REACTIONS OF METHACRYLALDEHYDE–STYRENE COPOLYMER. II.*
THE REACTION WITH BUTYLAMINE
IN THE PRESENCE OF ACETIC ACID

F.Švec and J.Kálal

Department of Macromolecuar Chemistry,
Institute of Chemical Technology, Prague 6

Chemical transformation taking place in the system containing poly(methacrylaldehyde-*co*-styrene)–butylamine–acetic acid depends upon the reaction mixture composition. The reaction leading to aldimine formation was found to be second order overall; the value of the rate constant at 20°C is $6 . 10^{-2}$ mol l s^{-1} whereas that of the non-catalysed reaction at 50°C is by two orders of magnitude lower. The activation energy of the crosslinking reaction was determined to be 13·3 kcal/mol, judging from the temperature dependency of the gelation time; the crosslinking reaction is substantially influenced also by the solvent used.

The reaction of methacrylaldehyde–styrene copolymer with primary amines in the presence of carboxylic acid and a primary amine salt with carboxylic acid, resp. leads, under certain conditions to crosslinking resulting in the gelation of the solution[1]. The course of the crosslinking reaction is influenced by the basicity of the primary amine but it is independent of the type of the carboxylic acid. It was concluded from the infrared spectra and from the course of reaction under modified conditions, resp. that the polymerisation of the carbonyl group is probably responsible for the polymer network formation. We examined the influence of concentration of each reaction component upon the reaction of poly(methacrylaldehyde-*co*-styrene) with butylamine in the presence of acetic acid in benzene solution. Under these conditions a product containing aldimine groups is formed but in certain cases also a gel formation is seen.

EXPERIMENTAL

The preparation of block methacrylaldehyde–styrene copolymer and the determination of free aldehyde groups by oximation was described in our previous paper[1]. The reaction with amines was carried out in closed glass ampoules placed in a constant temperature bath. The acid followed

---

*   Part I: This Journal *36*, 3947 (1971).

by the amine was added to a tempered benzene solution (10% w/w) of copolymer. The gelation time was defined as the time of reaction after which a conical body (base diameter 11·3 mm, height 2·2 mm, weight 15·70 g) did not penetrate the gel contents of the reaction vessel. The conversion of the aldehyde groups into aldimine was calculated from the bonded nitrogen content in an extracted gel. The nitrogen concentration was determined by the Kjeldahl's method and it was expressed as a ratio (in %) of bonded nitrogen to the aldehyde group contents determined in the initial copolymer. The determination of gel content and swelling capacity resp. has already been described[1].

RESULTS AND DISCUSSION

The Influence of Reaction Conditions

There are two principal processes taking place in the reaction system containing poly(methacrylaldehyde-*co*-styrene)–butylamine–acetic acid: the crosslinking reaction characterised by the gelation time, swelling capacity, and gel content in the final product and the imine groups formation reaction. The acetic acid influences the course of both reactions unequally. It acts as a catalyst activating the carbonyl group thus increasing the electron affinity of carbon atom so that both the crosslinking and the
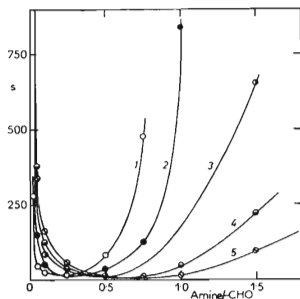

Fig. 1

Dependence of the Gelation Time upon the Molar Ratio Butylamine/Aldehydic Groups in Methacrylaldehyde–Styrene Copolymer

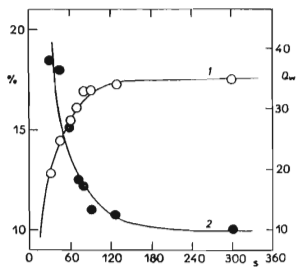Molar ratio acid/aldehydic groups: *1* 0·25, *2* 0·5, *3* 0·75, *4* 1·00, *5* 1·5.

Fig. 2

Reaction of Poly(Methacrylaldehyde-*co*-styrene) with Butylamine in the Presence of Acetic Acid at 20°C

Copolymer concentration in benzene solution 10%, molar ratio acid/amine 2, amine : : aldehyde 0·25; curves: *1* conversion, *2* swelling capacity.

TABLE I

The Influence of Molar Ratio Amine/Aldehydic Groups upon the Course of Methacrylaldehyde–Styrene Copolymer Reaction with Amine in the Presence of Acetic Acid

Temperature 50°C, 10% benzene solution of copolymer, concentration of aldehyde in copolymer 0·131 mol/100 g.

Amine/—CHO mol/mol	Conversion %	Gelation time, s	Gel content %	Swelling capacity
	AcOH/—CHO = 0·25 mol/mol			
0·025	2·6	280	57·0	26·6
0·05	5·2	44	72·3	13·8
0·1	11·7	24	76·7	11·1
0·25	14·6	18	74·3	14·7
0·5	23·1	83	73·3	15·4
0·75	38·8	478	68·8	17·7
	AcOH/—CHO = 0·5			
0·025	—	1 320	—	—
0·05	6·3	150	47·5	24·8
0·1	12·9	50	95·8	21·5
0·25	29·6	15	96·6	18·1
0·5	48·0	35	84·2	22·5
0·75	63·8	125	78·3	26·3
1·0	87·5	840	69·3	29·4
1·5	100·3	3 000	54·0	34·2
	AcOH/—CHO = 0·75			
0·1	11·8	85	72·5	18·2
0·5	44·4	16	86·8	15·5
1·5	78·7	53·6	53·6	34·0
	AcOH/-CHO = 1·0			
0·025	—	1 390	55·2	36·4
0·05	—	380	65·1	29·4
0·1	12·8	128	72·3	18·5
0·25	24·2	34	85·4	13·9
0·5	42·7	15	87·5	11·1
0·75	46·0	15	87·0	12·3
1·0	59·6	49	85·3	16·4
1·5	83·8	225	71·3	21·7

TABLE I

(*Continued*)

Amine/—CHO mol/mol	Conversion %	Gelation time s	Gel content %	Swelling capacity
		AcOH/—CHO = 1·5		
0·05	– –	337	71·3	24·1
0·1	13·4	163	78·2	18·0
0·25	22·9	58	78·9	12·9
0·5	34·3	15	81·9	12·7
0·75	46·5	12	84·2	12·0
1·0	56·0	15	82·7	13·0
1·5	72·0	93	78·3	16·2
3·0	94·7	341	60·3	26·4

reaction with amine are favourably influenced (Table 1). The amine concentration region within which gelation occurs in a relatively short time, is broadening with the increased acid concentration (Fig. 1). The acid, however, reacts with the free base forming a salt which is inactive in the reaction leading to aldimine. Because of this, the increasing concentration of acid causes the decrease in the rate of imine groups formation (Table II). The molar ratio of acetic acid to butylamine at which the gelation time is the shortest, the gel content the highest and the swelling capacity minimal is, in the above mentioned cases, practically constant being equal to two, provided that the concentration of free aldehyde groups is taken unity. The rate of aldimine formation is, even at 20°C, quite high; the nitrogen content in gel reaches almost its equilibrium value as early as after 70 seconds (Fig. 2). Also the gel content keeps almost constant (77%) from the start of the reaction whereas the swelling capacity decreases. This suggests that the reaction leading to aldimine groups formation does not proceed farther, whereas the reaction of crosslinking continues. The order of the first condensation reaction was experimentally determined to be second order overall. The rate constant of the reaction taking place in the presence of acetic acid at 20°C was calculated to be approximately $6 \cdot 10^{-2}$ mol l^{-1} s^{-1}; the non-catalysed reaction is also of second order overall and the value of the rate constant at 50°C is $4 \cdot 10^{-4}$ mol l^{-1} s^{-1} (Fig. 3).

As the formation of the gel requires the formation of crosslinks among macromolecular chains and because the gelation process is carried out in solution, the gelation time will depend on the reactive groups concentration (Table III). The gel is not formed during the first hour of the reaction when the concentration of copoly-

TABLE II

The Influence of Acetic Acid Concentration of the Reaction of Equimolar Quantities of Methacrylaldehyde–Styrene Copolymer and Butylamine

Temperature 50°C, 10% benzene solution of copolymer, aldehyde concentration in copolymer 0·154 mol/100 g.

Acid/amine mol/mol	Conversion %	Gelation time s	Gel content %	Swelling capacity
0·5	63·2	750	51·1	31·0
1	58·9	171	57·3	26·0
2	48·9	48	68·0	21·1
3	44·2	109	62·8	22·3
4	42·5	264	53·9	24·0
5	41·4	440	57·0	24·5
6	41·5	534	53·0	25·2
8	37·3	630	49·6	25·9
10	35·9	756	51·1	26·5

TABLE III

The Influence of Copolymer Concentration on Reactions Taking Place in the System Containing Poly(Methacrylaldehyde-co-styrene)–Butylamine–Acetic Acid–Benzene at 50°C

Concentration of aldehyde in copolymer 0·154 mol/100 g, molar ratio amine/aldehyde groups 0·5, amine/acid 1.

Concentration g/l	Conversion %	Gelation time s	Gel content %	Swelling capacity
100	17·6	20	78·3	15·6
90	17·3	26	77·0	16·5
80	16·8	31	75·1	17·1
70	17·9	50	70·8	20·0
60	17·6	140	56·2	27·4
50	17·7	3 600	19·3	165
40	17·5	—	0	—

mer is lower than 50 g/l. The reaction of amine with carbonyl group is, however, not influenced by decreasing concentration of polymer solution.

Also the kind of a solvent substantially influences the course of the crosslinking reaction. The gel is formed in pyridine, nitrobenzene, ethyl acetate and tetrahydro-

furane, resp. but values of the gelation time are very high (more than 1 hour). In chlorobenzene, benzene and toluene, resp. the formation of gel is, under identical conditions, very rapid (Table IV). In nitrobenzene solvent the gel is formed only if the molar ratio acetic acid/butylamine exceeds the value of 4. If it is assumed that the crosslinking is caused by a heterolytic reaction then the role of solvents

TABLE IV

Ratio of Acetic Acid/Butylamine that is Optimal for the Formation of Maximum Amount of Gel with Low Swelling Capacity; Different Solvents at 50°C

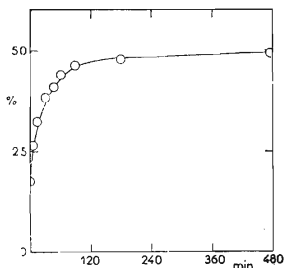| Solvent	Ratio	Gelation time, s
Tetrahydrofurane	1	3 600
Benzene	2	12
Toluene	2	15
Chlorobenzene	2	26
Pyridine	4	3 600
Ethyl acetate	4	3 600
Nitrobenzene	10	3 600

FIG. 3

Reaction of Equimolar Amounts of Butylamine and Aldehydic Groups in Methacrylaldehyde–Styrene Copolymer Performed in 10% Benzene Solution at 50°C
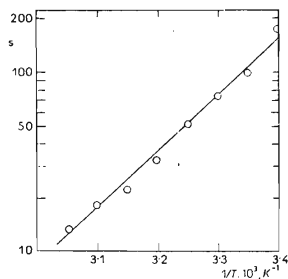

FIG. 4

Arrhenius Plot of Gelation Time *vs* Temperature

will consist in solvatation of particles initially present and those formed during the reaction. The degree of solvatation is dependent on the character of both the particle and the solvent. The solvent can also participate in a chemical reaction. The molecules of solvents in which the reaction time is long, contain atoms possessing a free electron pair; this blocks the reaction centra of crosslinking reaction thus retarding the cross-linking process. The values of molar ratio acetic acid/butylamine (unit concentration of aldehydic groups) at which a maximum amount of gel is formed whereas the swelling capacity is minimal, vary for different solvents (Table IV). The gelation time is shortened to one half of the original value when the temperature is increased by 10°C. This holds for the whole range of temperatures measured (Table V). This means that the gelation is a chemical process because physical processes depend much less on the temperature. The gelation time t is defined as a time of reaction during which always the same swelling capacity is reached independently of temperature. If it is assumed that the constant swelling capacity corresponds to a certain density of network, it is possible to use the values of the gelation time for calculation of activation energy of the crosslinking reaction by means of the Arrhenius equation in form $\ln t = E/RT + A$. The value of activation energy was then calculated from the slope of the linear plot of logarithm of gelation time vs. reciprocal of absolute temperature (Fig. 4). Its value was found to be 13·3 kcal/mol; the activation energy of the reaction of copolymer aldehydic groups with amine in the absence of carboxylic acid was reported[2] to be 8·6 kcal/mol.

TABLE V

Temperature Dependence of the Reaction of Methacrylaldehyde–Styrene Copolymer with Butylamine in the Presence of Acetic Acid

Molar ratio amine/aldehydic groups 0·25, acid/amine 2, aldehyde concentration in copolymer 0·131 mol/100 g.

Temperature °C	Gelation time s	Gel content %	Swelling capacity
20	191	65·9	13·5
25	100	67·0	13·0
30	74	72·1	12·9
35	51	76·1	12·8
40	32	78·5	12·4
45	22	83·1	11·4
50	18	83·3	11·9
55	13	83·7	12·0

Reaction Mechanism

The main reaction taking place in the system containing poly(methacrylaldehyde-*co*-styrene)–butylamine–acetic acid is the nucleophilic addition of primary amine to the carbonyl group carbon, leading to the formation of aldimine groups. This reaction can proceed even in the absence of acid. Its occurrence was confirmed by the equimolarity of bonded nitrogen and water, resp.[2,3] and by the inspection of the infrared spectra of the product[1]. The reaction takes place even under conditions that are optimal for gel formation.

Another assumed reaction is the polymerization of free aldehyde groups leading to the formation of ether bonds that are easily split namely in acid solution. The acidolysis of the gel has already been reported[1]. The assumption about the formation of crosslinks of this type can be made both on the basis of found reaction conditions and according the general properties of aldehydes; the aldehydes easily polymerise to give oligomeric and polymeric products. The reaction of aldehydic group are quite fast and they are catalysed by water; the traces of carboxylic acids, however, accelerate the reactions by several orders of magnitude[4,5]. This hypothesis is farther corroborated by the fact that the rate of carboxylic group reaction in aqueous media is markedly dependent on the value of pH. The highest values of the reactions

TABLE VI

Reaction of Methacrylaldehyde–Styrene Copolymer with Aniline in the Presence of Acetic Acid

Temperature 50°C, 10% benzene solution of copolymer, molar ratio amine/aldehydic groups 0·5, aldehyde concentration in copolymer 0·126 mol/100 g.

Acid/amine mol/mol	Reaction time s	Conversion %	Gel content %	Swelling capacity
0·05	3 600	10·2	22·8	103
0·1	3 600	11·1	28·0	89
0·2	3 600	27·5	28·6	88
0·5	3 600	29·4	38·0	71
1	3 600	32·3	51·0	40·4
2	3 900[a]	34·5	48·4	36·3
4	1 080[a]	38·4	59·4	24·7
10	660[a]	39·0	62·8	19·5
15	505[a]	37·7	63·8	20·2
20	450[a]	38·7	67·5	18·8
20	3 600	38·2	68·1	18·0
24	900[a]	38·0	66·4	19·7

[a] Reaction time is also the gelation time.

constants were observed at pH 4 (ref.[6]). It has been found, however, that even in medium of lower polarity than that as in the case of our experiments, the influence of acidity upon the reaction rate is substantial.

The acid HA (Scheme I) can generally be the proton of dissociated carbonyl group, carbonyl group, conjugated acid RNH_3^+, carboxylic acid, water or other compounds such as those formed through the coordination with a solvent molecule. Each change of the reaction conditions will then be accompanied by the change of the equilibrium ratios causing the concentration changes of individual components;
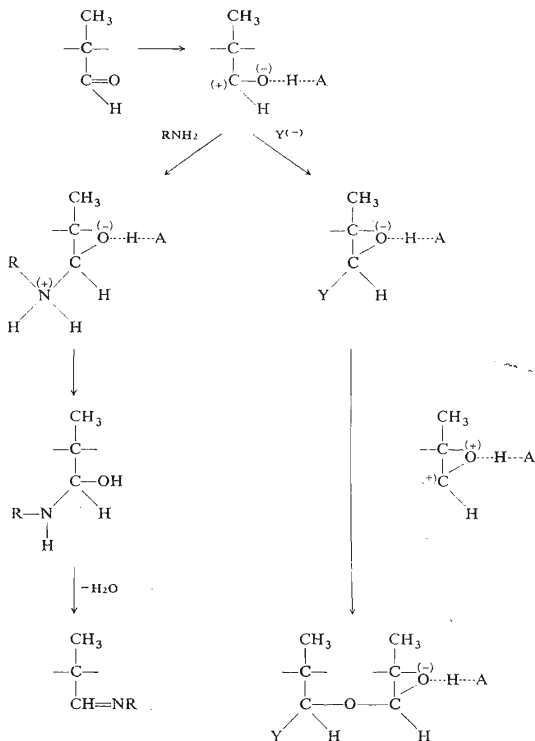
SCHEME 1

it will eventually result in the acidity changes of the system. This can account for the different reaction conditions required for the formation of the gel in the case of butylamine and aniline resp. It is thus obvious that under exactly defined conditions characterised by the molar ratio acid/amine at given concentration of aldehydic groups, the highest rate of the crosslinking process will be seen.

Neither the chemical structure of amine nor acid influences the course of the cross-linking reaction. The reaction is dependent only on the value of rate constant[1]. Strong acids such as hydrochloric and *p*-toluenesulphonic acid resp. as well as stronger basis (*e.g.* dibutylamine and triethylamine in non-polar media) have quite restricted possibilities to stabilise their cations by formation of the hydrogen bonding. They thus create the environment possessing either too high or too low acidity *i.e.* the acidity which is not suitable for the gel formation.

REFERENCES

1. Švec F., Kálal J.: This Journal, in press.
2. Kálal J., Švec F., Navrátil M.: *International Symposium on Macromolecular Chemistry*, Preprint 10/20, Budapest 1969.
3. Houska M.: *Thesis*. Institute of Chemical Technology, Prague 1969.
4. Plesch P. H.: *The Chemistry of Cationic Polymerization.* Pergamon Press, Oxford 1963.
5. Furukava J., Saegusa T.: *Polymerization of Aldehydes and Oxides.* Interscience, New York 1963.
6. Sykes P.: *Guidebook to Mechanism in Organic Chemistry.* Longmans, London 1962.

Translated by J. Sedlář.