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Polymerization and Copolymerization of Allyl Allyl Sulfonate*

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SUMMARY

Allyl allyl sulfonate (AAS) has been polymerized under the influence of azobisisobutyronitrile to low molecular weight polymers containing cyclic structures. This is in contrast to the behavior of allyl ethane sulfonate (AES) and of propyl allyl sulfonate (PAS) which did not polymerize under the same conditions. AAS has been copolymerized with styrene, methyl acrylate, and vinyl acetate. The following copolymerization reactivity factors have been found:

r_{AAS} 0.01 ± 0.01 $r_{styrene}$ 13 ± 1
r_{AAS} 0.37 ± 0.09 $r_{methyl\ acrylate}$ 5.3 ± 0.7
r_{AAS} 1.54 ± 0.08 $r_{vinyl\ acetate}$ 0.5 ± 0.15

The results indicate that AAS has a higher reactivity than AES or PAS.

INTRODUCTION

Polymerization of monomers containing two double bonds and leading to linear polymers containing cyclic structures is well known under the name

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of cyclopolymerization [1-5]. In most of the monomers which have been studied the double bonds were situated in such a manner that five- or six-membered rings were formed. Several authors observed that the number of cyclic recurring units in the polymer is markedly higher than what would be expected from theoretical calculations [6] or from the polymerization behavior of monomers in which the same kind of double bonds are isolated [7-9]. The reactivity of the allyl group in allyl acrylate [7] and in allyl ethene sulfonate [8], for instance, was markedly higher than that of monomers in which the allyl function alone was present.

The polymerization of allyl allyl sulfonate (AAS) is described in this paper. In order to find out if the reactivity of the double bonds in this monomer is normal or enhanced, copolymerization with several vinyl monomers was studied and compared to the polymerization and copolymerization behavior of propyl allyl sulfonate and of allyl ethane sulfonate.

RESULTS AND DISCUSSION

AAS (I) was synthesized by reaction of allyl sulfonyl chloride with allyl alcohol in the presence of pyridine:

$$CH_2{=}CH{-}CH_2SO_2Cl + CH_2{=}CH{-}CH_2OH \xrightarrow[\text{in } CH_2Cl_2]{\text{pyridine}}$$

$$CH_2{=}CH{-}CH_2SO_2OCH_2{-}CH{=}CH_2$$

(I)

AAS has been polymerized under the influence of azobisisobutyronitrile (AIBN) in benzene. As shown in Fig. 1, the polymerization is rather slow but yields of more than 80% can be obtained. Poly(AAS) is a white substance with a softening point of 140°C. It is soluble in acetone, dimethylformamide, dimethylsulfoxide, and sulfolane; insoluble in benzene, chlorinated hydrocarbons, and ethers. Formula II shows the general structure of poly(AAS).

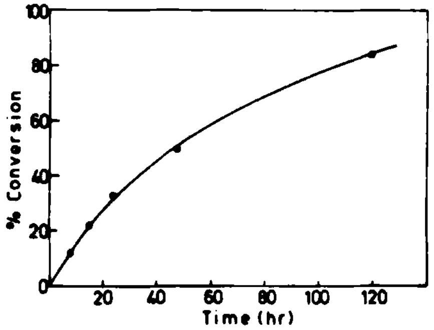
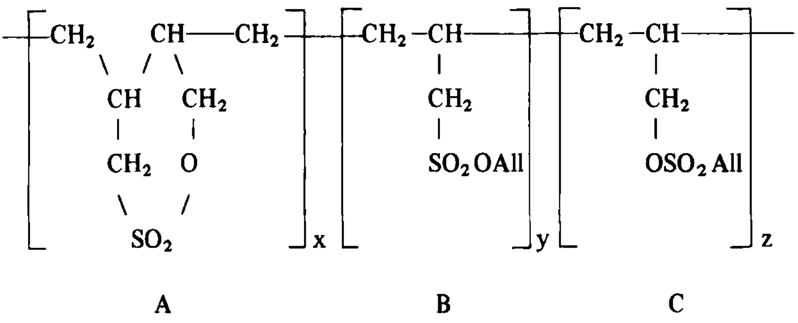


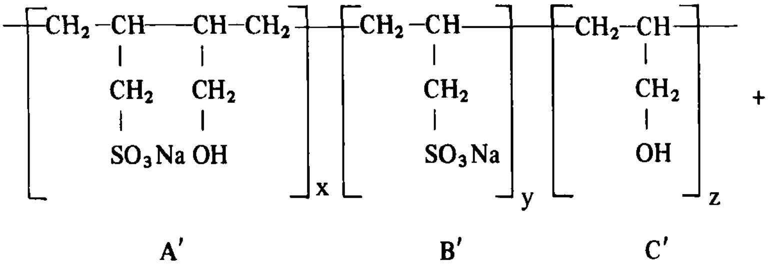
Fig. 1. Time conversion curve of the polymerization of AAS. [M] = 1.18 mole l^{-1} in benzene with AIBN as catalyst. [AIBN] = 0.05 mole l^{-1}.



II

Cyclic units A are formed by alternating intermolecular and intramolecular propagation steps. They have been formulated as six-membered rings although seven-membered ring structures are also possible. Units B are formed when the allyl radical of the sulfonic part propagates intermolecularly, and units C when the allyl radical of the alcohol part propagates intermolecularly. It is possible that some other structures formed by hydrogen transfer from an allyl group to a radical are also present in the polymer, but it was not possible to distinguish them from the units of general Formula II by chemical or spectroscopic methods.

In order to determine the composition of the polymer, the amount of allylic groups in the polymer was determined. Therefore the polymer was hydrolyzed by aqueous sodium hydroxide and gave a mixture of water-soluble products III. For each unit B in the original polymer, a molecule of allyl alcohol is formed, and for each unit C, a molecule of sodium allyl sulfonate.



$-[CH_2-CH(CH_2SO_3Na)-CH(CH_2OH)-CH_2]_x-[CH_2-CH(CH_2SO_3Na)]_y-[CH_2-CH(CH_2OH)]_z- \; +$

$yCH_2{=}CHCH_2OH + zCH_2{=}CHCH_2SO_3Na$

III

The remaining polymer has the structure of a copolymer of sodium allyl sulfonate and allyl alcohol. Bromination of the aqueous solution thus obtained gives the total amount of allylic groups present in the polymer. The amount of units B were determined as follows: After hydrolysis of the polymer in aqueous sodium hydroxide and neutralization of the excess sodium hydroxide with hydrogen chloride, water and other volatile components were removed by freeze drying of the solution. The only volatile substance formed by hydrolysis is allyl alcohol and from the amounts of polymer, sodium hydroxide, and hydrogen chloride and from the weight of the residue it was calculated how much allyl alcohol was present.

Table 1 shows the results of a series of experiments carried out to determine the influence of the monomer concentration on the number of cyclic units in the polymer. From Table 1 it follows that the number of cyclic

Table 1. Polymerization of AAS.[a] Influence of Monomer Concentration on Polymer Structure

[M] (mole/l^{-1})	Time (hr)	Yield (%)	Average [M]	%B + C	%C	Av MW
0.28	46.5	32.6	0.23	34.3	19.8	–
0.74	15	20.1	0.67	41.4	20.5	–
1.57	8.25	17.0	1.44	45.4	22.1	–
4.73	8.25	32.0	3.97	50.7	25.2	1100
8.94	4.5	24.0	7.72	52.6	27.0	1200

[a] Catalyst: AIBN. Solvent: benzene. Temperature: 60°C.

units varies from 47.5 to 65.7 mole % depending on the monomer concentration. The ratio of recurring units B and C remains practically constant between values of 0.90 and 1.02 except for the lowest monomer concentration.

The number of cyclic recurring units increases with decreasing monomer concentration because cyclic units are formed by a monomolecular reaction whereas units B and C are formed by a bimolecular propagation step. As expected for an allylic monomer, the molecular weights of the polymers were low. The influence of the temperature on the ratio of cyclic units to unsaturated units is shown in Table 2. By plotting log f_{unsat}/f_{cycl} against 1/T a straight line was obtained, the slope of which gave the difference in activation energy for cyclization (E_{cycl}) and for propagation of a noncyclized radical with another monomer molecule (E_{prop}):

$$E_{cycl} - E_{prop} = 1.1 \text{ kcal/mole}$$

This value is lower than the values reported for other cyclopolymerizations [4].

Table 2. Influence of Temperature on the Structure of Poly(AAS)[a]

Temp. (°C)	Time (hr)	Yield (%)	% Cyclic units
38	48	9	52
60	8	12	55
80	7	9	61

[a] Monomer concentration: 1.50 mole l^{-1}. [AIBN] = 0.075 mole l^{-1}.

The polymerization behavior of AAS is in sharp contrast to the behavior of allyl ethane sulfonate (AES) (IV) and propyl allyl sulfonate (PAS) (V). Indeed, both substances

$CH_3CH_2SO_2OCH_2CH{=}CH_2$ IV

$CH_2{=}CHCH_2SO_2OCH_2CH_2CH_3$ V

did not polymerize when treated with AIBN in benzene at 60°C during 48 hr. Also, an equimolar mixture of IV and V did not polymerize under the same conditions.

Copolymerizations

AAS has been copolymerized with styrene, methyl acrylate, and vinyl acetate. Figure 2 shows the copolymerization curves. From these curves the monomer reactivity ratios were derived by the "intersecting slopes" method. They are summarized in Table 3.

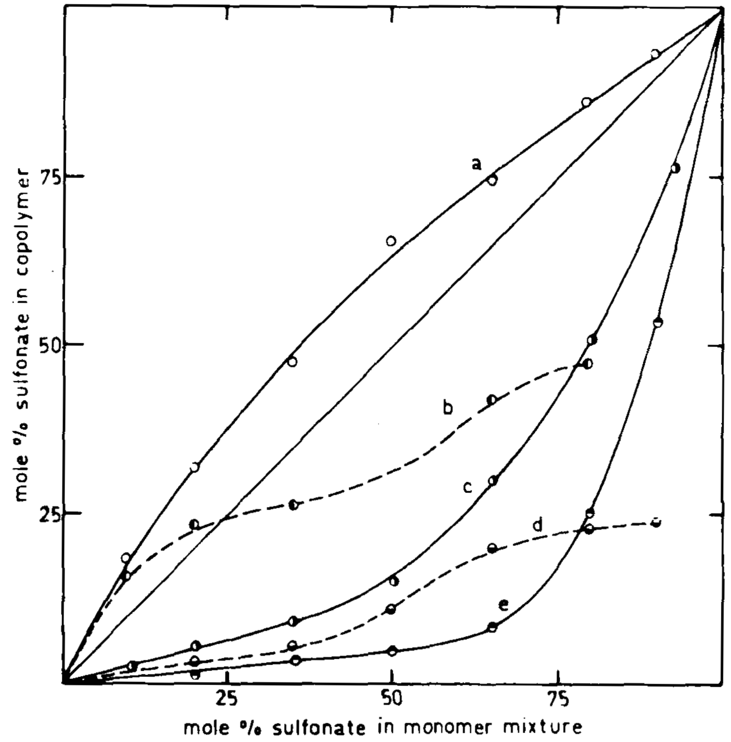


Fig. 2. Copolymerization of AAS: (a) with vinyl acetate; (b) mole % of unsaturation in the AAS-vinyl acetate copolymers; (c) with methyl acrylate; (d) mole % of unsaturation in the AAS-methyl acrylate copolymers; (e) with styrene.

Table 3. Monomer Reactivity Ratios in Copolymerizations of AAS (M_1)

M_2	r_1	r_2
Styrene	0.01 ± 0.01	13 ± 1
Methyl acrylate	0.37 ± 0.09	5.3 ± 0.7
Vinyl acetate	1.54 ± 0.08	0.50 ± 0.15

The dotted lines in Fig. 2 show the mole fraction of unsaturated units in the methyl acrylate and vinyl acetate copolymers. In both cases the ratio of cyclic to linear units of AAS in the copolymer increases considerably with increasing AAS fraction in the monomer mixture. The AAS-styrene copolymers could not be analyzed because they could not be hydrolyzed to water soluble substances.

In order to find out if the allyl groups in AAS have an increased reactivity compared to that of isolated allyl groups, copolymerizations of AES (IV) and of PAS (V) with the same comonomers have been carried out. The results, summarized in Table 4, show that AAS is more reactive than AES or PAS in copolymerizations with styrene and with vinyl acetate and roughly equally reactive,in copolymerization with methyl acrylate.

CONCLUSION

The experiments described in this paper show that allyl allyl sulfonate is capable of forming low molecular weight polymers containing cyclic structures. This behavior is in sharp contrast to the nonpolymerizability of allyl ethane sulfonate and propyl allyl sulfonate. It is an example of a 1,7-diene in which the reactivity of the double bonds is greater than that observed in analogous monomers in which only one double bond is present. In copolymerizations also allyl allyl sulfonate sometimes shows an increased tendency to enter into the copolymer in comparison with monomers where only one allylic group is present.

Table 4. Copolymerizations of AAS, AES, and PAS[a]

Monomers	Time (hr)	Yield (%)	Mole % sulfonate in copolymer
AAS-styrene	15	7.5	4.9
AES-styrene	24	5	0
PAS-styrene	15	9.8	3.3
AAS-methyl acrylate	0.5	10	17.4
AES-methyl acrylate	1	9	12.6
PAS-methyl acrylate	1	9	14.4
AAS-vinyl acetate	3	9.5	65.4
AES-vinyl acetate	24	0	–
PAS-vinyl acetate	24	0	–

[a] Equimolar amounts of both comonomers. Total monomer concentration: 1.2 mole l^{-1}. [AIBN] = 0.06 mole l^{-1}. Solvent: benzene. Temperature: 60°C.

EXPERIMENTAL

Synthesis of Monomers

Allyl allyl sulfonate (I). Pyridine (12 ml) was added dropwise to a solution of 21.4 g of allyl sulfonyl chloride and 8.7 g of allyl alcohol in 100 ml of methylene chloride. The stirred mixture was kept between 0 and 5°C by external cooling. The mixture was washed with 0.1 N hydrogen chloride and with water, and dried over sodium sulfate. After evaporation of the solvent, fractionation yielded 14.5 g of AAS (60%) ($bp_{0.02\ mm}$ 62-65°C).

$C_6H_{10}O_3S$ (MW 162). Calculated: C, 44.5; H, 6.18; S, 20.2. Found: C, 44.6; H, 6.11; S, 19.8

Allyl ethane sulfonate (IV) has been described previously [8].

Propyl allyl sulfonate (V) was synthesized starting from allyl sulfonyl chloride and propyl alcohol as described for allyl allyl sulfonate. It is a colorless liquid with $bp_{0.02\ mm}$ 78-80°.

$C_6H_{12}O_3S$ (MW 164). Calculated: C, 43.8; H, 7.31; S, 19.4. Found: C, 43.4; H, 6.92; S, 20.0.

POLYMERIZATIONS

Polymerizations were carried out in glass vials of 10-50 ml capacity with benzene as solvent and AIBN as catalyst. Before polymerization, the vials containing the solution of monomer(s) and catalyst were connected to a high-vacuum line, degassed twice, and melted off under high vacuum. The vials were then transferred into a waterbath thermostated at the desired temperature.

Poly(AAS) precipitated from the solution and was isolated by filtration. It was purified by dissolving in acetone and precipitating in benzene.

Copolymers from AAS and styrene remained in solution and were isolated by pouring the solution into a tenfold volume of methanol followed by filtration of the precipitate obtained. AAS-vinyl acetate and AAS-methyl acrylate copolymers were isolated by pouring the solution into a tenfold volume of n-hexane. All copolymers were purified by dissolving in acetone and reprecipitating in n-hexane.

Copolymers composition was determined by sulfur analysis (Schöninger combustion method). Molecular weights were determined by means of a Mechrolab Vapor Pressure Osmometer with dimethylformamide as solvent.

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