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F. E. Bailey Jr.^{ab}; E. M. La Combe^{ac}

^a Research and Development Department, Chemicals and Plastics Union Carbide Corporation, South Charleston, West Virginia ^b Union Carbide Corporation, New York, New York ^c Technical Center, Union Carbide Corporation, Tarrytown, New York

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Synthesis and Some Properties of Some Sulfonium Polyelectrolytes: Polymers and Copolymers Derived from Methylthioethyl Acrylate

F. E. BAILEY, JR.* and E. M. LA COMBE†

*Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia*

SUMMARY

Methylthioethyl acrylate, prepared by ester exchange from methylthioethanol and methyl acrylate, behaves in copolymerization like a typical acrylate ester such as butyl acrylate. This monomer can be alkylated to yield corresponding sulfonium monomers. With dimethyl sulfate, (2-acryloxyethyl) dimethylsulfonium methyl sulfate is obtained. This latter monomer has a predictable lower relative copolymerization rate with alkyl acrylates than methylthioethyl acrylate. Water-soluble sulfonium polymers are polymeric cations and can act effectively as flocculants.

*Present address: Union Carbide Corporation, 270 Park Ave., New York, New York 10017.

†Present address: Technical Center, Union Carbide Corporation, Tarrytown, New York 10591.

INTRODUCTION

Interest in cationic polyelectrolytes that can function as effective flocculants for organic matter suspended at relatively high dilution in water led to the synthesis and investigation of sulfonium polymers derived from methylthioethyl acrylate [1]. More commonly, polymeric cations studied are nitrogen based and are the quaternary or hydrohalide salts of amine-containing polymers. Occasionally, phosphonium-containing polymers may be involved. In the case of polymers of methylthioethyl acrylate, synthesis of a wide range of polymer structures of varying sulfonium content was possible using alkylating agents such as dimethyl sulfate, chloroacetic acid, or methyl iodide. The acrylate polymer or copolymer can be first prepared and subsequently alkylated to the desired degree or, alternatively, methylthioethyl acrylate can be alkylated to yield the "sulfonium monomer" which can be subsequently polymerized.

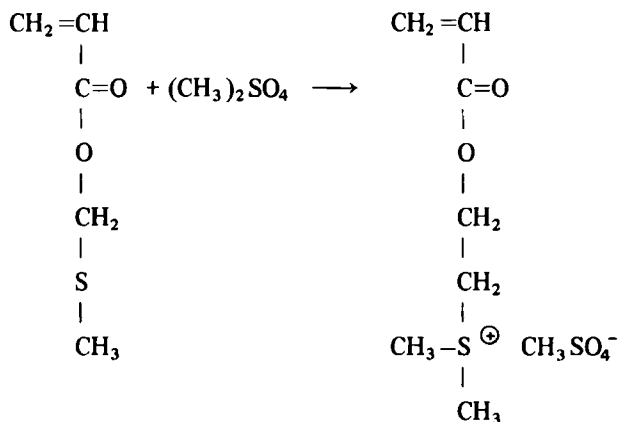
EXPERIMENTAL

Preparation of 2-Methylthioethyl Acrylate

Methyl acrylate, 1290 g (15 moles); 2-methylthioethanol, 460 (5 moles); Age-rite powder, 3.5 g; and magnesium methoxide, 50 ml of an 18 wt/vol% solution in methanol, were mixed together in a 2-liter boiling flask that was attached to an efficient fractionation column. The mixture was heated under reflux, and during 12 hr, 175 g of methanol was distilled off as an azeotrope with methyl acrylate boiling at 62.5 to 64°C. The kettle material was cooled to about 30°C and treated with water to destroy the catalyst. The product was filtered through gravity filters and about 300 g of gelatinous residue remained. The residue was broken up with 500 g of water and 20 ml of conc HCl and an additional quantity of oil layer was recovered and combined with the previous filtrate in a 2-liter boiling flask. The material was fractionally distilled in an efficient fractionation column to give 431 g (59% yield) of high purity 2-methylthioethyl acrylate boiling at 65°C at 5 mm pressure and having a refractive index of 1.4776, $n_{30/D}$. Analysis calculated for: $C_6H_{10}O_2S$: 49.3% C; 6.85% H; 21.9% S. Found: 49.4% C; 7.4% H; 19.16% S. The preferred ester exchange catalysts are alkali metal and alkaline earth metal alkoxides.

Preparation of "Sulfonium Acrylate" Monomers

The sulfonium salt of methylthioethyl acrylate can be prepared by alkylation with dimethyl sulfate to yield (2-acryloxyethyl) dimethylsulfonium methyl sulfate:

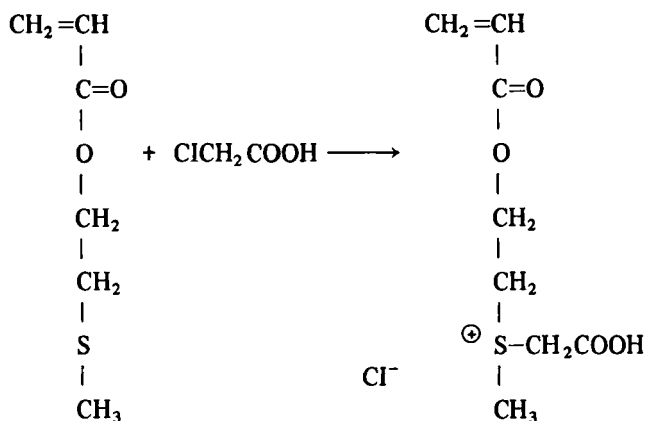


The reaction proceeds rapidly and quantitatively and can be carried out, for example, in benzene solution with the sulfonium acrylate monomer separating from solution as a separate, viscous liquid layer containing about 15% benzene.

Alkylation of methylthioethyl acrylate with chloroacetic acid proceeds more slowly than with dimethyl sulfate but leads to an interesting ampholytic sulfonium monomer, (2-acryloxyethyl) carboxymethylsulfonium chloride. To a 300-ml Pyrex pressure bottle there were charged 73 g of 2-methylthioethyl acrylate, 47 g of chloroacetic acid, 50 g of acetonitrile, and 0.06 g of hydroquinone. The bottle was purged with nitrogen, capped, and tumbled in a constant temperature rotary water bath at 75°C. The next day the contents were poured into 1200 ml of isopropyl ether with continued stirring. Forty-three grams of (2-acryloxyethyl) carboxymethylsulfonium chloride settled out and was recovered as a liquid. (Structure is shown on following page.)

Polymerization

Methylthioethyl acrylate readily homopolymerizes in benzene solution with azobisisobutyronitrile initiator at 50°C to yield high molecular weight homopolymer at reaction rates of the order of 8 to 10% conversion per



hour. In copolymerization, methylthioethyl acrylate behaves like a typical alkyl acrylate. A comparison of the copolymerization of methylthioethyl acrylate and of butyl acrylate with vinylidene chloride is shown in Fig. 1. Copolymers of methylthioethyl acrylate can be quantitatively alkylated with dimethyl sulfate to yield the corresponding sulfonium containing copolymer.

(2-Acryloxyethyl) dimethylsulfonium methyl sulfate also readily homopolymerizes to yield a high molecular weight, water-soluble polymer which demonstrates typical polyelectrolyte behavior. For example, a homopolymer with a reduced viscosity in 0.2% water solution of 3.5, typically has a reduced viscosity at the same concentration in 0.5 M sodium acetate solution of about 1.2. In copolymerization, presumably because of the ionic nature of the monomer, (2-acryloxyethyl) dimethylsulfonium methyl sulfate has a lower relative rate than a typical acrylate. Copolymerization behavior with 2-ethylhexyl acrylate is shown in Fig. 2. Relative reactivity ratios in the copolymerization of 2-ethylhexyl acrylate and (2-acryloxyethyl) dimethylsulfonium methyl sulfate are, respectively, +2.5 and +0.40.

Preparation of a Copolymer with Acrylamide

Copolymer is prepared from a solution in acetonitrile (600 parts) of acrylamide (60 parts), 2-methylthioethyl acrylate (40 parts), and dimethyl sulfate (35 parts) at 50°C using 2.5 parts α, α' -azobisisobutyronitrile as catalyst. After a short induction period (about 30 min), polymerization occurs rapidly and may be complete in 1 to 2 hr. Copolymer separates from solution and is recovered by filtration, washing, and drying in an air oven.

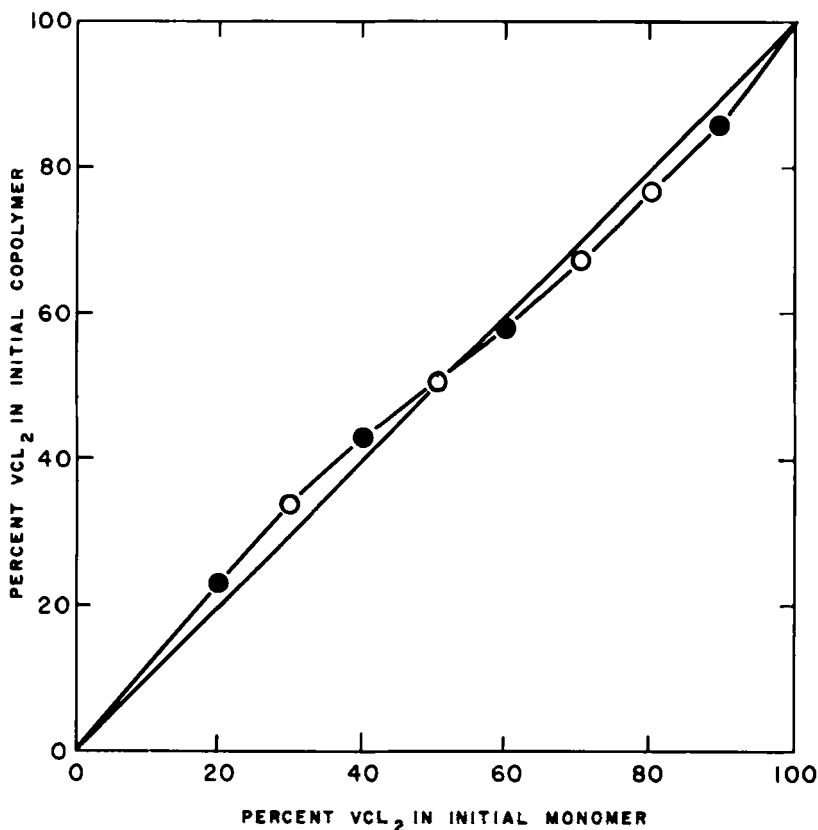


Fig. 1. Copolymerization of methylthioethyl acrylate and butyl acrylate with vinylidene chloride.

Alternatively, polymerization can be carried out in a solution of 8 g of 2-methylthioethyl acrylate and 12 g of acrylamide in 100 g of dry acetonitrile, initiated with 0.2 g of azobisisobutyronitrile at 50°C. Copolymer forms as a suspension in acetonitrile with a composition of about 75 mole% acrylamide. A solution of 7 g of dimethyl sulfate in 100 g of acetonitrile is then added with stirring. The methylthioethyl acrylate units in the copolymer are quantitatively alkylated.

Similarly, at 50°C a copolymer was prepared in acetonitrile containing 50 wt% of acrylamide and 50 wt% of (2-acryloxymethyl) carboxy-methyl-sulfonium chloride. Such a copolymer having a reduced viscosity in 0.2%

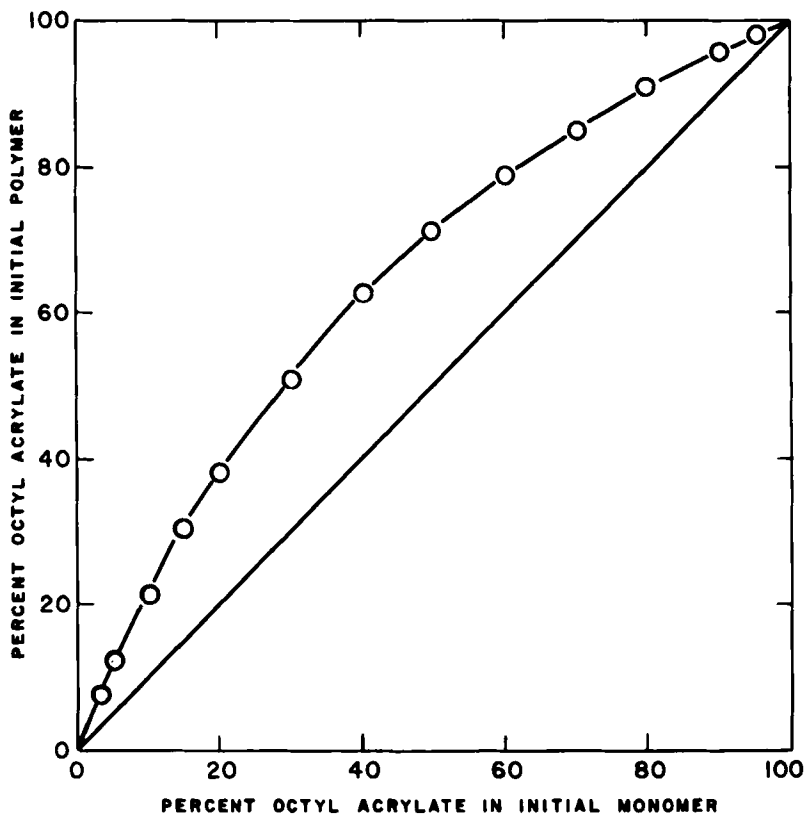


Fig. 2. 2-Acryloxyethyl dimethyl sulfonium methyl sulfate relative rate with 2-ethylhexyl acrylate.

water solution of 11.2 was found to have a reduced viscosity in 0.5 M sodium acetate solution, at the same copolymer concentration of 2.1.

DISCUSSION

Principal interest in the synthesis of these sulfonium polymeric cations centered in the study of the behavior of these polyelectrolytes in flocculation of suspended organic matter in water. Screening of a number of water-soluble sulfonium polymers prepared as described led to the selection of copolymers of (2-acryloxyethyl) dimethylsulfonium methyl sulfate with

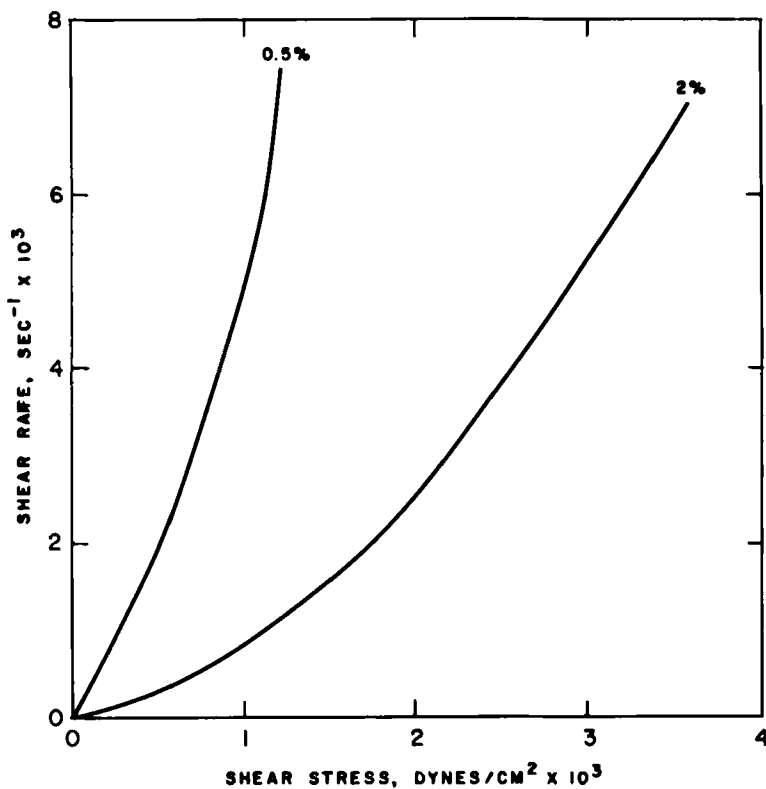


Fig. 3. Flow curves at 25°C.

acrylamide for further study. Particular emphasis was given to copolymers with a composition of 60 parts by weight acrylamide and 40 parts by weight of 2-methylthioethyl acrylate, completely alkylated with dimethyl sulfate. Preparation of this copolymer as a one-step process as a suspension in acetonitrile was found to be a particularly facile synthesis.

A copolymer of (2-acryloxyethyl) dimethylsulfonium methyl sulfate and acrylamide prepared in acetonitrile suspension as described above is readily water soluble. More concentrated water solutions, 0.5 and 2.0%, are mildly pseudoplastic as shown in Fig. 3. Behavior in water solution is that of a typical cationic polyelectrolyte and this copolymer is quite effective as a flocculant in "white water," for example.

Defining filtration ratio as the ratio of the filtration rate of treated "white water" to that of untreated, the effectiveness of this copolymer was

Table 1. Filtration Ratio of "White Water" With Solids Level of 290 ppm

Clay or pigment	Concentration of copolymer (ppm)	Filtration ratio
Clay	0.1	2.4
Clay	1.0	3.1
TiO ₂	0.1	1.2
TiO ₂	1.0	2.7
CaCO ₃	0.1	2.4
CaCO ₃	1.0	1.7
Alum at 700 ppm with clay		1.5

tested on a "white water" consisting of 15 g of bleached sulfit pulp and 1.5 g of clay or pigment at a total solids level of 290 ppm in water. Results are shown in Table 1.

REFERENCE

- [1] U.S. Patents 3,238,276; 3,278,500; 3,278,501; 3,207,656.

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