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# 3-Acrylamido-3-methylbutyltrimethylammonium Chloride: A New Cationic Monomer*

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## ABSTRACT

The monomer 3-acrylamido-3-methylbutyltrimethylammonium chloride was synthesized by two routes which differed in the first reaction of the synthetic sequence. Dimethylaminomethylation of isobutylene or dimethylamination of isoprene gave intermediate amino-olefins which could be reacted with acrylonitrile in a Ritter reaction to yield 3-acrylamido-3-methylbutyldimethylamine. Subsequent quaternization with methyl chloride gave the subject monomer. The purity of the monomers from the two routes was found to differ greatly; however, extensively purified monomer was not necessary for high molecular weight polymer formation.

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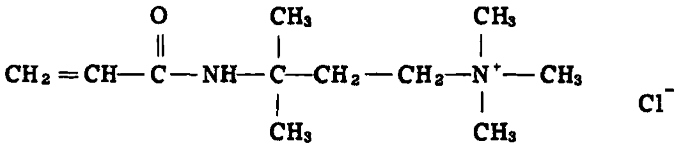
*For a preliminary account of this work, see Boothe, Sharpe, and Noren [1].

## INTRODUCTION

Over the past several years the importance of polyelectrolytes has increased immensely [2]. Synthetic cationic polyelectrolytes find many applications from increasing the dyeability of fabrics to liquid/solids separations. Either step-growth or chain-growth polymerization techniques have been employed for the preparation of cationic polyelectrolytes, although the latter mode is preferred in order to obtain high molecular weight polymer and allow easy copolymerization with commercial monomers. Our interest in the synthesis of new and novel polyelectrolytes led to an investigation of the synthesis and polymerization of 3-acrylamido-3-methylbutyltrimethylammonium chloride (I). This monomer contained an amide linkage,



$$CH_2=CH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{N^+}}-CH_3 \qquad Cl^-$$

I

in contrast to the commercially available quaternary ammonium alkyl (meth)acrylates.

## EXPERIMENTAL

### Dimethylaminomethylation of Isobutylene

Acetic acid (477 g) was weighed into a 2-liter, three-necked flask which was equipped with a Dry Ice–isopropanol condenser, thermometer, magnetic stirrer, addition funnel, and a wet ice bath. Sulfuric acid (100 g) was added in a dropwise manner while cooling and stirring. Dimethylamine (226 g, 3.0 mole of 60% aqueous solution) was added dropwise from a second addition funnel while cooling and stirring. Reaction temperature did not exceed 35° C during these additions. Paraformaldehyde (90 g, 3 mole) was then added as a solid via a powder funnel which had been substituted for the second addition funnel; a white suspension resulted. The ice bath was replaced with a heating mantle and the suspension was heated to 94° C over ca. 1 hr to obtain a yellow-green homogeneous solution. The solution was then allowed to cool to room temperature, then cooled to about 0° via an ice bath.

The solution was subsequently transferred to a precooled, 2-liter Parr bomb. Isobutylene (175 g, 3.1 mole) was condensed into an Erlenmeyer flask at Dry Ice–isopropanol temperature and added to the bomb. The reactor was assembled rapidly, tested for leaks, and placed in a furnace. The reaction mixture was heated to 96-99° C with stirring for 15 hr. The maximum pressure attained was 210 psig; pressure had decreased to 99 psig after 15 hr.

The product, a clear, homogeneous, orange liquid (98% recovery), was collected in a 3-liter Erlenmeyer flask. The solution was diluted with ice and neutralized with 50% aqueous sodium hydroxide while cooling in an ice bath: two phases formed on neutralization. The upper, organic phase was collected; the aqueous phase was extracted with several portions of ethyl ether. After evaporation of the ether, the two portions were combined (total 312 g). The major product was 2-methyl-4-dimethylamino-1-butene; two minor products were observed which are believed to be 2-methyl-4-dimethylamino-2-butanol and 2-methyl-4-dimethylamino-2-butyl acetate. The yield of 2-methyl-4-dimethylamino-1-butene was calculated to be ca. 80% based on isobutylene.

The dimethylamination reactions were performed according to a known procedure [3] by using freshly distilled isoprene, dimethylamine (Matheson Gas Co.), and the appropriate alkali metal.

## 3-Acrylamido-3-methylbutyldimethylamine

Sulfuric acid (292 g, 3.0 mole) was combined with chloroform (208 g) in a 1-liter, four-necked flask which was equipped with a thermometer, condenser, paddle stirrer, addition funnel, and wet ice bath. The crude dimethylaminomethylation product (167 g, 1.5 mole) and acrylonitrile (149 g, 2.7 mole) were combined in the addition funnel and added dropwise to the cooled, stirred sulfuric acid/chloroform mixture over 110 min at 13-25° C, stirred at 25-27° C for ca. 3 hr, then warmed to 59° C and maintained at that temperature overnight.

After separation of the chloroform, the reaction solution was diluted with ice and neutralized with aqueous 50% sodium hydroxide. The organic product separated and was collected: 260 g crude product, 96% yield. The product was vacuum-distilled to obtain 148 g of 3-acrylamido-3-methylbutyldimethylamine, 55% yield. Pot residue was 35 g of polymerized material.

### 3-Acrylamido-3-methylbutyltrimethylammonium Chloride

A solution of 3-acrylamido-3-methylbutyldimethylamine (29.0 g, 0.16 mole) was combined with dry acetone (75 ml) in a 200-ml four-necked round-bottomed flask which was equipped with a thermometer, paddle stirrer, condenser, and gas inlet tube. Excess methyl chloride was bubbled through the reaction mixture over a 2.5-hr period at 18-27° C to produce a voluminous white precipitate which was isolated via vacuum filtration: 34.8 g (94% yield, mp 232 °C).

### Homopolymerization of 3-Acrylamido-3-methylbutyltrimethylammonium Chloride

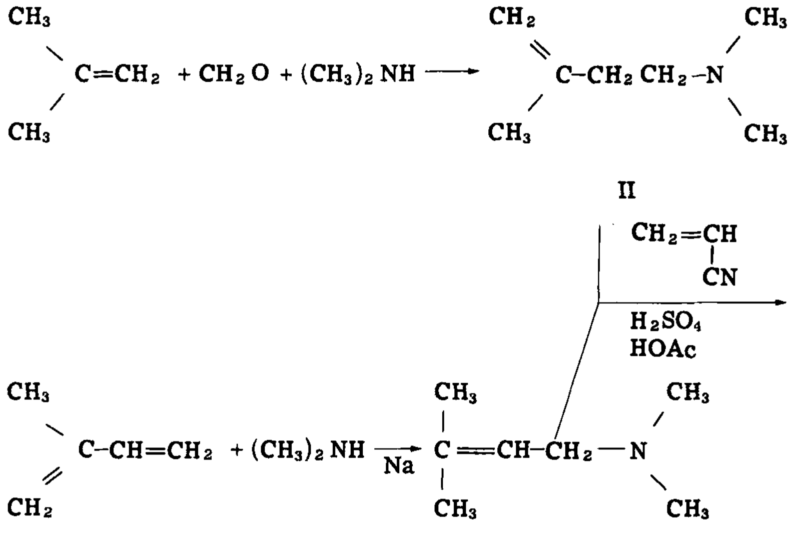
A solution of 293 g (1.25 mole) of 3-acrylamido-3-methylbutyltrimethylammonium chloride in 207 g of distilled water was prepared in a 1-liter resin kettle, and the pH was adjusted to 8.0-8.1 (if necessary) by addition of 5% HCl. The kettle was equipped with a stirrer, thermometer, nitrogen inlet, and a condenser. The solution was stirred and purged with nitrogen for 1 hr, the temperature adjusted to 30 °C, and the free-radical catalyst system introduced. In about 50 min, polymerization reaction began which was followed adiabatically with an oil bath to its maximum temperature and held there for 2 hr. After cooling, the gel was removed and dried to a solid polymer containing about 10% moisture. The yield was always greater than 95%.

## RESULTS AND DISCUSSION

The monomer 3-acrylamido-3-methylbutyltrimethylammonium chloride was prepared by two synthetic routes. The first route employed a dimethylaminomethylation of isobutene [4-6] as the initial step to form amino-olefin II, while the second utilized the dimethylamination of isoprene [7] to obtain a similar amino-olefin intermediate III.

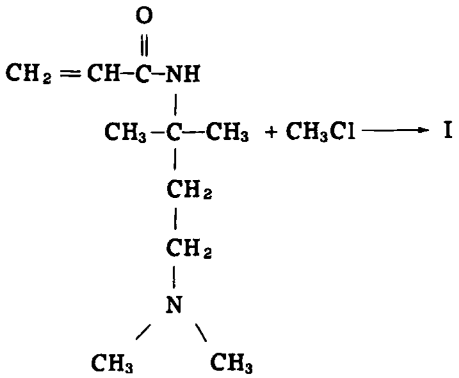
In both methods the crude product from the first reaction could be converted to 3-acrylamido-3-methylbutyldimethylamine IV, which was in turn quaternized to the subject monomer.

The dimethylaminomethylation of isobutylene had been reported to give the desired amino-olefin intermediate 2-methyl-4-dimethylamino-1-butene II [4-6]. However, the reaction produced only low



II

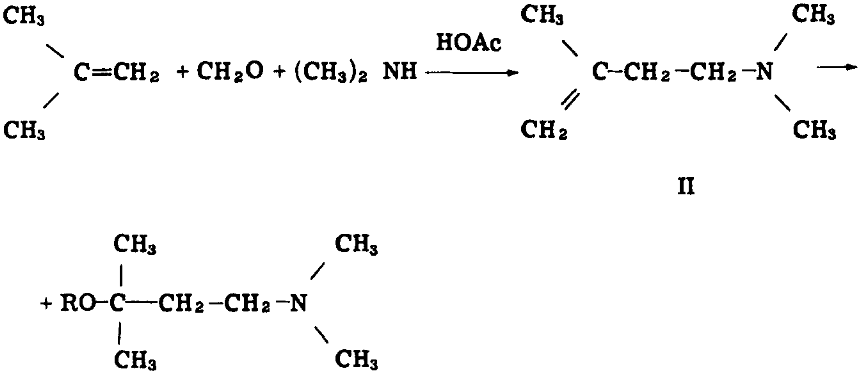
III



IV

yields of II when conducted according to the previously reported procedure [4-6]. Gas chromatographic analysis of the crude reaction mixtures showed that in addition to II, both Va and Vb were present. Normal distillation could not be used to separate Va and Vb, but IR and NMR spectral studies of the distillate containing Va and Vb provided the necessary evidence for their presence.

An investigation of the reaction variables for the dimethylaminomethylation reaction was undertaken. It can be seen from the results



$$(CH_3)_2C=CH_2 + CH_2O + (CH_3)_2NH \xrightarrow{HOAc} CH_2=C(CH_3)-CH_2-CH_2-N(CH_3)_2 \longrightarrow + RO-C(CH_3)_2-CH_2-CH_2-N(CH_3)_2$$

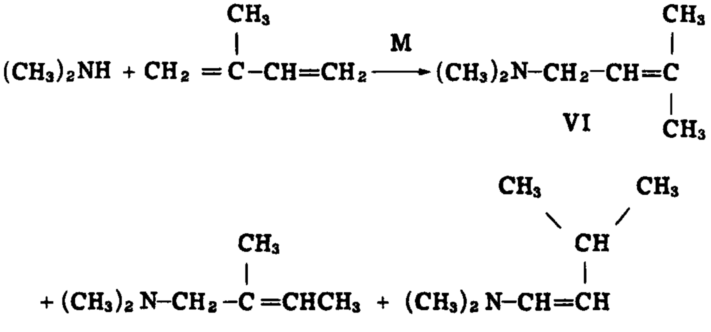
II

Va: $R=H$

Vb: $R=CH_3-\overset{\displaystyle O}{\overset{\|}{C}}$

in Table 1 that the optimum conditions for this reaction can be approached by the employment of (a) approximately 0.3 mole of sulfuric acid per mole of amino product, (b) a reaction temperature of 95-105° C, and (c) a certain minimum quantity of water added with the dimethylamine.

The sodium catalyzed addition of dimethylamine to isoprene was reported to give 95% N,N 3-trimethyl-2-butenylamine VI, which was an alternate amino-olefin intermediate [8]. Other investigations [3, 7] have shown that the product was a mixture of 75% VI, 21% VII, and 4% of the enamine VIII. Isomer VI was reported to be the only



$$(CH_3)_2NH + CH_2=C(CH_3)-CH=CH_2 \xrightarrow{M} (CH_3)_2N-CH_2-CH=C(CH_3)_2 + (CH_3)_2N-CH_2-C(CH_3)=CHCH_3 + (CH_3)_2N-CH=CH-CH(CH_3)_2$$

VI

VII

VIII

TABLE 1. Conditions for the Dimethylaminomethylation of Isobutylene[a]

| Run | Isobutylene[b] (mole) | Acetic acid (mole) | $H_2SO_4$ (mole) | Temp (°C) | Yield (%) |
|---|---|---|---|---|---|
| 1 | 1.3 | 2.3 | 0.2 | 60-63 | 54 |
| 2 | 1.3 | 2.5 | 0.1 | 70-75 | 66 |
| 3 | 1.3 | 2.2 | 0.2 | 75 | 5 |
| 4 | 1.2 | 2.6 | 0.4 | 77-84 | 50 |
| 5 | 1.3 | 2.6 | 0.3 | 85 | 66 |
| 6 | 1.2 | 2.6 | 0.3 | 95-103 | 72 |
| 7 | 1.2 | 2.6 | 0.3 | 96-101 | 86 |
| 8 | 1.0 | 2.6 | 0.3 | 96-99 | 87 |
| 9 | 1.1 | 2.6 | 0.3 | 95-100 | 88 |
| 10 | 1.1 | 2.6 | 0.3 | 97-100 | 32[c] |
| 11 | 1.1 | 2.0 | 0.2 | 100-115 | 36[d] |

[a] Dimethylamine/paraformaldehyde ratio 1; dimethylamine always added as 60% aqueous solution; reaction time, 15-20 hr; reaction pressure, 200-250 psi.

[b] Moles relative to dimethylamine.

[c] Anhydrous dimethylamine was used.

[d] Pressure reached 330 psi.

reactive component in the subsequent Ritter reaction [7] and thus, some investigations into enhancing the amount of VI obtained from the reaction were undertaken.

The variation of the alkali metal catalyst employed for the reaction was found to affect the isomer ratio as shown in Table 2. The reactions were all run at 22-25°C for 5 hr. Total yields of 70-90% were obtained, along with small amounts of hydrocarbon polymer formation and unreacted isoprene. The percentage of VI increased with decreasing reactivity of the alkali metal [9].

Of additional interest was the rearrangement of II obtained from the dimethylaminomethylation reaction to the more thermodynamically stable internal olefin VI which occurred during distillation.

TABLE 2. Effect of Alkali Metal Catalyst on the Reaction of Dimethylamine With Isoprene

| Alkali metal | Product composition (%)[a] VI | VII | VIII | Total yield (%) |
|---|---|---|---|---|
| Lithium | 76.6 | 16.6 | 6.8 | 72 |
| Sodium | 71.8 | 22.4 | 4.0 | 88 |
| Potassium | 64.4 | 32.2 | 3.5 | 70 |

[a] Determined by GLC on a 15% 1,2,3,-tris-2-cyanoethoxypropane on Chromasorb W, 12 ft × 1/4 in. stainless column at 60° C.

This rearrangement was characterized by a shift in the IR absorption frequency for the double bond from 1650 to 1670 $cm^{-1}$.

The Ritter reaction [10] of acrylonitrile with both the product from the dimethylaminomethylation of isobutylene and the dimethylamination of isoprene [4-6] gave 3-acrylamido-3-methylbutyldimethylamine IV in 50-75% yields. Our investigations were concentrated on the dimethylaminomethylation product which was utilized in the Ritter reaction at two levels of purity: (1) II was isolated by neutralization and distillation (bp 122° C/1 atm); and (2) the acetic acid and water were vacuum-stripped from the crude product prior to use. Some of the conditions studied are summarized in Table 3. The two orders of addition that were studied included the addition of a solution of the amino-olefin in acrylonitrile to concentrated sulfuric acid and the addition of acrylonitrile to a solution of the amino-olefin in concentrated sulfuric acid. Equally high yields of IV could be obtained by using either process, and in both cases the purity of the amino-olefin precursor did not adversely affect the yield.

Fully optimized conditions for this reaction were not obtained; however, the following observations can be made. The reaction requires at least 2 moles of sulfuric acid/mole of amine reactant in process 1, while lesser amounts are tolerated in process 2. The reaction is not instantaneous; i. e., reaction at 50-60° C for 3-5 hr following the mixing of the reactants is necessary to obtain respectable conversion. If the reaction temperature is too high (>80-90° C) and the reaction time too long, conversion of acrylonitrile to acrylamide is noted.

TABLE 3. Conditions Investigated for the Ritter Reaction with Acrylonitrile (AN)

| Run | Process[a] | Amine purity[b] | $H_2SO_4$ (mole) | AN (mole) | Solvent[c] | Addition temp (°C) | Reaction temp (°C) | Reaction time (hr) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1.8 | 1.7 | HOAc | 10-19 | 82-86 | 9 | 24 |
| 2 | 1 | 2 | 2.0 | 1.9 | $CHCl_3$ | 13-25 | 59 | 15 | 55 |
| 3 | 1 | 1 | 9.6 | 1.4 | $CCl_4$ | 11-21 | 51 | 1-2 | 92 (crude) |
| 4 | 1 | 1 | 2.0 | 1.2 | $ClCH_2CH_2Cl$ | 12-51 | 52-61 | 1 | 37 |
| 5 | 1 | 1 | 1.5 | 1.2 | N.S. | 11-24 | 20-47 | 4-5 | 36 |
| 6 | 2 | 2 | 3.0 | 2.5 | N.S. | 14-27 | 108 | 1-2 | 52 |
| 7 | 2 | 1 | 1.0 | 1.3 | HOAc | 9-35 | 50 | 17 | <10 |
| 8 | 2 | 2 | 2.9 | 2.6 | N.S. | 8-10 | 26-100 | 2 | 48 |
| 9 | 2 | 2 | 0.4 | 0.4 | N.S. | 3-4 | 14 | 0.25 | 0 |
| 10 | 2 | 2 | 0.5 | 1.2 | N.S. | 5 | 24 | 1.5 | 2 |
| 11 | 2 | 2 | 0.5 | 1.2 | N.S. | 5-6 | 23 | 17 | 23 |
| 12 | 2 | 2 | 0.4 | 1.2 | N.S. | 4 | 6-45 | 3 | 9 |
| 13 | 2 | 2 | 0.4 | 1.4 | N.S. | 8 | 55 | 2 | 33 |
| 14 | 2 | 2 | 1.0 | 1.2 | N.S. | 49-61 | 61-67 | 0.5 | 49 |

(continued)

TABLE 3 (continued)

| Run | Process[a] | Amine purity[b] | $H_2SO_4$ (mole) | AN (mole) | Solvent[c] | Addition temp (°C) | Reaction temp (°C) | Reaction time (hr) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 15 | 2 | 2 | 1.3 | 1.1 | N.S. | 42-84 | 84 | 2 | 45 |
| 16 | 2 | 2 | 1.4 | 1.2 | N.S. | 44-76 | 76-109 | 1 | 55 |
| 17 | 2 | 2 | 1.1 | 1.2 | N.S. | 49-58 | 45-74 | 3 | 45 |

[a] Process 1 was a solution of amino-olefin and acrylonitrile added to the sulfuric acid. Process 2 was the addition of acrylonitrile to a solution of the amino-olefin in sulfuric acid.

[b] 1 mole of amino-olefin used in each reaction. Purity 1 is distilled amine; purity 2 is crude amino-olefin minus the water and acetic acid from the dimethylaminomethylation reaction.

[c] N.S. = no solvent.

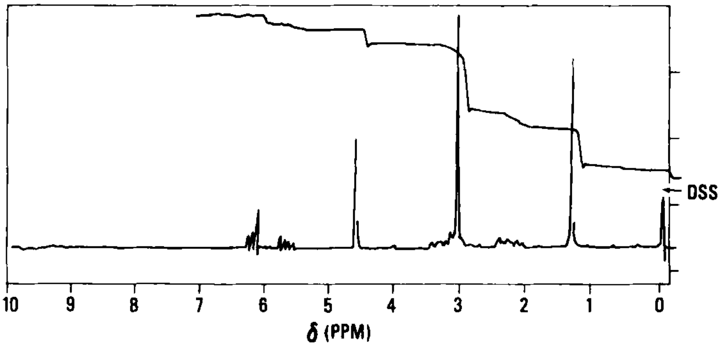


FIG. 1. NMR spectrum of 3-acrylamido-3-methylbutyltrimethylammonium chloride (I).

Distilled IV from the Ritter reaction was reacted with excess methyl chloride in dry acetone to form 3-acrylamido-3-methylbutyltrimethylammonium chloride (I), which separated as a white crystalline solid. Benzene and chloroform were also effective solvents for this reaction. The monomer is a moderately hygroscopic white solid having a melting point of 235° C as determined by differential scanning calorimetry. The product was further characterized by the secondary amide carbonyl absorptions at 1660 and 1690 $cm^{-1}$ in the infrared region and a $\lambda_{max}$ 249-258 nm in the ultraviolet. The NMR spectrum is shown in Fig. 1. The monomer is soluble in water, alcohols, formamide, and dimethyl sulfoxide.

Purity of the monomer was determined by thin-layer chromatography and liquid chromatography. Pure 3-acrylamido-3-methylbutyltrimethylammonium chloride could only be prepared from highly purified IV obtained by distillation of crude IV obtained via the dimethylaminomethylation route through a 12-in., glass bead-packed, heated distillation column. The monomer obtained from the isoprene route following a similar distillation always contained at least one impurity which could not be removed by either recrystallization or chromatography. However, when the quaternization of IV from the isoprene route was carried out by using benzene as a solvent instead of acetone, slightly purer monomer resulted from the isoprene route.

The activity of I was shown by homopolymerization of the monomer with typical free-radical initiators. Under these conditions, monomer from either route produced polymers with intrinsic viscosities as high as 7.1 dl/g in 1 *M* sodium chloride. This magnitude of viscosity corresponds to an intrinsic viscosity of 2.2 dl/g in 1 *M* sodium nitrate and a number-average molecular weight of $1.6 \times 10^5$ as determined by membrane osmometry in 1 *M* sodium nitrate.

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