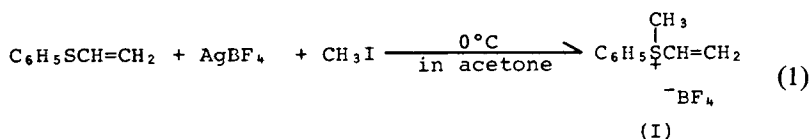


SYNTHESIS AND COPOLYMERIZATION OF METHYLPHENYLVINYLSULFONIUM TETRAFLUOROBORATE

Some papers and patents have been published concerning syntheses and use of sulfonium-containing polymers (1-4). However, the structures in many cases of these polymers have been achieved by syntheses based on the sulfonium salts of chloromethylated polystyrene-divinylbenzene copolymers (1), or the acrylates or the methacrylates of alcohols such as methylthioethanol or the sulfonium derivatives (2-4).

Attempts to polymerize vinylsulfonium salts were unsuccessful because of the low polymerization ability of vinylsulfonium salts and some difficulty existing in the syntheses of vinylsulfonium salts. Therefore, we synthesized poly(vinylsulfonium salts) by a polymer reaction (5).

Alkylvinylsulfonium salts and dimethylvinylsulfonium salts were synthesized by Doering and Schreiber (6) and Caserio et al. (7) in 1955 and 1966, and they reported that alkylvinylsulfonium salts were unstable compounds. In 1971, LaRoche and Trost (8) obtained for the first time arylvinylsulfonium salt in the products of the elimination reaction of acetoxyethylsulfonium salt. However, this is not suitable for the syntheses of vinylsulfonium salts because of its troublesome procedure and low yield. Therefore, we synthesized phenylvinylsulfonium salt from phenylvinylsulfide, methyl iodide, and silver tetrafluoroborate, as shown in eq. (1).



Under nitrogen stream, equimolar amounts of phenylvinylsulfide and silver tetrafluoroborate were mixed in acetone, and the same amount of methyl iodide was added to the solution at 0°C . After 2 hr, methylphenylvinylsulfonium salt (I) was obtained as a white solid. Recrystallization from chloroform-ether yielded 67% of I, mp $54-55^\circ\text{C}$. The NMR spectrum ($\text{DMSO}-d_6$) showed $\delta = 3.90$ ppm(s, 3H), 6.41 (t, 2H), 7.10 (q, 1H), and 7.85 (m, 5H). The infrared spectrum showed $\nu_{\text{BF}_4} = 1000-1150 \text{ cm}^{-1}$.

Anal. Calcd for $\text{C}_9\text{H}_{11}\text{SBF}_4$: C, 45.40%; H, 4.67%. Found: C, 45.03%; H, 4.88%.

Polymerization of I was attempted by radical (AIBN), cationic ($\text{BF}_3 \cdot \text{OEt}_2$), and anionic (n-BuLi) methods. Since polymer and I behave the same in the solubility (5), the presence of polymer was examined by NMR. However, sulfonium polymer could not be obtained by any method. However, in the case of copolymerization with vinyl monomers, such as acrylonitrile (AN), acrylamide (AA), methyl methacrylate, methyl acrylate, and styrene, radical copolymerization proceeded at 60°C in acetonitrile.

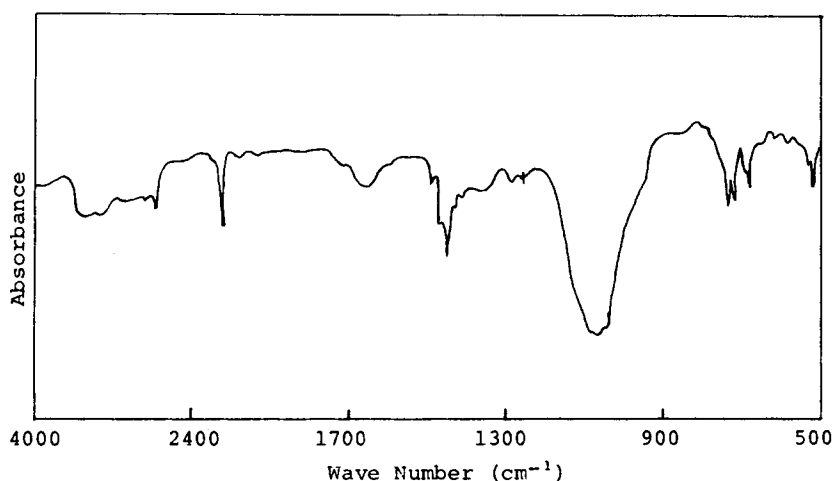
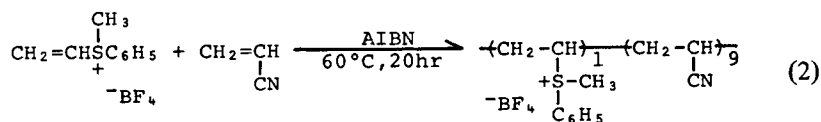


Fig. 1. Infrared spectrum of methylphenylvinylsulfonium tetrafluoroborate (I) and acrylonitrile copolymer.

For example, copolymerization with AN was carried out with 0.5 g (2.1 mmole) of I and 0.11 g (2.1 mmole) of AN using 0.02 g (0.12 mmole) of AIBN as an initiator in 2 ml of acetonitrile at 60°C for 20 hr. After the copolymerization, the reaction mixture was poured into 80 ml of methylene chloride to precipitate the copolymer; yield, 0.08 g. The structure of copolymer was confirmed by the characteristic infrared absorption of tetrafluoroborate at 1000-1150 cm^{-1} and cyano group at 2230 cm^{-1} (Fig. 1). NMR spectra of copolymer and I also supported the copolymer structure from the signal of phenyl protons at $\delta = 7.6\text{--}8.2$ ppm; on the other hand, the signal of vinyl protons of I completely disappeared in the copolymer. The composition of copolymer was found that the ratio of I to AN was about 1:9 by the elemental analysis of copolymer.



It is very difficult to isolate the copolymer which consists of higher contents of sulfonium salt units, because the solubilities of this copolymer and I are similar. Therefore, the monomer reactivity ratio was determined in the range of low sulfonium salt monomer concentration (under 50%) by the method of Finemann and Ross. In the copolymerization with AN, $r_{\text{I}} = 0.1$ and $r_{\text{AN}} = 2.2$ were obtained, and Q and e values for I were calculated as $Q = 1.19$ and $e = 2.43$. The AA copolymer precipitated from the polymerization solvent as the polymerization proceeded, and it was then separated by filtration. Copolymerization parameters were obtained as follows: $r_{\text{I}} = 0.1$; $r_{\text{AA}} = 3.4$; $Q_{\text{I}} = 1.13$; and $e_{\text{I}} = 2.23$.

Q and e values which are obtained from the copolymerization with AN or AA are in good agreement within the experimental error. In the case of methyl acrylate, the copolymer was extracted by benzene because I did not dissolve in that solvent.

The reactivity of vinylsulfonium salts, separation method of copolymer which consists of higher sulfonium salt, and the composition and the nature of the copolymer of this high sulfonium salt unit are now under investigation.

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