

REACTIONS OF METHACRYLALDEHYDE-STYRENE COPOLYMER. I.  
THE REACTION WITH AMINES  
IN THE PRESENCE OF ACID CATALYSTS

J. KÁLAL and F. ŠVEC

*Department of Macromolecular Chemistry,  
Institute of Chemical Technology, Prague 6*

Received May 26th, 1970

The reaction of methacrylaldehyde-styrene copolymer with primary amines in the presence of carboxylic acids or its reaction with the amine salt and carboxylic acid leads, under certain conditions, to the formation of a gel. The presence of the acid also accelerates the reaction leading to imine group formation. The type of carboxylic acid used has no effect upon the reaction. Judging from infrared spectra there is no qualitative difference between the products of reaction catalysed and non-catalysed. This, together with the considerable swelling ability of the product, indicates low concentration of cross-links. The results suggest that the gel is formed by the polymerisation of aldehyde groups.

Reactions of polymers and copolymers of unsaturated aldehydes with amines has been the subject of a considerable interest. These reactions are also being employed technologically. The reaction has been followed particularly from the point of view of use of polyfunctional amines, *e.g.* hexamethylenediamine, hexamethylenetetramine, ethylenediamine, benzidine, urea, thiourea, melamine *etc.*<sup>1-4</sup> as potentially useful vulcanising agents for aldehyde-type rubbers. In some cases, carboxylic acids *e.g.* oxalic acid<sup>1</sup>, salicylic acid<sup>1,3</sup>, have been used to accelerate the reaction. The reactions were usually carried out on calender rolls and the product has not been analysed. Using polymer polyamines it is also possible to prepare the product possessing a network structure<sup>5</sup>. An optically active, modified polyacrylaldehyde<sup>6</sup> resulted when a suitable amine was used. Paronjanc and coworkers<sup>7</sup> reported on the reaction product of methacrylaldehyde-butadiene copolymer with aniline, prepared in the solid state at 70–100°C, which could be used as a polymeric antioxidant. The authors suggested a probable course of the reaction as well as the product structure on the basis of analogical behaviour of low molecular aldehydes. These hypotheses are, however, not supported by experimental results.

We have studied<sup>8,9</sup> the reaction of methacrylaldehyde-styrene copolymer with primary amines; judging from the nitrogen content in the product and from the amount of water formed, we have concluded that the reaction leads to the formation of imino groups in a significant yield. We have also determined kinetic parameters of this reaction. Similarly as in the case of reaction of low molecular aldehydes with amines, the polymeranalogical reaction is significantly accelerated by the presence

of a carboxylic acid. At the same time, quite substantial amount of a gel is formed. It is the purpose of this work to try to explain this phenomenon.

## EXPERIMENTAL

### Chemicals

Methacrylaldehyde (Spolana Neratovice) was cooled down to  $-70^{\circ}\text{C}$  so that most of the water present could be removed by filtration. Then it was rectified on a 0.5 m long column (the  $68.0^{\circ}\text{C}$  fraction collected) and further dried over the A-4 molecular sieve. The purity of the final product was checked by gas-chromatography and it was found to be better than 99%. Styrene (Kaučuk, Kralupy nad Vltavou) was repeatedly extracted with sodium hydroxide solution prior to use in order to remove the stabiliser; it was then washed with water, dried over anhydrous magnesium sulphate and rectified *in vacuo* (B.p.  $46^{\circ}\text{C}/20$  Torr,  $n_{\text{D}}^{20}$  1.563). Benzoyl peroxide was purified by double recrystallisation from chloroform.

### Copolymerisation

Always 0.1% of an initiator was added to the mixture of monomers. The starting copolymerisation mixture in glass ampoules was deaerated by the repeated freeze-pump-thaw process carried out under oxygen free nitrogen. The ampoules were then sealed off. The overall time of reaction was 24 hours; the temperature was kept at  $70^{\circ}\text{C}$  for the first 18 hours and then increased to  $110^{\circ}\text{C}$  at which value it was maintained for the remaining 6 hours. After the ampoule had been cooled down, the contents were dissolved in benzene, precipitated by addition of ethanol and the precipitate was dried to a constant weight at room temperature at 6 Torr.

The limiting viscosity number of benzene solutions was determined at  $30 \pm 0.1^{\circ}\text{C}$  using an Ubelohde viscometer; the average value was found to be 0.3 dl/g. The concentration of free aldehyde groups was determined by oximation: The reagent solution was prepared by dissolving 7 g of hydroxylamine hydrochloride and 7.2 g of 2,2',2''-trihydroxyethylamine in 200 ml of water and the solution was diluted to 1000 ml with ethanol. To 5 ml of this solution 50 mg of the copolymer dissolved in 10 ml of benzene was added and the mixture was refluxed for 2 hours. The condenser was washed down with 10 ml of benzene and then the excess of hydroxylamine was titrated by 0.02M-HCl in ethanol. The end point was indicated potentiometrically using saturated calomel electrode in combination with high resistance glass electrode.

The reaction of copolymer with amines was carried out at  $50^{\circ}\text{C}$  in closed test tubes containing 10% benzene solution of the copolymer. The gel obtained after the reaction was extracted with boiling ethanol several times, was separated and dried to a constant weight at room temperature at 6 Torr. The amount of bonded nitrogen was determined by the Kjeldahl method. The time interval in which a conical body (11.3 mm base diameter, 2.2 mm height, 15.7 g weight) did not penetrate the gel contents of the tube, was used for definition of the gelation time. The amount of gel formed, is the fraction of insoluble residue remaining in the mixture after five-fold extraction with benzene at  $25^{\circ}\text{C}$ . The swelling capacity was defined as a ratio of benzene-swollen gel weight to the weight of the dried gel. The equilibrium of the swelling process at  $20^{\circ}\text{C}$  was reached within 5 days.

## RESULTS AND DISCUSSION

The reaction of carbonyl compounds with amines, can, in general, be accelerated by the presence of acid catalysts<sup>10</sup>. The use of carboxylic acids as catalysts substantially

increases the rate of the reaction of free aldehyde groups of methacrylaldehyde-styrene copolymer with benzylamine. This enables to complete the reaction during relatively short time (Fig. 1) provided that the reaction is carried out in benzene solution at the boiling point temperature, the water formed being removed in form of an azeotrop by continuous distillation; the degree of conversion was, in this case, followed by determining the water by titration with the Fisher reagent<sup>11</sup>. The extent of the polymeranalogical reaction catalysed in this way is smaller when the reaction is carried out in a closed system; the degree of conversion was followed by determining the bonded nitrogen contents. The crosslinking of the copolymer, leading as far as gelation of the solution, takes place at a certain optimum concentration of the reaction components. The gel isolated after the extraction of soluble fractions is insoluble even in boiling solvents such as benzene, toluene, dimethylformamide, pyridine, dioxane, tetrahydrofurane, nitrobenzene, chlorobenzene, methyl ethyl ketone and others. The gel only swells in these solvents. It was possible to dissolve the gel only in the mixture of benzene with formic or hydrochloric acid. The soluble product, however, was not possible to cross-link using the above described procedure. The dissolving of the gel is, in this case, probably a chemical reaction leading to the modification of the reactive groups of the chain.

The infrared spectra of the original copolymer differ from those of the product of the reaction with amine: The absorption bands at  $1720\text{ cm}^{-1}$  corresponding

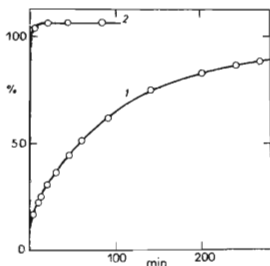


FIG. 1

Reaction of Methacrylaldehyde-Styrene Copolymer with Benzylamine

Aldehyde concentration in the copolymer  $0.204\text{ mol}/100\text{ g}$ , molar ratio amine/aldehyde =  $4.49$ , acid/amine =  $0.3$ , temperature  $80^\circ\text{C}$ , 1 non catalysed reaction, 2 reaction catalysed by benzoic acid.

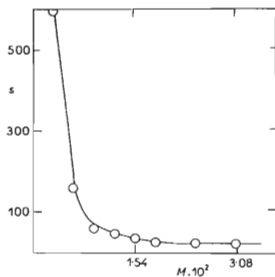


FIG. 2

The Dependence of the Gelation Time upon the Molar Ratio of Butylammonium Acetate to Carbonyl Group ( $M$ )

Aldehyde concentration in copolymer  $0.287\text{ mol}/100\text{ g}$ , temperature  $2^\circ\text{C}$ .

to the C=O vibrations of the aldehyde group, and the  $2650\text{ cm}^{-1}$  absorption due to C—H vibrations of an aliphatic aldehyde group are substantially weaker. On the other hand a new absorption at  $1675\text{ cm}^{-1}$  is seen to appear. This absorption was assigned to the valence vibration of the C=N bond. These differences are observed both in the case of soluble and insoluble (gel-like) products and are characteristic for a polymeranalogical reaction leading to the formation of aldimine groups<sup>8</sup>. Although the infrared spectrum of the product of catalysed reaction (gel) is not qualitatively different from that of the soluble copolymer which was modified in the absence of carboxylic acid, it is obvious that in the system containing a catalyst, the crosslinking reaction takes place beside the polymeranalogical change. Judging from the high swelling capacity of the gel (Table I) it may be concluded that the number of cross-links is small, so that their presence is not sufficiently reflected in the infrared spectrum.

It follows from the results summarised in Table I that the formation of the gel is significantly dependent upon the amine basicity. The differences between the aliphatic and aromatic amine reactivity as well as their ability to form the gel can be explained on the basis of these results. There is an order-of-magnitude difference between the dissociation constants of these amines (measured in water). Diamines, such as *p*-phenylenediamine because of their bifunctional character, form cross-links by a direct reaction of amino groups with aldehydic groups. The low reactivity

TABLE I

The Influence of the Amine Type upon the Reaction with the Methacrylaldehyde-Styrene Copolymer in the Presence of Acetic Acid

Aldehyde concentration in the copolymer 0.131 mol/100 g, molar ratio amine/carbonyl groups = 0.25, acid/amine = 2.

Amine	Gelation time, s	Conversion % <sup>a</sup>	Gel content, %	Swelling capacity
Propylamine	15	22.8	82.5	14.7
Butylamine	15	24.4	82.3	15.6
Hexylamine	15	24.4	82.5	16.2
Octylamine	15	25.4	82.4	16.6
Benzylamine	15	24.8	79.5	16.9
Aniline	960	18.5	45.7	46.5
<i>o</i> -Toluidine	1 800	13.4	18.2	70
Naphthylamine	1 800	13.8	10	— <sup>b</sup>
<i>p</i> -Phenylenediamine	230	18.4	71.0	13.3
Dibutylamine	—	4.5	0	—

<sup>a</sup> Ratio of bonded nitrogen to aldehydic group contents in the starting copolymer. <sup>b</sup> It was not determined because of a very high value.

of dibutylamine can be accounted for by the equilibrium directed towards the initial components. This equilibrium is particularly characteristic for the case of low molecular aldehydes reacting in acid solution<sup>12,13</sup>.

The gel formation is typical for the reaction catalysed by carboxylic acids (Table II). When stronger acids are used, the formation of amine salts is enhanced thus precluding both the aldimine formation reaction and crosslinking. If *e.g.* *p*-toluenesulphonic acid is employed, a product possessing high swelling capacity *i.e.* low gel contents, is formed; no gel is formed in the presence of hydrochloric acid. If, on the other hand, a salt of primary amine with carboxylic acid is applied, then the gel is formed easily. Fig. 2. shows the dependence of the gelation time upon the concentration of the salt of acetic acid with butylamine, the reaction being carried out at 2°C. The amount of the salt was, in average, by two orders of magnitude lower than the concentration of aldehydic groups. This signifies that the salt shows catalytic activity. In this concentration range the salt is still easily soluble in the reaction mixture so that the gel product is perfectly transparent. No nitrogen was found to be present in the extracted gel. This indicates that the crosslinking reaction had taken place and not the reaction leading to the aldimine groups formation. The formation of the gel is thus not connected with the formation of products formed by the reaction of amine with aldehyde group. This means that mechanisms considering mutual reactions of intermediates formed via nucleophilic addition of an amine to carbonyl

TABLE II

The Influence of the Acid Type upon the Reaction of the Methacrylaldehyde-Styrene Copolymer with Butylamine

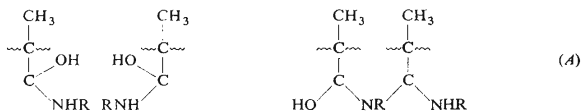
Aldehyde concentration in the copolymer 0.154 mol/100 g, molar ratio amine/carbonyl groups = 0.5, acid/amine = 2.

Acid	Gelation time, s	Conversion % <sup>a</sup>	Gel content, %	Swelling capacity
Acetic	47	16.3	77.4	13.2
Phenylacetic	58	15.2	65.4	13.2
Sebacic <sup>b</sup>	57	12.7	73.6	12.0
Citric <sup>c</sup>	227	15.9	82.4	10.5
Oxalic <sup>c</sup>	300	12.6	85.6	10.0
Oxalic <sup>b</sup>	64	13.1	84.8	10.2
<i>p</i> -Toluenesulphonic	80	15.7	34.2	31.8
Hydrochloric	—	—	0	—

<sup>a</sup> Ratio of bonded nitrogen to aldehydic groups contents in the starting copolymer. <sup>b</sup> Fine powder.

<sup>c</sup> Crystals.

group or reactions of these intermediates with the activated form of carbonyl group, can be excluded:



The absence of bonded nitrogen in the gel formed by crosslinking in the presence of small amounts of the above mentioned salt signifies that the polymerisation of aldimine groups does not take place. This is further corroborated by the fact that the gel is not formed even after the addition of acetic acid or its salt with primary amine to the solution of aldimine groups containing copolymer.

As the gelation rate is quite high even at low temperatures and the reaction of amine with carbonyl group is not significant, it may be assumed that the structure *I* is formed by ionic polymerisation.

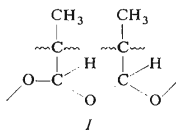


TABLE III

The Reaction of Methacrylaldehyde-Styrene Copolymer with Butylamine in the Presence of Acetic Acid and Ethanol

Aldehyde concentration in the copolymer 0.154 mol/100 g, molar ratio amine/carbonyl group = 0.25, acid/amine = 2; conversion 20.5%.

Molar ratio —OH/—CHO	Gelation time, s	Gel content, %	Swelling capacity
0.05	29	64.6	15.3
0.1	34	65.5	16.9
0.25	42	65.4	17.3
0.5	72	63.8	17.5
0.75	94	63.5	18.2
1	212	57.3	19.7
2	— <sup>a</sup>	50.0	43.0
4	— <sup>a</sup>	3.6	125

<sup>a</sup> Gelation time longer than 600 s.

The above suggested structure of the gel is also justified by the fact that additions of an alcohol suppress the crosslinking reaction whereas the reactions leading to aldime is not influenced (Table III). Low molecular alcohols are known to act as the terminating agent in the polymerisation of aldehydes. They make feasible the transfer of the proton to the growing end of the polymer chain. The increasing concentration of alcohol causes the decrease in the reaction rate and restricts the formation of crosslinks; the swelling capacity of the gel increases whereas the amount of the gel formed remains almost constant. From the series of carboxylic acids presented in Table II only acetic and phenylacetic acid are soluble in benzene. In such a case both the reaction with amine and the crosslinking reaction take place in a homogeneous system. In the case of insoluble acids, however, the dependence of the gelation time upon the surface area is apparent. It thus may be assumed that the amine salt remains a part of solid surface and acts as a heterogeneous catalyst of the crosslinking reaction.

The high rate of the crosslinking reaction even at temperatures as low as 2°C, together with the evidence about acidolysis of the product at 80°C, indicates the presence of unstable bonds that have probably been formed *via* ionic mechanism. The fact that the infrared spectrum of the resulting gel shows no absorptions corresponding to a disubstituted benzene ring, suggests that the polymerisation of aldehydic groups predominates over the formation of hydroxymethylenic bondings between the quarternary carbon and phenyl group.

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Translated by J. Sedlář.