

Copolymerization of Sodium 2-Acrylamido-2-methylpropanesulfonate with Vinyl Acetate

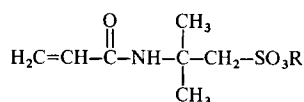
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Recently, copolymerizations of 2-acrylamido-2-methylpropanesulfonic acid (**1a**) with some vinyl monomers have been investigated for commercial applications. It can easily be copolymerized, especially with acrylonitrile or acrylamide, and the resultant copolymers have been found to be useful for many applications, including the improvement of the dyeing property of synthetic fibers¹⁾, endowing with the hydrophilicity to acrylic fibers²⁾, and preparation of water soluble copolymers based on polyacrylamide³⁾.

The copolymers of **1a** with vinyl acetate and with vinyl alcohol, derived therefrom, are also expected to be useful for some applications, for example, as a polymeric surfactant and flocculation agent, as well as a catalyst for acid hydrolysis reactions⁴⁾, although the copolymerization has seldom been reported so far.



1a: R = H

b: R = Na

This paper describes first results of the copolymerization of the sodium salt of **1a** (**1b**) with vinyl acetate and preliminary tests of its application.

Experimental Part

Reagents: Vinyl acetate was distilled under ordinary pressure. Methanol was dehydrated by passing a molecular sieve 3A column. **1a** was commercially available (from Nitto Kagaku Kogyo, Tokyo, Japan) and like the other reagents it was used without further purification.

Copolymerization: A methanol solution of **1a** was strictly neutralized with a solution of sodium hydroxide in methanol by means of a pH-meter, and vinyl acetate was added together with benzoyl peroxide (0.01 g) as initiator. The total amount of monomers and methanol were 0.10 mol and 120 ml, respectively. The reaction mixture was heated at 60°C under nitrogen to polymerize. After a given time, *p*-quinone was added to the solution, which was purified by dialysis in pure water for three days and then concentrated and dried *i.vac.*

Estimation of copolymer composition: The copolymer composition was estimated by two methods: the amount of vinyl acetate monomeric units in the copolymer was determined by the sulfuric acid hydrolysis-steam distillation method⁵⁾, and the monomeric units of **1b** by ion-exchanging of the copolymer solution, passing an Amberlite 120B column and subsequent titration with sodium hydroxide solution. The two methods gave practically the same values for the amount of monomeric units in the corresponding copolymer.

Estimation of the maximum amount of solubilized benzene: As an index of surface activity, the maximum amount of solubilized benzene in the aqueous solution of the copolymer was estimated. Benzene was added dropwise into the aqueous solution of the copolymer with stirring, and the amount of benzene just before turbidity appeared was considered as the maximum amount of solubilized benzene.

Flocculation test: The flocculation effect of the copolymer of vinyl alcohol and **1b** deriving from the copolymer of vinyl acetate and **1b**, towards a bentonite suspension, was examined. The copolymer of vinyl alcohol and **1b** contained only a little amount of vinyl acetate monomeric units (less than 5 mole-% based on vinyl alcohol monomeric units). 20 ml of the copolymer solution was added to 80 ml of 1.0 wt.-% of a bentonite suspension in a 100 ml graduated cylinder equipped with a cap. After having well shaken it was left at room temperature and the sedimentation rate was measured.

Results and Discussion

Fig. 1 shows the rates of the copolymerization of **1b** with vinyl acetate for several mole fractions of **1b** in the monomer feed. The conversion increases proportionally to the reaction time over the observed range of conversion. The initial reaction rate was calculated from the slope of the resulting straight line.

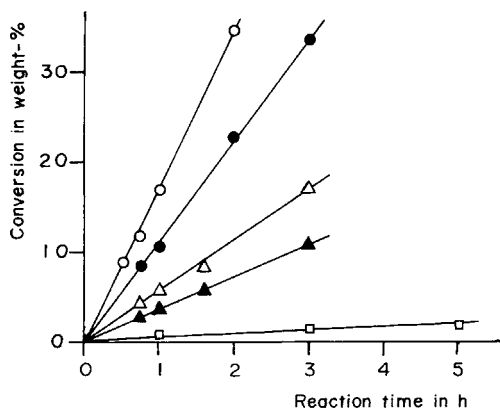


Fig. 1. Relationship between the conversion of the copolymerization of sodium 2-acrylamido-2-methylpropanesulfonate (**1b**) with vinyl acetate and reaction time at 60°C. Mole fraction of **1b** in the monomer feed: (○): 0.3; (●): 0.2; (△): 0.1; (▲): 0.1; (□): 0

Fig. 2 shows how the initial reaction rate and the mole fraction of monomeric units of **1b** in the resulting copolymer change with the mole fraction of **1b** in the monomer feed. It can be seen that the initial reaction rate increases proportionally to the mole fractions of **1b**, and that the mole fraction of monomeric units of **1b** in the resulting copolymer increases considerably in the lower range and moderately in the higher range of mole fractions of **1b**, with increasing mole fraction of **1b** in the monomer feed.

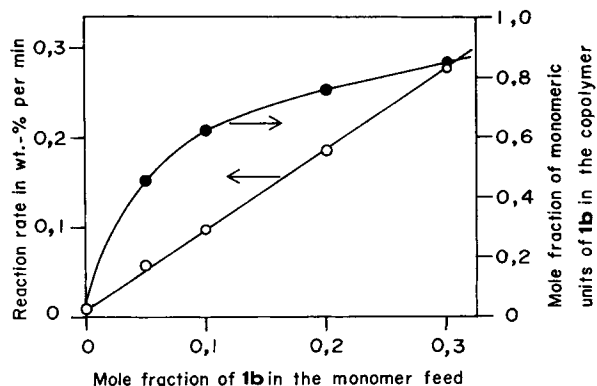


Fig. 2. Changes in initial reaction rate of the copolymerization of **1b** with vinyl acetate (○), and in mole fraction of monomeric units of **1b** in the resulting copolymer (●), with increasing mole fraction of **1b** in the monomer feed

From the data obtained in the observed range of conversion (less than 12%), the monomer reactivity ratios in the copolymerization (M_1 = vinyl acetate, M_2 = **1b**) were calculated. Fig. 3 shows the Fineman-Ross plot⁶ of these data. A good straight line is obtained (the correlation coefficient being 0,989). The reactivity ratios are

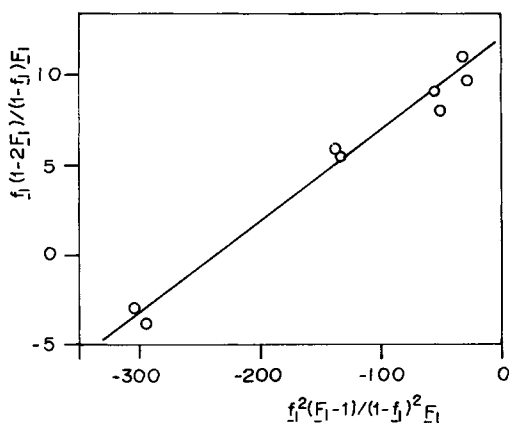


Fig. 3. The Finemann-Ross plot of the copolymerization data of **1b** with vinyl acetate:

$$f_1(1-2F_1)/(1-f_1)F_1 = r_2 + [f_1^2(F_1-1)/(1-f_1)^2 F_1] r_1$$

where f_1 and F_1 are mole fractions of vinyl acetate in the monomer feed and vinyl acetate monomeric units in the resulting copolymer. r_1 and r_2 are reactivity ratios of vinyl acetate and **1b**, respectively

$r_1 = 0,05$ (error for 95% confidence limit: $\pm 0,01$) and $r_2 = 11,6$ ($\pm 0,8$), respectively, showing **1b** to be very preferentially copolymerized. These values are in the range expected from the monomer reactivity ratios in the copolymerizations of **1b** and vinyl acetate with some acrylic monomers²⁾.

Preliminary tests on the application of the resulting copolymers were carried out. First, as an index of surface activity, the maximum amount of solubilized benzene in the aqueous solution of the copolymer was evaluated. The copolymers were easily soluble in water but not in benzene. Fig. 4 shows the relationship between the maximum amount of solubilized benzene and the mole fraction of monomeric units of vinyl acetate in the copolymer, keeping the concentration of the copolymer constant at 2,5 wt.-%. The maximum amount of solubilized benzene increases with increasing mole fraction of monomeric units of vinyl acetate, although the points are rather scattered.

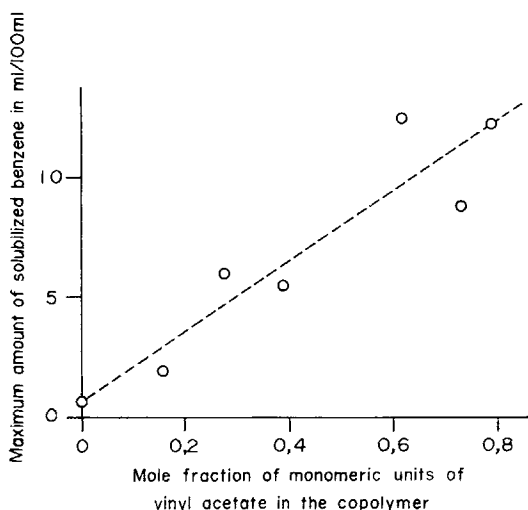
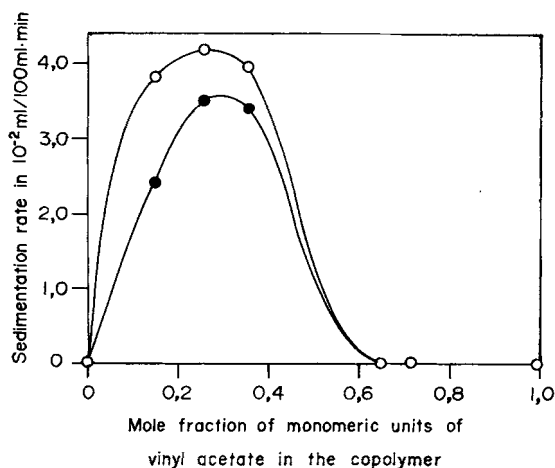


Fig. 4. Relationship between the maximum amount of solubilized benzene in the aqueous solution of the copolymer of **1b** with vinyl acetate and the mole fraction of monomeric units of vinyl acetate in the copolymer, keeping the concentration of the copolymer constant at 2,5 wt.-% at room temperature

This result indicates that the copolymers may have some surfactant ability, although, strictly speaking, the solubilization of benzene is not a direct proof of surfactant ability.

The flocculation effect of the copolymer of vinyl alcohol and **1b**, deriving from the copolymer of vinyl acetate and **1b** by saponification, towards a bentonite suspension, was examined. Fig. 5 shows the relationship between the sedimentation rate and the mole fraction of monomeric units of vinyl alcohol in the copolymer, keeping the concentration of the copolymer constant at 0,4 and 0,8 g/100 ml. The sedimentation rate is accelerated by the addition of the copolymer having mole fractions of monomeric units of vinyl alcohol in the range of 0,1 to 0,5, although poly(vinyl alcohol), poly(**1b**), and the copolymer having mole fractions of monomeric units of vinyl alcohol higher than 0,6, have no effect on the flocculation of a bentonite suspension.

Fig. 5. Relationship between the sedimentation rate of a 0,8 wt.-% bentonite suspension and the mole fraction of monomeric units of vinyl alcohol in the copolymer of **1b** with vinyl alcohol, at room temperature. Amount of the copolymer added: (●): 0,4 g/100 ml; (○): 0,8 g/100 ml



This effect, obtained by the addition of the copolymer, but not observed upon addition of either of the corresponding homopolymers, is interesting although it is not so outstanding as compared with that obtained by the addition of aluminium sulfate which gave a sedimentation rate of 0,39 ml/100 ml · min at a concentration of 0,1 wt.-%.

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