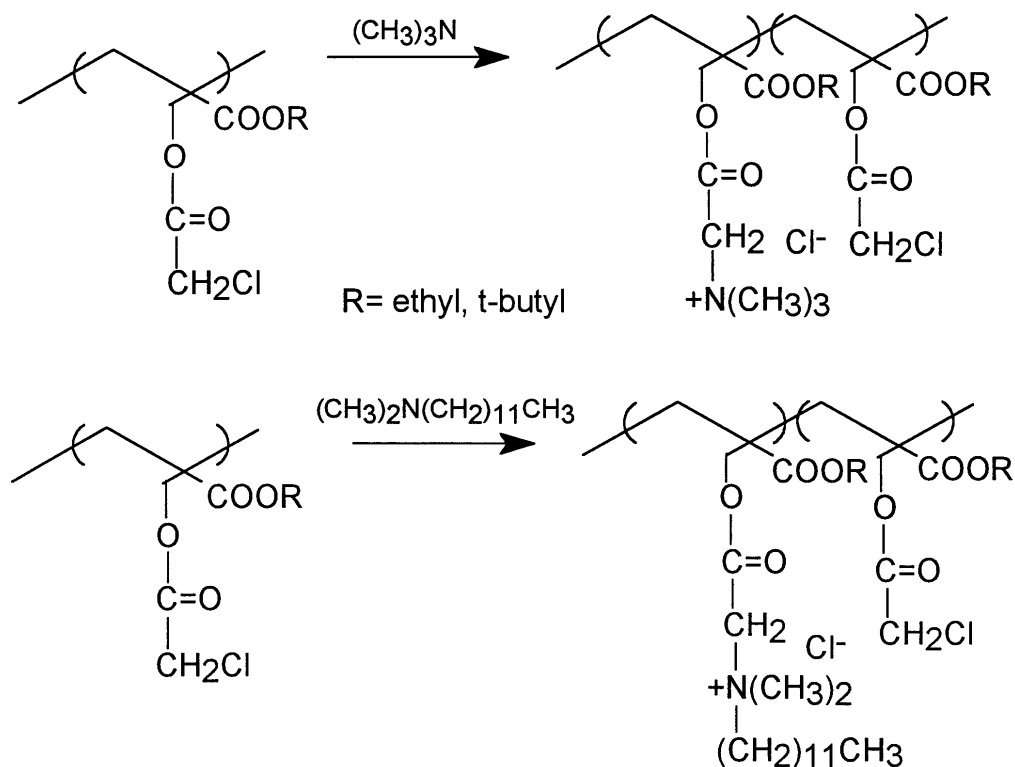


Figure 2. General synthetic scheme for quaternization reactions

The ^{13}C -NMR spectra of the poly-ECAM in CDCl_3 and quaternized poly-ECAM in D_2O are given in Figure 3. They show a new sharp peak due to the three methyl groups at 53.9 ppm in the quaternized polymer. Also, the intensity of the characteristic $-\text{CH}_2\text{Cl}$ carbon peak at 41 ppm decreased relative to the backbone carbon peaks at 45 and 48 ppm in the quaternized polymer.

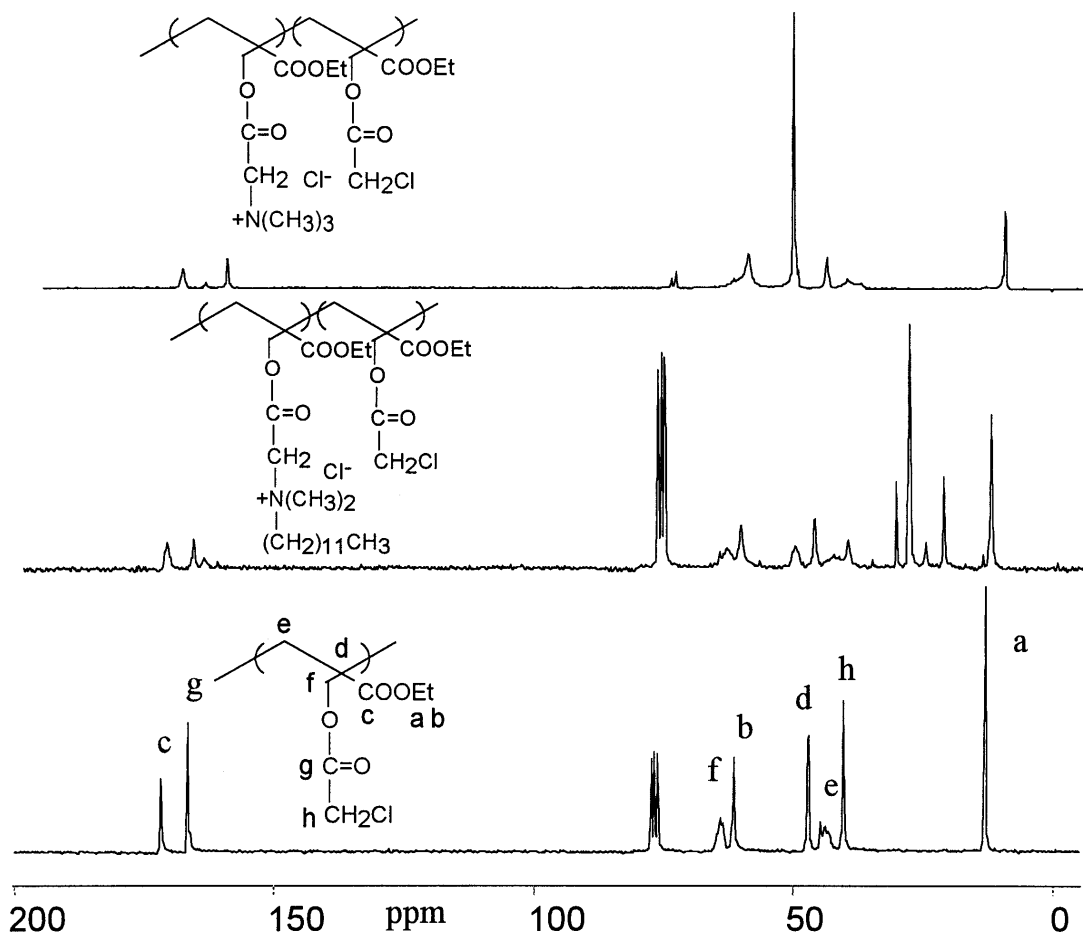


Figure 3. ^{13}C -NMR spectra of poly-ECAM and the quaternized polymers

The ^1H -NMR measurements were used for the determination of the DQ values of the quaternized polymers. A ^1H -NMR spectra of poly-ECAM and quaternized poly-ECAM showed backbone protons and methyl protons of the ester group between 1 and 2.5 ppm, and other protons between 2.8 and 4.7 ppm (Figure 4). The DQ values were calculated from the ratio of peak areas of these two regions. The resultant DQ value of poly-ECAM quaternized with TMA at room temperature after 1 h was found to be 84 %.

Quaternization reactivity of poly-TBCAM was lower than that of poly-ECAM. From the ^1H -NMR spectrum, the DQ value of poly-TBCAM quaternized with TMA at room temperature for 4 h was found to be 19 %. Low reactivity of poly-TBCAM is due to steric hindrance around the $-\text{CH}_2\text{Cl}$ group due to the t-butyl group.

Reactions of poly-ECAM and poly-TBCAM were also performed by displacement of the pendant chlorine with N,N-dimethyldodecylamine. This reaction was carried out homogeneously in DMF at 12-17 w/v % polymer concentration at room temperature. Temperature, polymer concentration and time dependence of the quaternization reaction were also studied. When the quaternization of poly-ECAM (12 % in DMF) was carried out at room temperature for 2-10 h, a soluble polymer was obtained. The molar ratio of tertiary amine to polymer was five. The ^{13}C -NMR spectrum of the

quaternized poly-ECAM in D₂O showed new peaks (31.8, 29.5, 29.3, 26.3, 22.6, 14 ppm) due to the dodecyl chain and a new peak at 51.3 ppm due to the methyl groups (Figure 3). Results of ¹H-NMR measurements indicate the DQ value of 37 %. Increasing reaction temperature to 60 °C at the same polymer concentration resulted in crosslinked polymer in 2 h. Also, increasing the polymer concentration (>17 %) resulted in crosslinked polymer at room temperature after 4 h. Similar results were obtained when chloromethylated polystyrene was quaternized with trialkylamine. A fraction of the polymer becomes insoluble because of the gelation through intermolecular crosslinkage involving the trialkyl amine. This result suggest that one trialkylamine can react or interact with two halogens groups, perhaps by an aggregation mechanism (12). Quaternization poly-TBCAM (17 w/v % in DMF) with N,N-dimethyldodecylamine at room temperature after 4 h gave a soluble polymer with the DQ value of 9 %.

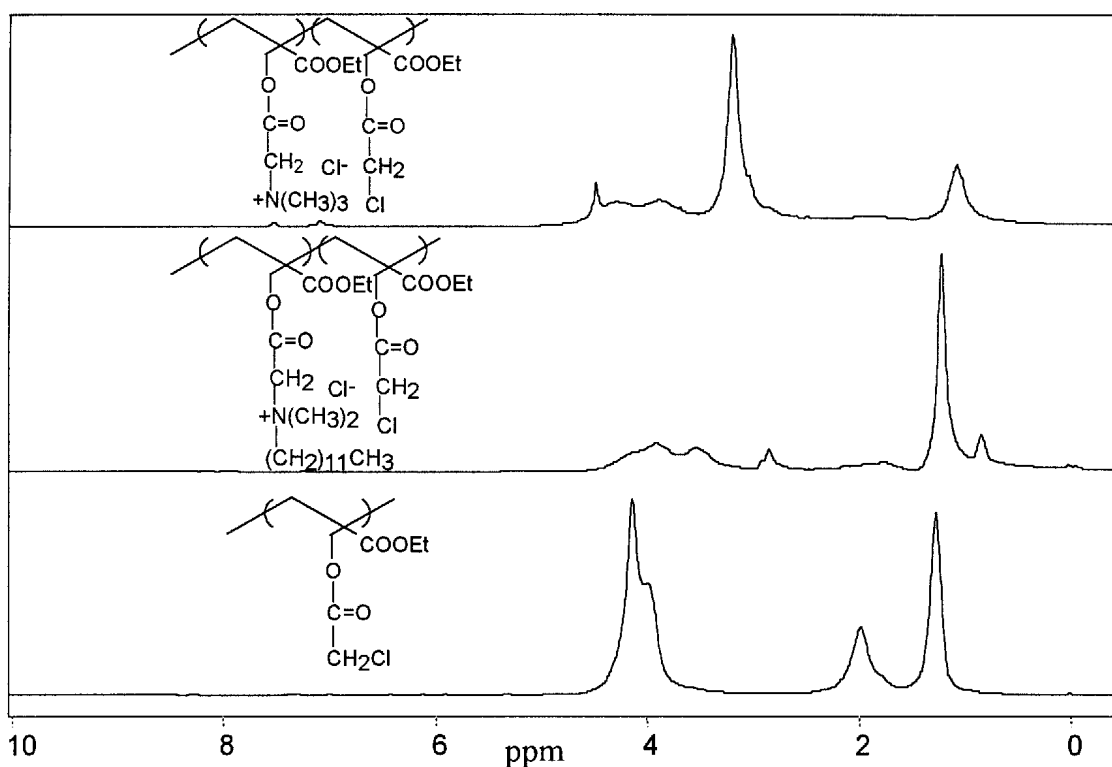


Figure 4. ¹H-NMR spectra of poly-ECAM and the quaternized polymers

The IR spectra of all quaternized polymers show broad absorption at 3440 cm⁻¹ due to the presence of absorbed water. The peak is more intense for highly hydrophilic TMA substituted polymers compared to that of the N,N-dimethyldodecyl amine substituted polymers.

The solubilities of the polymers in some standard solvents are listed in Table 1. Poly-ECAM and poly-TBCAM polymers dissolved in rather non-polar solvents such as acetone, CHCl₃ and THF but not in polar solvents such as methanol and water. In contrast, TMA substituted polymers did not dissolve in acetone, CHCl₃ and THF but did dissolve in methanol and water. Even at the low DQ value (19 %) poly-TBCAM

quaternized with TMA became water soluble. Aqueous solutions of these polymers foamed, indicating reduced surface tension.

The N,N-dimethyldodecylamine substituted polymers dissolved both in non-polar solvents such as CHCl_3 , acetone and THF and polar solvents such as methanol. These polymers did not dissolve in water due to the hydrophobic character of the dodecyl group. Ether is a non-solvent for all the polymers.

The T_g (from DSC) of the original poly-ECAM was 60 °C before the quaternization reaction. The TGA thermogram under nitrogen showed a one-step weight loss started at about 280 °C. The TMA substituted polymer was found to be less stable than the original poly-ECAM. It did not display an apparent T_g and showed multistep weight loss due to evaporation of water at 116 °C (5.8%), hydrolysis of ester groups and Hoffman degradation of ammonium salts. N,N-Dimethyldodecylamine substituted poly-ECAM showed 9.5 % weight loss at 193 °C and started to decompose at 280 °C as did the original polymer. The T_g of the poly-TBCAM was 118 °C before the quaternization reaction. Its TGA thermogram showed a two-step decomposition starting at 150 °C due to thermolysis of the t-butyl groups, and a 60 % weight loss at 350 °C (Figure 6). The TMA and N,N-dimethyldodecylamine substituted polymers showed a single-step decomposition starting at 150 °C. Lower stabilities of the substituted polymers were probably due to the autocatalyzed decomposition induced by the acid groups liberated by thermolysis of t-butyl groups.

Table I. Solubility of the polymers in various solvents

Polymer	THF	Acetone	H ₂ O	MeOH	CHCl ₃	Ether
Poly-ECAM	+	+	-	-	+	-
Poly-TBCAM	+	+	-	-	+	-
Poly-ECAM-TMA	-	-	+	+	-	-
Poly-ECAM-DMDO*	+	+	-	+	+	-
Poly-TBCAM-TMA	-	-	+	+	-	-
Poly-TBCAM-DMDO*	+	+	-	+	+	-

*N,N-Dimethyldodecylamine

In conclusion, homopolymers of ECAM and TBCAM can be converted to new cationic polymers with quite different structures using different tertiary amines. The DQ values of the polymers can be controlled by the size of the ester group and the structure of the amines.

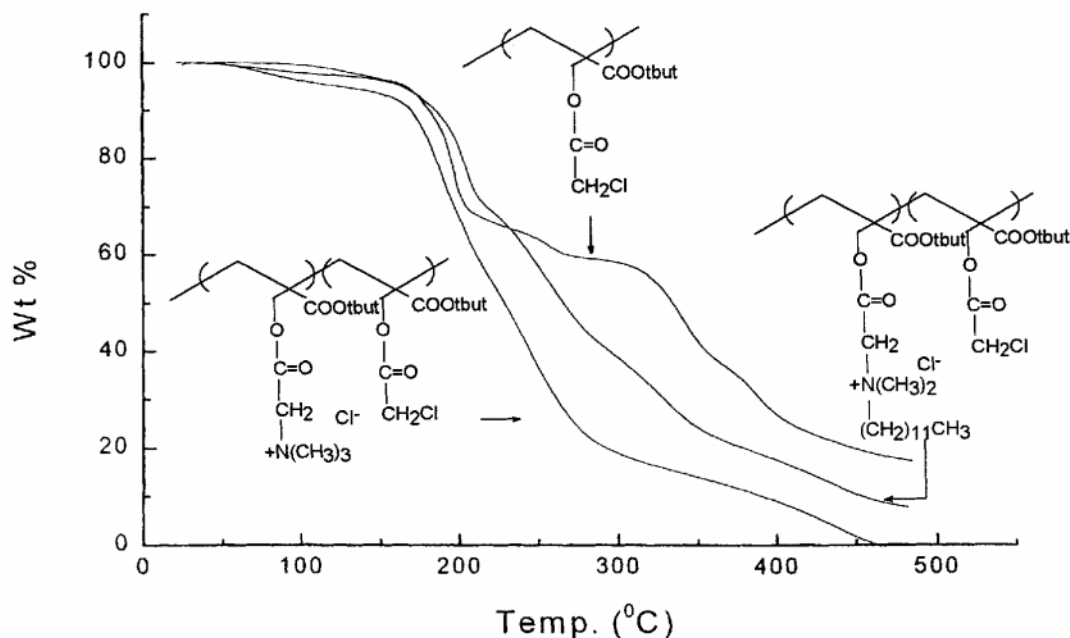


Figure 6. TGA curves of the poly-TBCAM and the quaternized polymers

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