

# REACTION OF METHACRYLALDEHYDE-STYRENE COPOLYMER IV.\* REACTION IN THE PRESENCE OF AMINE SALTS AND CARBOXYLIC ACID

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The crosslinking reaction of the copolymers of styrene and methyl- and 2-ethylacrylaldehyde in the presence of the catalytic system carboxylic acid-primary amine was investigated. An increase in the substituent at the  $\alpha$ -position to the carbonyl group leads to a decrease in its reactivity and stability of the crosslink. The insoluble products thus obtained were subjected to thermal degradation which led to breaking of the crosslinks and enabled the polymers to dissolve again. The mechanism of decomposition of the polymer network was suggested, and the activation energy of the reaction determined.

It has been stated in earlier papers<sup>1,2</sup> of this series that the methacrylaldehyde-styrene copolymer becomes crosslinked in the presence of carboxylic acid and a primary amine with formation of three-dimensional gels. The effect of the individual components of the system on the reaction course was investigated and the reaction mechanism was suggested. In another paper<sup>3</sup> the degradation of these gels was investigated, and the mechanism of splitting was discussed. This paper is devoted to the problem of the effect of the  $\alpha$ -substituent on aldehyde on the formation and splitting of the gel, to an investigation of the course of the gelation reaction based on the change in viscosity, and to the effect of the system components on this reaction.

## EXPERIMENTAL

The purification of monomers (methacrylaldehyde, styrene, 2-ethylacrylaldehyde) and the preparation of copolymers have been described earlier<sup>1,3</sup>. The salts of butyl amine and 2-aminoethanol with acetic acid were obtained by a reaction of an equimolar amount of the respective amine and acid in toluene solution at room temperature. After completion of the reaction the salt, which is soluble in toluene to a limited extent only (solubility of the butyl amine salt is 0.44 mol/100 ml at 20°C, that of the 2-aminoethanol salt is zero), becomes separated. Both salts are viscous liquids, turning yellow in the air. The white crystalline butylammoniumphenyl acetate was prepared by a reaction with an excess of butyl amine, which afterwards was extracted with ether. The identity of the salts thus obtained was proved by their infrared spectra.

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The gelation of the polymer solutions was carried out in thermostated sealed test tubes. The gel time is a subjectively recorded time after which a glass bead,  $4.0 \pm 0.1$  mm in diameter and  $0.0892 \pm 0.0014$  g by weight, does not pass through the contents of the test tubes any more. The gel was (if not mentioned otherwise) extracted several times with ethanol and dried at  $20^\circ\text{C}$  : 6 Torr to constant weight. The determination of the degree of swelling and gel content has been described<sup>1</sup>.

The viscosity of the solution was calculated from Stokes' relationship

$$\eta = \frac{2}{9} \frac{gr^2(s - \rho)}{v_m}, \quad (1)$$

where  $\eta$  is viscosity in cP,  $g$  is gravity acceleration,  $r$  is the bead radius (0.2 mm),  $s$  is the solvent density,  $\rho$  is the bead density ( $2.663 \text{ g/cm}^3$ ),  $v_m$  is the limiting velocity determined from the relationship  $v_m = h/t$  ( $h$  is the path of the bead, 3.38 cm in regions remote from the gel point and 0.94 cm in those close to it;  $t$  is the time needed for covering this distance). The limiting viscosity number of the starting copolymer  $[\eta]_0$  was determined in an Ubbelohde viscometer in benzene solution at  $30 \pm 0.1^\circ\text{C}$ . The limiting viscosity number of the gelating product before the gel point was determined under the same conditions in a solution obtained by transferring the contents of the test tube into toluene with 2% by vol. of ethanol.

The degradation of insoluble samples of poly(methacrylaldehyde-co-styrene) was carried out in the absence of the solvent at  $100\text{--}190^\circ\text{C}$  in glass ampoules sealed after oxygen had been completely removed. After degradation the solution was reprecipitated from benzene solution into ethanol and dried *in vacuo*.

## RESULTS AND DISCUSSION

It has been found earlier<sup>2</sup> that poly(methacrylaldehyde-co-styrene) undergoes cross-linking by a reaction catalyzed with the salt of acetic acid and butylamine ( $S_1$ ). It has also been established that already a salt concentration lower by three orders of magnitude with respect to methacrylaldehyde is sufficient to give rise to a gel within a comparatively short time. If the catalyst is used in an amount comparable to the concentration of methacrylaldehyde (Fig. 1), the dependence of the gel time on its concentration is linear for both salts under investigation. It is obvious that with increasing concentration of the salt partly soluble in toluene the composition of the system changes, and the reaction conditions are more remote from the optimum which has been defined earlier<sup>2</sup>. For the salt of acetic acid and 2-aminoethanol ( $S_2$ ) which is virtually insoluble in toluene the dependence is quite different. After a concentration of  $S_2$  of approximately  $1.5 \cdot 10^{-2}$  mol/mol of aldehyde (A) has been reached, the gel time ( $t_g$ ) remains constant, which may be due to the fact that the solution is divided into two phases, and a constant catalyst concentration is maintained in the polymer solution, or a phase boundary with a constant area<sup>1</sup> is formed. The addition of ethanol leads to a considerable extension of the gel time, as is documented by the following data (participation of aldehyde in the copolymer  $c_A = 20.6\%$ ,  $[\eta]_0 = 0.51 \text{ dl/g}$ ,  $[S_2]/[A] = 0.13 \cdot 10^{-4}$ , temperature  $T = 50^\circ\text{C}$ ):

$([\text{EtOH}]/[\text{A}]) \cdot 10^3$ :	0	1.73	4.08	5.78
$t_g$ , min	2.5	300	441	531

Retardation is due to the proton transfer by alcohol and to the termination of the polymerization reaction, or also to the formation of semiacetal bonds and a decrease in the concentration of the reactive aldehyde groups.

The course of gelation of the solution may be followed by measuring its viscosity during the reaction. It can be seen from Fig. 2 that at the beginning the viscosity does not change, and only near the gel point a steep increase is observed. Within brief time viscosity reaches infinite value; the contents of the reaction vessel becomes solidified. If one simultaneously follows the changes in the limiting viscosity number of the copolymer, its increase is easy to see (Fig. 2). However, the methods used do not allow the reaction to stop in the immediate proximity of the gel point; neither do they allow the determination of the limiting viscosity number of critically branched

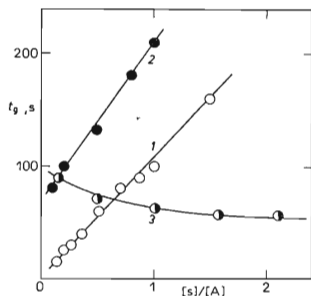


FIG. 1

Gel Time of Poly(methacrylaldehyde-co-styrene) as a Function of the Catalyst Concentration at 50°C

Copolymers (symbols *cf.* the text): 1  $c_A = 20.3\%$  by wt.,  $[\eta]_0 = 0.51$  dl/g, catalyst-salt  $S_1$ ; 2  $c_A = 16.8\%$  by wt.,  $[\eta]_0 = 0.44$  dl/g, catalyst-salt of phenylacetic acid and butylamine; 3  $c_A = 21.9\%$  by wt.,  $[\eta]_0 = 0.50$  dl/g, catalyst-salt  $S_2$ .

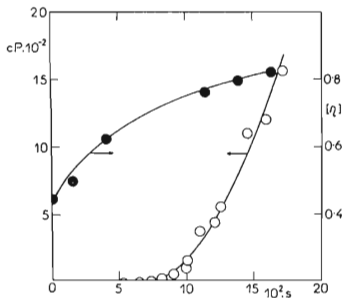


FIG. 2

Viscosity and Limiting Viscosity Number of the Gelatinizing Solution of Poly(methacrylaldehyde-co-styrene)

$c_A = 20.6\%$  by wt.,  $[\eta]_0 = 0.51$  dl/g,  $[S_1]/[A] = 2.90 \cdot 10^{-2}$ .

macromolecules. The gelation can be performed by the procedure described above also at low temperatures ( $-25^{\circ}\text{C}$ ), but the solution of the copolymer itself is very viscous, and the measurements of the gel time are inaccurate.

A remarkable tendency to the formation of crosslinked gels may be documented by an example of the copolymer methacrylaldehyde-butadiene. The crosslinking reaction proceeds spontaneously and – as shown in Fig. 3 – the changes in the limiting viscosity number adequately describe the process occurring in the system. The initial slow decrease represents the formation of branched macromolecules which later become larger units, and the limiting viscosity number increases again. The butadiene structure units in the chain allow a better flexibility of the latter; at the same time, the negative steric effect of the bulky substituent is not operative as in the case of poly(methacrylaldehyde-co-styrene); consequently, the carbonyl group is more accessible to mutual reactions. The further changes in the limiting viscosity number cannot be measured any more, since the insoluble phase becomes separated.

It was observed that in some cases also the copolymers of methacrylaldehyde and styrene after separation and drying were insoluble in common solvent<sup>3</sup>. In contrast with the copolymer acrylaldehyde-styrene<sup>4</sup>, these crosslinked products may be made soluble by heating to a higher temperature. From the temperature dependence of the time needed for solubilization of the insoluble copolymer ( $t_d$ ), and assuming

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$T_d, ^{\circ}\text{C}$	100	110	120	130
$t_d, \text{min}$	45	20	15	9

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that on attaining solubility the degree of the degradation reaction is always the same, the apparent activation energy of degradation was calculated and found to be 14.4 kcal/mol.

The investigation of the limiting viscosity numbers of degraded gels at 140–160°C shows that the degradation proceeds to the same degree, *viz.*, that at these temperatures the same bonds are split, most likely only “weak” crosslinks of the semiacetal type

$$(c_A = 4.46, [\eta]_0 = 1.52 \text{ dl/g}, [S_1]/[A] = 0.138):$$

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$T_d, ^{\circ}\text{C}$	140	140	160	160	190	190
$t_d, \text{h}$	6	24	6	24	6	24
$[\eta], \text{dl/g}$	0.284	0.284	0.283	0.283	0.250	0.250

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At 190°C and more, some deeper changes in structure occur than those described above, which leads to a decrease in the molecular weight of the primary chains.

The originally insoluble copolymers subjected to thermal degradation may be crosslinked again if treated by salts. In this case, the gel time of products degraded at 100–120°C is independent of the time of the preceding degradation, if the product obtained after degradation was perfectly soluble. However, for a product degraded at  $T_d$  130°C it is quite evident that the gel time increases with the time of heating, which again is connected with the incipient deeper structural changes of the functional groups of macromolecules (Table I). Such crosslinked product can again be made soluble by heating<sup>3</sup>, but the latter product cannot be crosslinked again. Further experiments allowed this finding to be generalized, since it was found that no gels obtained by a reaction between the solution of copolymer in the presence of catalyst could be crosslinked by the described procedure after thermal destruction.

The heating of the polymer leads to the formation of volatile products which were collected and analyzed by GC and mass spectroscopy. These are mainly aliphatic hydrocarbons, especially the saturated ones, aromatic hydrocarbons (benzene, toluene, styrene), and oxygen-containing derivatives (3-phenylacetaldehyde, benzaldehyde). The infrared spectra of an isolated gel confirm the decrease in the carbonyl groups to 35–50% of the original amount present in the starting copolymer in accordance with earlier papers<sup>1–3</sup>. At the same time, the decrease in the average content of the aldehyde units is accompanied by an increase in the ether skeletal absorption in the region from 850 to 1200  $\text{cm}^{-1}$ .

A similar crosslinking reaction was carried out under similar conditions also with the 2-ethylacrylaldehyde-styrene copolymer. It was found that in contrast with butylammonium acetate, the salt of 2-aminoethanol and acetic acid is not catalytically active in the crosslinking reaction. The condition for gel formation is a higher concentra-

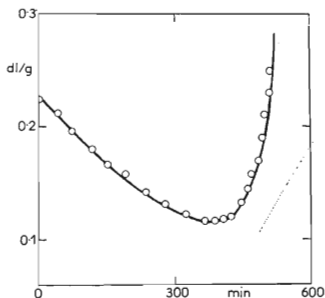


FIG. 3

Limiting Viscosity Number of the Gelatinizing Solution of Poly(methacrylaldehyde-co-butadiene)

$c_A = 48.2\%$  by wt., concentration 1 g copolymer/100 ml of toluene solution, temperature 30°C.

tion of solutions of this copolymer (at least 20% by wt. compared to solutions of poly(methacrylaldehyde-co-styrene), when crosslinking can be carried out already in a 5% solution). This fact is given by the steric effect of the bulkier substituent near the reaction site. The gel thus obtained is very unstable, and is perfectly dissolved once again in the reaction medium after the gelatinized product has been left to stand for several hours. The infrared spectra of both products (gel and the solution formed of it) do not differ qualitatively, because the changes occurring here are insignificant.

As has been described<sup>2</sup>, two parallel reactions take place in the system containing the copolymer and the salt of the acid and amine, *viz.*, a fast crosslinking reaction, which is strongly dependent on the composition of the system, and a comparatively slow reaction leading to the formation of aldimine<sup>2</sup>. It is also known<sup>5</sup> that the carbo-

TABLE I

Effect of the Time of Degradation ( $t_d$ , min) and Temperature ( $T_d$ , °C) on the Gel Point (s) of Degraded Poly(methacrylaldehyde-co-styrene)

$$c_A = 12.1\% \text{ by wt.}, [S_2]/[A] = 1.38 \cdot 10^{-3}.$$

$t_d$	100°C	$t_d$	110°C	120°C	130°C
40	45.5	10	—	—	48
50	42.0	15	55	55.7	67
60	42.0	21	43	54.7	68
120	60.5	25	52	47.5	170
		30	44	51.8	—
		35	50	50.7	—

TABLE II

Effect of the Extractant on the Properties of Poly(methacrylaldehyde-co-styrene) Gel

$$[S_1]/[A] = 2.99 \cdot 10^{-2}, [\eta]_0 = 0.50 \text{ dl/g}, T = 50^\circ\text{C}, t_d = 649 \text{ s.}$$

Extractant	Content of methacrylaldehyde, % by wt.			Gel content %	Degree of swelling
	by oximation	by elem. analysis	IR		
—	21.2	21.5	20.5	0	—
Ethanol	—	37.7	12.7	30	96.5
Light petroleum	—	33.2	14.5	60	38.1

nyl group of poly(2-ethylacrylaldehyde-co-styrene) is less reactive than the same group in the copolymer based on methacrylaldehyde. It can be deduced therefrom that the crosslinking reaction too will in the first case be much more sensitive to changes in the composition of the system. On mixing of the reaction components, the crosslinking reaction is the first to occur in the case of a suitable composition of the initiator. At the same time, however, a reaction takes place which leads to the formation of aldimine, thus removing amine from the system and releasing free acetic acid. In this way, the conditions suited for gel formation (acidity) deviate from the optimum, and "depolymerization" takes place. It is also possible that the released acetic acid not only leads to a deviation from the optimum conditions, but that it itself attacks the semiacetal crosslinks formed in the reaction, thus causing their splitting which eventually leads to the dissolution of the crosslinked macromolecules. The gel thus obtained could not be isolated and characterized owing to the easy splitting of the crosslinks.

Taking into account the conditions of gel formation, the splitting due to free acetic acid may be regarded as an easier process, because from an analogy for poly-(methacrylaldehyde-co-styrene) the acids are known to exert a degradative effect on the copolymer<sup>6</sup>. With respect to the relatively large amount of salt having buffer properties, a change in the acidity of the system cannot be too important. If this were not the case, the gel decomposition should have to be accelerated with decreasing salt concentration in the system, which however has not been observed.

A statistical calculation of the distribution of aldehyde units in the styrene-aldehyde-styrene sequences demonstrates that if the participation of aldehyde in the copolymer does not exceed 40%, these sequences become predominant, and the homopolymer aldehyde sequences become little probable, which to a great extent precludes the formation of tetrahydropyrane rings<sup>7</sup>. Thus, no formation of such structures can be assumed in the case of gelation. It is evident that the reacted carbonyl groups are bonded in crosslinks having an intermolecular (crosslinking) and intramolecular (cyclization) character. The presence of both types of bonds is borne out by the fact that the formation of merely intermolecular bonds should give a considerably higher crosslinking density than the value found experimentally for the spectrometrically determined loss of reactive groups. In the opposite case, a state may be reached when cyclic structures (intermolecular bonds) are formed almost exclusively, if the system is sufficiently diluted. The effect of concentration is especially obvious if the copolymers of styrene and 2-methylacrylaldehyde, on the one hand, and of styrene and 2-ethylacrylaldehyde on the other are compared: in the latter case the steric effect of the ethyl group must be compensated for by "concentrating" the chains by an increase in concentration (irrespective of the decrease in reactivity due to the inductive effects).

The C—O—C type bond is comparatively unstable and splits readily by heating or by hydrolytic agents, similarly to other semialdehydes, *e.g.* polyformaldehyde.

This fact is corroborated by data on the effect of alcohol on gel during the extraction of the catalyst (Table II). It also follows from these data that the gel alone (after extraction of the soluble fractions with benzene) predominantly contains copolymer fractions with the methacrylaldehyde content higher than corresponds to the average determined value. However, for a gel from which the catalyst was extracted with ethanol, the aldehyde content (calculated from the oxygen content determined by elemental analysis) also includes the alcohol bonded in the gel. Such bond may arise, on the one hand, by a direct action of alcohol on the crosslink, and on the other, by a consecutive reaction, because the originally high-swollen gel is compressed in the alcohol owing to a change in the quality of the solvent, which is accompanied by breaking of some crosslinks, and the ends thus formed may be "terminated" by the alcohol. The breaking of the crosslinks then leads to a decrease in the gel content, and at the same time to an increase in its swelling owing to a lower crosslinking density. The degradative effect of alcohol in the case of uncrosslinked copolymers has been pointed out earlier<sup>8</sup>.

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