

REACTION OF CROSSLINKED COPOLYMERS BASED ON STYRENE-METHACRYLALDEHYDE WITH DIAMINES*

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Received February 20th, 1975

The reaction of crosslinked polymers containing free aldehyde groups with diamines was investigated. Conditions were determined under which only one amino group of diamine enters into the reaction.

For the modification of polymers in order to obtain new types of polymeric compounds it is possible to use the high reactivity of the aldehyde group bonded in the polymer chain or network. In this work we investigated reactions of the copolymers of methacrylaldehyde with amines, diamines, and particularly with ethylenediamine.

EXPERIMENTAL

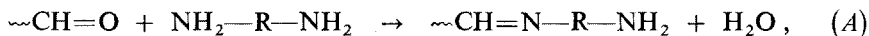
Crosslinked copolymers having the composition styrene-methacrylaldehyde-divinylbenzene were prepared by suspension radical polymerization initiated by 2,2'-azobis(isobutyronitrile) in an amount of 0.5% by wt. per monomer mixture with poly(vinylpyrrolidone) as the suspension stabilizer. The content of free aldehyde groups ($[-CHO]$) in the copolymer was determined titrimetrically by oximation¹; the overall content of methacrylaldehyde ([MA]) was calculated from the elemental analysis of the copolymer (with respect to oxygen).

Copolymers having the particle size ranging from 100 to 200 μ were used in the reaction. The polymer (1 g) was left to swell in a chosen solvent (20 ml) in an ampoule for 12 h; after that, an amine compound was added into the ampoule (1–20 mol/mol of aldehyde groups), the ampoule was closed and placed in a thermostat (continuous rotation of the ampoule about the longitudinal axis at a rate of 10 r.p.m.). After the chosen reaction time had passed, the content of the ampoule was transferred into methanol, the undissolved fraction was filtered off after being washed several times with methanol and dried *in vacuo* at room temperature to constant weight. Nitrogen was determined in the products according to Kjeldahl, free amino groups were determined by conductometric titration in a mixture phenol-propanol (2 parallel determinations). Infrared spectra of the original samples and of the reaction products were recorded with a Perkin-Elmer 325 apparatus using the KBr technique.

* Part VI in the series Reactions of Methacrylaldehyde-Styrene Copolymer; Part V: *Angew. Makromol. Chem.* 38, 35 (1974).

RESULTS AND DISCUSSION

In the first part of the work, the course of the reaction of the copolymer styrene-methacrylaldehyde-divinylbenzene with aniline and benzyl amine was investigated basing on the facts known about soluble polymers²⁻⁷. The reaction course is similar to that of soluble polymers and can be seen in Fig. 1. The experience gained with primary monoamines was used for studying the reaction of the aldehyde group bonded on the polymer chain with aliphatic and aromatic diamines. The results are interesting particularly in those cases when the aldehyde group has a limited mobility or is completely immobilized by bonding on the polymer network. The immobilized group in a crosslinked polymer could offer only one amino group for the reaction, namely,



because the other amino group has a restricted possibility of reacting with another aldehyde group.

It was found that in the reaction between ethylenediamine and a crosslinked copolymer containing aldehyde groups, ethylenediamine participates predominantly by one amino group only. With increasing content of the aldehyde groups in the copolymer the fraction of completely reacted diamine increases, as shown by Figs 2a-c and Tables I and II. A direct proof of the free primary amino group by means of infrared spectra and by the direct potentiometric titration of the NH_2 groups showed a very good agreement. It can be seen from both tables that at the lowest relative concentration of aldehyde groups in the primary chain an equivalence was reached between the reacted aldehyde groups and the primary amino group bonded on the chain. With increasing concentration of the aldehyde groups in the chain

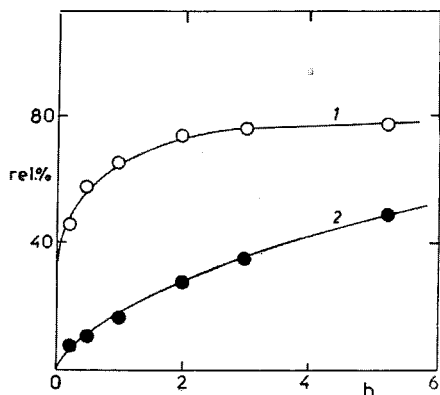


FIG. 1
Reaction of Copolymer Styrene-Methacrylaldehyde (MA)-Divinylbenzene with Aniline (2) and Benzyl Amine (1)

Conditions: [MA] 20.6% by wt., tetrahydrofuran as reaction medium, $[-\text{NH}_2]/[-\text{CHO}]$ 10, 40°C.

the probability that the amino group will react by its second primary amino group with another aldehyde group in the chain also increases. The amino group bonded on the polymer chain participates in the reaction only in a later stage when the concentration of unreacted aldehyde groups has dropped. Bearing in mind that the reaction proceeded at a tenfold molar excess of ethylenediamine related to the free aldehyde group, the reactivity of the immobilized amino group seemingly increases during the reaction. This can be explained by a local concentration effect. Ethylenediamine is in a large excess in the solution, but its molecules are uniformly scattered throughout the volume. On the other hand, amino groups of the residue after the reaction of diamine with the aldehyde group must be concentrated near the polymer chains, because their mobility is restricted to the mobility of the group proper and to the mobility of the network sequence to which they are bonded. For this reason,

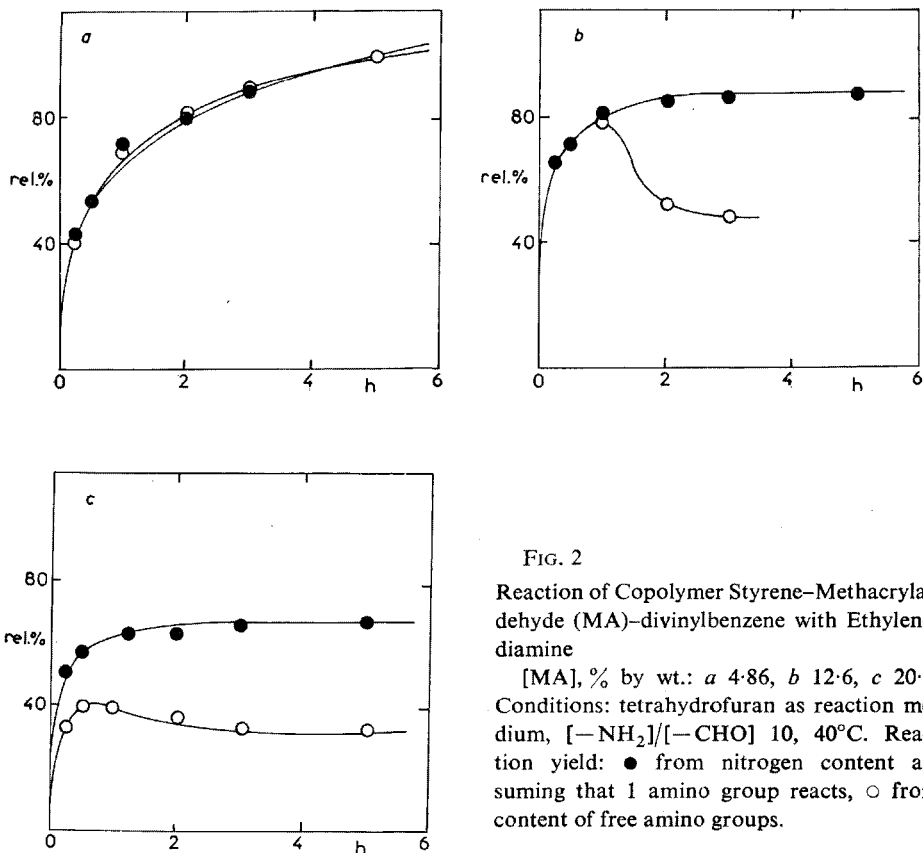


FIG. 2
Reaction of Copolymer Styrene-Methacrylaldehyde (MA)-divinylbenzene with Ethylenediamine

[MA], % by wt.: *a* 4.86, *b* 12.6, *c* 20.6.
Conditions: tetrahydrofuran as reaction medium, $[-NH_2]/[-CHO]$ 10, 40°C. Reaction yield: ● from nitrogen content assuming that 1 amino group reacts, ○ from content of free amino groups.

TABLE I

Reaction of Copolymer Styrene–Methacrylaldehyde (MA)–Divinylbenzene with Ethylenediamine (EDA)

Conditions: reaction time 5 h.

[—CHO]	[MA]	Solvent	$\frac{[EDA]}{[—CHO]}$	°C	$\frac{[NH_2]}{[—CHO]}$
% by wt.					
4.86	9.06	tetrahydrofuran	1.995	65	10
12.60	20.28	tetrahydrofuran	1.72	65	10
12.60	20.28	benzene	1.65	80	10
20.60	31.94	tetrahydrofuran	1.32	40	10
20.60	31.94	benzene	1.20	40	10
20.60	31.94	tetrahydrofuran	1.08	40	2
20.60	31.94	benzene	0.98	40	2

TABLE II

Time Dependence of $[-NH_2]/[N]$ in the Reaction of Ethylenediamine with Copolymer Styrene–Methacrylaldehyde (MA)–Divinylbenzene

Conditions: $[-NH_2]/[-CHO]$ 10, 40°C.

[MA]	Reaction time, h				
	% by wt.	0.25	0.5	1.0	2.0
4.86	1.08	1.00	1.01	0.98	0.99
12.60	1.00	1.00	0.96	0.61	0.56
20.60	0.64	0.69	0.62	0.52	0.50 ^a
20.60 ^b	0.74	1.25	0.58	0.35	0.32

^a After 5h reaction: 0.49; ^b For $[-NH_2]/[-CHO] = 2$.

the local concentration of the amino groups of the $—CH_2—CH_2—NH_2$ type in the vicinity of so far unreacted aldehyde groups increases with proceeding reaction, while the concentration of ethylenediamine somewhat decreases. This effect is still better seen if the molar ratio $[-NH_2]/[-CHO]$ 2 is used.

The reaction of hexamethylenediamine proceeded initially only to the first degree. Owing to the higher flexibility of the longer chain the second amino group also entered into reaction in a later stage. The results are summarized in Table III.

TABLE III

Reaction of Copolymer Styrene-Methacrylaldehyde (MA)-Divinylbenzene with Hexamethylenediamine

Conditions: [MA] 20.6% by wt., tetrahydrofuran as reaction medium. $[\text{NH}_2]/[-\text{CHO}]$ 10, 40°C.

Reaction time, h	$\frac{[\text{N}]}{[-\text{CHO}]}$	$\frac{\text{Equivalent } -\text{NH}_2}{100 \text{ g product}}$
0.25	0.702	3.66
0.50	0.797	5.08
1.00	0.848	4.14
2.00	0.929	0
3.00	0.985	0
5.00	0.996	0

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Translated by L. Kopecká.