Copolymerization of Sodium Styrene Sulfonate with Sodium Chloroacrylate

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SUMMARY

Sodium styrene sulfonate was copolymerized with sodium chloroacrylate in water–isopropanol mixtures by radical initiation at 70°C. Analysis of the copolymers showed that due to dehalogenation reaction chloroacrylate units underwent various transformations with predominant formation of lactone structures. The copolymer composition was evaluated from NMR spectra. Monomer reactivity ratios were calculated using the integrated copolymerization equation.

INTRODUCTION

Many studies have been made on synthesis and characterization of ion-containing polymers, primarily because of their many industrial applications, but also because of the challenge they pose to polymer chemists. In the present communication, we wish to report the preparation and characterization of copolymers of sodium styrene sulfonate and sodium chloroacrylate. The study indicates a rather complex structure of the copolymer as a result of intramolecular cyclization reactions.

EXPERIMENTAL

Sodium styrene sulfonate (SSS) was twice recrystallized from ethanol. Sodium chloroacrylate (SCA) was obatined by neutralization of the twice sublimed chloroacrylic acid (m.p. 62°C). The initiator 2,2'-azobisisobutyronitrile (AIBN) was twice recrystallized from ethanol. A mixture of freshly quartz bidistilled water and analytical grade isopropanol (3:1 v/v) was used as polymerization media.

Copolymerization of SSS and SCA was carried out using AIBN and total monomer concentration 0.1M in water–isopropanol mixture. Polymerization tubes, thoroughly degassed, were kept at a constant temperature 70°C. The copolymerization was stopped by freezing the tube in liquid nitrogen; the frozen solution is then quickly melted and diluted. The diluted solutions were transferred quantitatively into a Spectrapor dialysis tubing (m.w. cutoff 2,000) and dialyzed until external solution was free of SSS and SCA. Dialyzed polymers were concentrated and dried in vacuo at 40°C.

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The IR analysis was made on dried potassium bromide pellets of 1.3 cm diameter containing 0.5 mg of copolymer sample in 200 mg of KBr. The pellets were prepared in a hydraulic press using a force of 10 tons, under vacuum. The spectra were recorded with a Beckman Model 4230 Spectrophotometer, using a scan rate of 150 cm^{-1}/min and a 0.3mm slit width.

NMR spectra of the polymer solutions in D_2O were recorded with a Bruker WP 270SY spectrometer at 270 MHz. Sulfur and chlorine elemental analysis was performed by Galbraith Laboraties, Inc.

RESULTS AND DISCUSSION

Copolymerization of SSS and SCA initiated by AIBN in water-isopropanol mixture resulted in a polymer which was analyzed for chlorine and sulfur content (Table 1).

Table 1. Copolymerization of SSS and SCA in water-isopropanol mixture.

| Sample No.	SSS in feed mole fr.	Yield, % (wt)	SSS in copolymer, mole fr.*)	Elemental Analysis, %		
				S	Cl	Cl**)
CONO 1	0.7	59	0.78	12.08	0.56	6.14
CONO 2	0.6	54	0.68	11.76	1.09	6.71
CONO 3	0.5	54	0.62	10.95	1.29	6.71
CONO 4	0.4	47	0.54	9.82	2.21	10.20
CONO 5	0.3	39	0.46	8.53	2.66	12.46
PSCA	–	40	–	–	0.67	27.24

Time: 3 hrs; temperature: 70°C

*) Determined by proton NMR analysis

**) Calculated on the basis of $(CH_2-\overset{Cl}{\underset{COONa}{C}}-)$ SCA structural unit

Analytical data for sulfur and chlorine could be used for the determination of the copolymer composition provided one knows the structure of repeating units in the copolymer.

The copolymer composition calculations based on idealized copolymer structure (I) yielded ambiguous results. Specifically, all the

$$\sim(-CH_2-\underset{\underset{SO_3Na}{\bigcirc}}{CH}-)_x-(-CH_2-\overset{Cl}{\underset{COONa}{C}}-)_y \qquad (I)$$
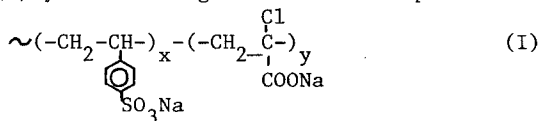
copolymers have a much lower chlorine content than one could expect from the structure (I). Homopolymerization of SCA using the same conditions also resulted in a polymer with a low chlorine content (Table 1). Marvel and coworkers (MARVEL 1940) mentioned the possibility of lactone formation during the polymerization of esters of chloroacrylic acid to explain the low halogen content of their products. Later, Minsk (MINSK 1950)
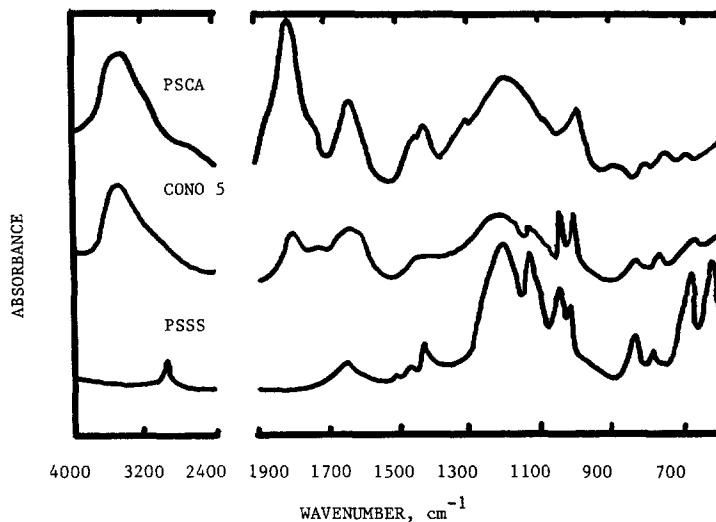

Figure 1. IR spectra of the homopolymers PSSS, PSCA and copolymer CONO 5 with 46% (mole) SSS content.

showed that poly(chloroacrylic acid) undergoes simultaneous esterification and lactonization when heated in alcohol solutions. Addition of water to the mixture increases carboxyl and lactone content.

To elucidate the structure of SSS-SCA copolymers, their IR spectra were analyzed together with the spectra of homopolymers poly(sodium styrene sulfonate) (PSSS) and poly(sodium chloroacrylate) (PSCA) obtained in water-isopropanol mixture (Figure 1). The spectra of the copolymers show almost all characteristic absorptions of the homopolymers with the exception of the strong peak at 1790 cm^{-1} of PSCA. This fact, as well as the appearance of new band near 1720 cm^{-1}, indicates that the copolymerization products are true copolymers and not mixtures of homopolymers. The carbonyl absorption in the region 1800-1500 cm^{-1} provides information about the structure of the SCA unit in the polymer (Figure 2). In this region PSCA IR spectrum shows a very strong absorption at 1790 cm^{-1} with a shoulder at 1760 cm^{-1} and a band at 1630 cm^{-1}. The absorption at 1790 cm^{-1} is characteristic of a carbonyl group part of a lactone structure (BELLAMY 1975). Upon lactonization, the most probable head-to-tail structure may yield either of the two forms (IIa or IIb) or a mixture
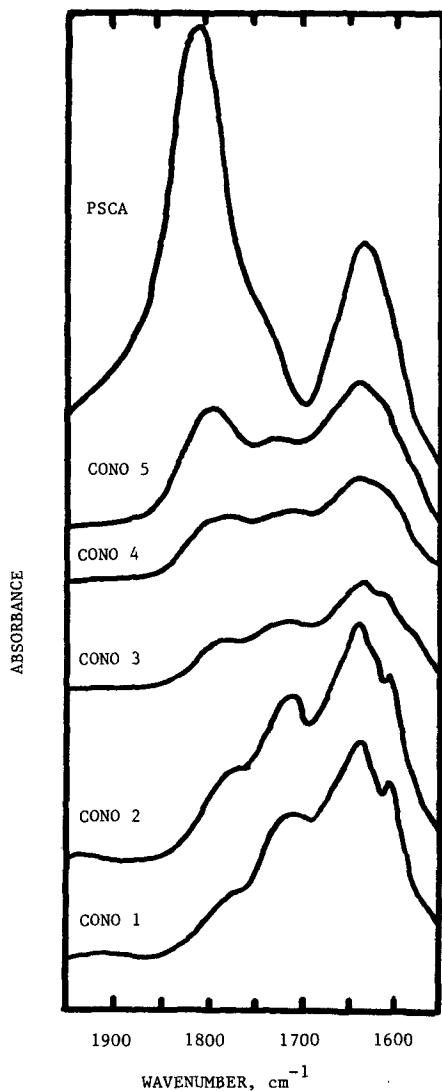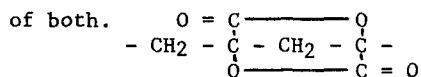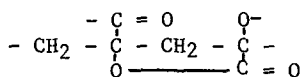
Figure 2.   Carbonyl band region in IR spectra of SSS–SCA
            homo- and copolymers.

of both. $O = C$ ——————— O $- C = O$ $O-$
           $- CH_2 - C - CH_2 - C -$ $- CH_2 - C - CH_2 - C -$
              O ——————— $C = O$ O ——————— $C = O$

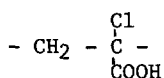   (IIa)   (IIb)

The carbonyl absorption band in five–membered lactone rings is located
usually near 1780 cm^{-1} (BELLAMY 1975) and due to dipolar interactions
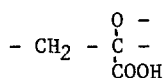of the α-oxygen or the α-chlorine could shift to higher frequencies.

The gradual shift of the band at 1760 cm^{-1} toward 1800 cm^{-1} with increase of SCA content in the copolymer is probably a direct consequence of the formation of the δ-lactone structures. With increased content of SSS units, the tendency toward lactone formation declined as evidenced by the absence of lactone carbonyl absorption above 1760 cm^{-1} in the spectrum of copolymer CONO 1 (Figure 2).

The mechanism of the reaction cannot be determined from the available data. Hydrogen chloride would be the by-product of the reaction.

The double absorption of the copolymers in the 1770-1600 cm^{-1} range may be assigned to the units with carboxylic groups (IIIa and IIIb), which could arise in a water-isopropanol mixture.
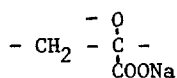
$$
\begin{array}{cc}
\quad\quad\text{Cl} & \quad\quad\text{O} - \\
- \text{CH}_2 - \text{C} - & - \text{CH}_2 - \text{C} - \\
\quad\quad\text{COOH} & \quad\quad\text{COOH} \\
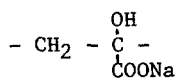\\
\text{(IIIa)} & \text{(IIIb)}
\end{array}
$$

It is known that the IR spectrum of poly(acrylic acid) shows a double carbonyl absorption at 1725 - 1740 cm^{-1} (SIMON 1958). The presence of a -chlorine or oxygen atom would increase the frequency of the carbonyl band. A very strong absorption in 3800 - 2400 cm^{-1} range, which was found in the spectra of all copolymers and PSCA, supports this assignment. The absorption in this region could also arise from hydroxyl groups (BELLAMY 1975). The formation of hydroxyl groups due to dehalogenation reaction was observed for poly(chloroacrylic acid) (MINSK 1950) on heating in alcohol-water soultion.
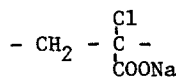
The peak at 1630 cm^{-1}, though it overlapped with the absorption of SSS unit for the copolymers, might be seen clearly in the spectrum of PSCA. The carbonyl absorbence in this region is usually associated with salts of carboxylic acid in the 1610 - 1550 cm^{-1} range (BELLAMY 1975). There again such electronegative substituents as oxygen (IVa and IVb) or chlorine (IVc) give rise to higher carbonyl frequency.

$$
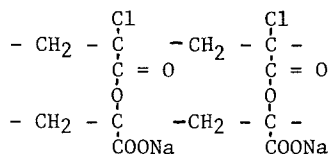\begin{array}{ccc}
\quad - \text{O} & \quad\quad\text{OH} & \quad\quad\text{Cl} \\
- \text{CH}_2 - \text{C} - & - \text{CH}_2 - \text{C} - & - \text{CH}_2 - \text{C} - \\
\quad\quad\text{COONa} & \quad\quad\text{COONa} & \quad\quad\text{COONa} \\
\\
\text{(IVa)} & \text{(IVb)} & \text{(IVc)}
\end{array}
$$

In addition to the structures discussed above, formed as a result of intramolecular reactions, there is a possibility of intermolecular

esterification (V) which would lead to an insoluble

$$
\begin{array}{ccc}
& Cl & Cl \\
- CH_2 - & C & - CH_2 - \ C - \\
& C = O & C = O \\
& O & O \\
- CH_2 - & C & - CH_2 - \ C - \\
& COONa & COONa
\end{array}
$$

(V)

polymer. From solubility studies of PSCA and SSS-SCA copolymers in water, it can be concluded that intermolecular reactions do not play a significant role in water-isopropanol mixtures at 70°C. Furthermore, the presence of isopropanol could lead to esterification of isolated carboxylic groups (VI) (MINSK 1950).

$$
\begin{array}{c}
- O \\
- CH_2 - C - \\
O = C - OC_3H_7
\end{array}
$$
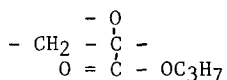
(VI)

The extent of the esterification is difficult to estimate on the basis of IR data. The isopropyl ester carbonyl absorption would overlap with other carbonyl bands. Proton NMR provides the evidence of isopropyl groups in these polymers due to the prominence of the resonance peak. Indeed, proton NMR spectrum of PSCA (Figure 3) shows signals of low intensity in the methyl resonance region. In the NMR spectra of the copolymers, this absorption peak is hardly noticeable. In the case of SCA homopolymer, however, NMR analysis shows that the esterification reaction takes place but not to a large extent.

The content of SSS and overall acrylic structures may be evaluated from proton NMR spectra of the copolymer (Figure 3). Phenyl protons of SSS unit absorb in 5-8 ppm range, while signals of all backbone protons are in 0.5-3.8 ppm region. Since the measurements were conducted in D_2O solutions, there is no interference of hydroxyl protons from the converted SCA units due to deuterium exchange. The composition of the SSS-SCA copolymers was determined from proton NMR spectra using the relation: $m_1/m_2 = 2S_1/(4S_2 - 3S_1)$, where m_1 and m_2 are molar fractions of M_1 (SSS) and M_2 (SCA) monomer units in the copolymer, respectively; S_1 is the area of the peaks corresponding to the absorption of SSS aromatic protons, S_2 is the peaks area of all backbone protons (SSS and SCA). The composition of the copolymers obtained in water-isopropanol mixtures is given in Table 1.

The reactivity ratios for SSS and SCA are calculated from composition
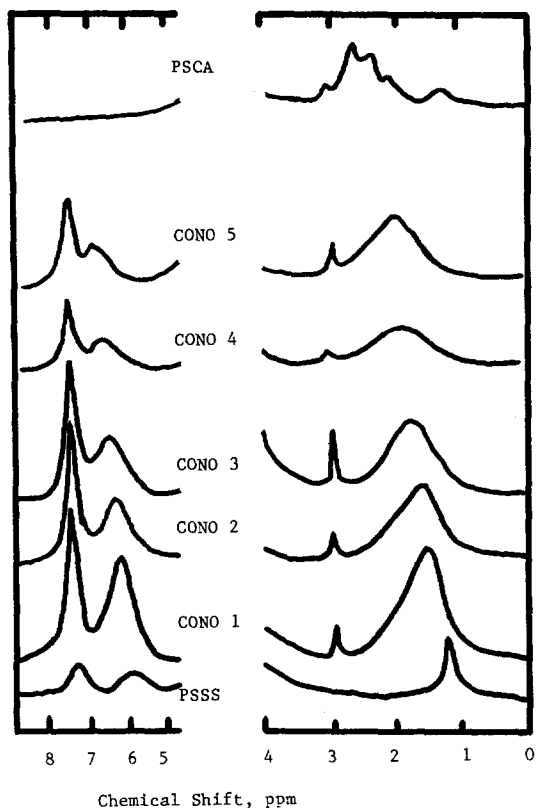
Figure 3. Proton NMR spectra of PSSS, PSCA and SSS-SCA
copolymers.

data for the copolymers given in Table 1, using the integrated copolymer
equation (TIDWELL 1965, 1970). Monomer reactivity ratios for M_1 = SSS
and M_2 = SCA were found as follows: r_1 = 1.39 ± 0.14 and r_2 = 0.26 ± 0.05,
respectively.

The study shows that copolymerization of SSS and SCA in aqueous iso-
propanol solutions results in complex copolymer structures. The predominant
reaction taking place is the dehalogenation reaction of the chloroacrylate
unit, which results in the intramolecular cyclization leading to lactone
formation. The mechanism of this transformation is not understood at
present. Monomer reactivity ratios were determined using NMR data. It
can be seen from thus estimated copolymerization parameters that SSS
monomer molecules add faster to both SSS and SCA radicals than SCA mono-
mer molecules.

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