

CROSSLINKING OF THE STYRENE-ACRYLALDEHYDE COPOLYMERS AT ELEVATED TEMPERATURES

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A series of acrylaldehyde-styrene copolymers were heated to 80–240°C under inert conditions in the solid state and were found to undergo crosslinking by a reaction similar to aldol condensation. If the polymer was spontaneously crosslinked prior to heating through the formation of unstable hemiacetal bonds, the above reaction is preceded by a reversible splitting of the crosslinks. The effect of chemical agents on the behaviour of the copolymer at 100°C was also investigated.

A systematic investigation of the copolymers of styrene and α,β -unsaturated aldehydes has revealed that the presence of the hydrogen atom at the α -position to the carbonyl group, *e.g.* in acrylaldehyde copolymers compared to their α -alkyl homologs, is important for the behaviour and properties of the copolymers^{1,2}. Schulz has observed earlier³ that polymeric acrylaldehyde reacts with formaldehyde in the presence of basic catalysts with the formation of methylene-1,3-propanediol units in the chain. The use of other aldehydes, such as *e.g.* acetaldehyde, propionaldehyde or benzaldehyde, led to the formation of completely insoluble products which, however, were not further investigated. Bäder⁴ studied the reaction of poly(acrylaldehyde) in the presence of a base which yielded a gel insoluble even on boiling with *p*-toluenesulphonic acid. From comparison with the behaviour of poly(methacrylaldehyde) which showed no crosslinking under the same conditions he concluded that the crosslinks are of the C—C type, and are due to a reaction similar to aldol condensation. A reaction with the adduct poly(acrylaldehydebisulphite) in a basic medium also gave rise to a gel, which in contrast with the former readily split in an acidic medium. However, the structure of the crosslinks was not elucidated. Schilling⁵ studied the crosslinking of poly(acrylaldehyde) during moulding (800–18 000 kg/cm²) and heating (140–180°C). He does not assume the formation of a new type of bonding during crosslinking by moulding (comparison of the infrared spectra), which could be caused, *e.g.*, by the transformation of intramolecular oxygen bonds into intermolecular bonds, or by their reaction with the hydroxy group. On the other hand, the same samples after heating exhibit changes in their spectra (an increase in the intensity of the C=O band at 5.8 μ and a decrease in the intensity of the OH band at 2.8 μ), which could be due to the splitting off of water from the aldehyde-hydrate ether bonds or to the degradation reaction of poly(acrylaldehyde); at the same time, the aldehyde fragments remain "occluded" and cause a considerable increase in the concentration of the aldehyde groups.

It has been shown in an earlier paper⁶ that the copolymers of styrene with methacrylaldehyde and 2-ethylacrylaldehyde contain a large amount of crosslinks of the hemiacetal type and of the inter- and intramolecular character. These bonds can be

readily split in an inert medium by a mere increase in temperature, or even better by treating them with various chemical agents such as carboxylic acids, alcohol, inorganic acids, *etc.*^{2,7}. This paper is devoted to the behaviour of the copolymer styrene-acrylaldehyde which, if heated, differs principally from similar copolymers of methacrylaldehyde or 2-ethylacrylaldehyde.

EXPERIMENTAL

Chemicals. Acrylaldehyde (Lachema, Brno) was cooled to -70°C , water was removed by filtration, and acrylaldehyde was rectified on a column 0.5 m long, filled with metal coils, b.p. 52.3 to $52.5^{\circ}\text{C}/760$ Torr; purity according to GLC was higher than 99.4%. Styrene (Kaučuk, Kralupy) was repeatedly extracted with a solution of sodium hydroxide until all stabilizer (hydroquinone) had been removed, then washed with water, dried with anhydrous magnesium sulphate, and rectified, b.p. $46^{\circ}\text{C}/20$ Torr, n_D^{20} 1.563. 2,2'-Azobisisobutyronitrile (Porofor, Lachema, Brno) was crystallized twice from ether and used in a concentration of 0.062 mol% (with respect to monomers).

Methods

After polymerization the sample was dissolved in benzene, precipitated into an excess of light petroleum and dried *in vacuo* at room temperature. The amount of aldehyde bonded in the copolymer was followed by the oximation method (volumetrically)⁸, and also calculated from the elemental analysis of the copolymer. The viscosity measurements of the benzene solutions at $30 \pm 0.05^{\circ}\text{C}$ were carried out with an Ubbelohde viscometer. The copolymers used are listed in Table I. Some samples were crosslinked with hexamethylenediamine, in a 10% benzene solution at 50°C ; the reagent was added in the form of a solution in the mixture benzene-ethanol (90/10 vol.%).

The copolymers were heated in glass ampoules sealed after a preceding repeated evacuation ($5 \cdot 10^{-3}$ Torr) and rinsing with oxygen-free nitrogen. The temperature of the thermostating block was maintained during heating with an accuracy of $\pm 0.5^{\circ}\text{C}$. In some cases, the heated gels were swollen in toluene, or some other agents were also present.

The products of heating which were not completely soluble (designated as gels) were extracted five times in benzene at room temperature. The gel content represents the portion of the dry insoluble sample after extraction. The degree of swelling is defined as the ratio of the weight of the swollen extracted gel to that of the dried gel.

RESULTS AND DISCUSSION

The copolymers of styrene and acrylaldehyde exhibit a pronounced tendency to form crosslinked and thus insoluble products. This reaction often proceeds spontaneously during the sample treatment after opening of the polymerization ampoule.

A series of copolymers were heated to temperatures ranging from 80 to 240°C . With respect to their behaviour the copolymers can be divided into two groups. In samples with the aldehyde content in the copolymer up to roughly 3 wt.% (A1-A2) an insoluble portion (gel) is formed only in the temperature range from 140 to 220°C (Table II). At lower temperatures these copolymers do not even exhibit a marked change in the limiting viscosity number; at temperatures

above 200°C, degradation was observed accompanied by the formation of soluble products which can undergo further degradation. Under the same conditions, *i.e.* on heating to 120–200°C for 24 h the reference polystyrene sample undergoes degradation, but only very little; at 200°C the decrease in $[\eta]$ amounts to only about 8% of the original value.

If the original copolymer contains more than 3 wt.% of acrylaldehyde in the copolymer (A3–A8), then on heating within 90–240°C for 24 h gel is the final product (trace amounts in the case of samples A3 and A5 already at 80°C); this gel cannot be made soluble even at 240°C.

TABLE I

Characteristics of the Copolymers Styrene-Acrylaldehyde

$[A]_0$ Portion of acrylaldehyde in the copolymerization batch, $[A]_{ox}$ and $[A]_{el}$ aldehyde content in the copolymer determined by the oximation method or by calculations from elemental analysis.

Sample	$[A]_0$ mol.%	Conversion wt.%	$[\eta]$ dl/g	$[A]_{ox}$ wt.%	$[A]_{el}$ wt.%
A 1–1 ^a	3	98.0	1.96	1.43	—
A 1–2 ^a	3	98.0	1.86	1.70	2.05
A 2	3	34.4	0.97	2.63	3.05
A 3	3	5.36	0.85	5.62	6.05
A 4	8	56.2	gel ^b	5.58	7.61
A 5	8	5.0	0.97	11.21	11.21
A 6	15	58.0	gel	10.52	12.72
A 7	15	38.3	gel	13.58	16.15
A 8	15	3.3	0.91	16.90	20.35

^a Sample A 1: part A 1–1 was used without reprecipitation, part A 1–2 was treated in the standard manner (*cf.* Experimental). ^b Insoluble or containing insoluble portion (gel).

TABLE II

Effect of Temperature on Changes in the Limiting Viscosity Number (dl/g) of the Copolymers Styrene-Acrylaldehyde

Time of heating 24 h.

°C	A 1–1	A 1–2	A 2	°C	A 1–1	A 1–2	A 2
— ^a	1.86	1.86	0.97	140	1.96	gel	1.00
90	1.98	2.03	0.96	160	1.72	—	gel
100	—	2.03	0.91	180	1.58	gel	gel
110	1.96	—	0.89	220	0.97	1.38	gel
120	2.00	2.13	0.88	240	0.65 ^b	0.78 ^b	0.18 ^b

^a Without heating. ^b Part of the copolymers are degraded as much as to yield liquid products.

The temperature and time dependences of the gel content and of the degree of swelling of selected polymers, both originally soluble (A3) and insoluble (A4, A7), are shown in Figs 1 and 2. In the process of heating of the originally insoluble copolymer A4 (Fig. 1) we succeeded in recording the stage when after heating to 120°C for 2 h or to 100°C for 2–4 h the copolymer was transformed into a completely soluble form. Subsequent heating led again to the formation of a crosslinked product, which however could not be thermally degraded any more. The increase in the gel content and the decrease in its degree of swelling indicate the second crosslinking reaction which in its final stabilized form bonds in the network c. 90% of the polymer irrespective of the temperature applied. The temperature has a positive effect only on the reaction rate. The time dependence of the gel content of the copolymer A5 has a similar character. Owing to the higher temperature of heating the transformation of the soluble polymer into gel is faster, and practically quantitative after 8 h.

The increasing temperature of heating accelerates the crosslinking reaction, as is demonstrated by the experiments with the copolymers A3 and A7. In the case of the copolymer A3 (Fig. 2) the network density after 15 h of reaction at 100 and 120°C is still so low that the gel becomes mechanically degraded during separation and cannot therefore be isolated. Similarly, the gel content and concentration of crosslinks of the copolymer A7 (Fig. 2) increase with increasing temperature up to a maximum constant value. Compared to the copolymer A3, the latter copolymer contains

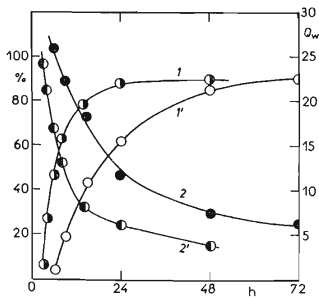


FIG. 1

Dependence of the Gel Content 1 and of the Degree of Swelling Q_w 2 on the Time of Heating of the Polymer A4

Temperature of heating, °C: ○, ● 100; ●, ● 120.

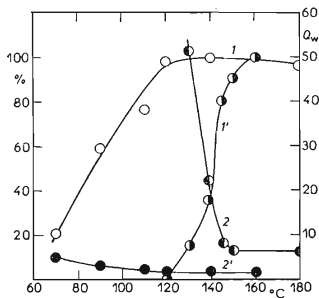


FIG. 2

Dependence of the Gel Content 1 and of the Degree of Swelling Q_w 2 on Temperature

Time of heating, h (polymer): ●, ● 15 (A3); ○, ● 24 (A7).

a larger amount of aldehyde groups capable of crosslinking, and the insoluble fraction is formed already at room temperature. By heating to 70°C, it was possible to isolate gel with a considerable network density.

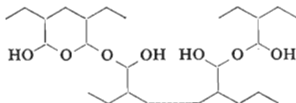
Apart from experiments involving heating of the copolymers in the solid state, we also checked the effects of hydrolytic agents (*cf.* degradation of copolymers based on methacrylaldehydes²) on spontaneously crosslinked copolymers (samples A4, A6), on gels formed by heating of the originally soluble copolymers (A3, A5) and separated from the soluble fractions, and for the sake of comparison also on the gel formed by crosslinking with hexamethylenediamine.

The spontaneously crosslinked copolymers split with a comparative ease at elevated temperatures, the more readily the smaller the content of the aldehyde groups in the copolymer. It was found that the sample A4 swollen in toluene (gel content 40.2 wt.%, degree of swelling 19.7) becomes completely dissolved after 45 min at 100°C. The addition of acetic acid, phenol and pyridine (50 vol.%) accelerates the decomposition in an extent corresponding to the given order. Methanol in the above concentration impairs the quality of the solvent to such a degree that the product is no more soluble in the given medium. Complete dissolution is also attained after 1.25 h by reducing methanol concentration to 10 vol.%. For the sample A6 (gel content 64.8 wt.%, degree of swelling 11.1), it was even possible to observe reversibility of the crosslinking and degradation reactions. The sample swollen in toluene was quantitatively dissolved at 100°C after 6.5 h; after standing for 48 h at 20°C it became crosslinked again. If heated repeatedly after this to 100°C, it dissolved again after 10 min. The addition of acetic acid or pyridine (in an amount of 50 vol.%) leads to an acceleration of degradation (dissolution within 3 or 1.5 h under the same conditions), similarly to the addition of methanol (10 vol.%; 4.5 h); however, no reversibility could be proved. After swelling in toluene, the sample crosslinked with hexamethylenediamine was also degraded at 100°C; its quantitative dissolution took 10 h.

On the other hand, insoluble products arising by heating of the originally soluble copolymers (A3, A5) and extracted with benzene cannot be made soluble even after heating to 100°C for 40–80 h, not even in the presence of hydrolytic agents (acetic acid, pyridine, methanol).

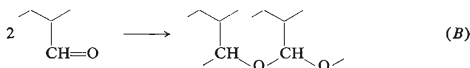
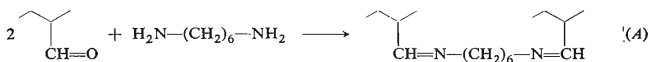
Reaction Mechanism

It can be deduced from the results described above that the copolymers of styrene and acrylaldehyde are readily crosslinked without catalysts. Two types of bonds participate in the formation of insoluble products. Those of the first type readily undergo hydrolytic and thermal splitting. The bonds involved here are probably hemiacetal bonds, the character of which and the mechanism of formation have been described for methacrylaldehyde⁵:

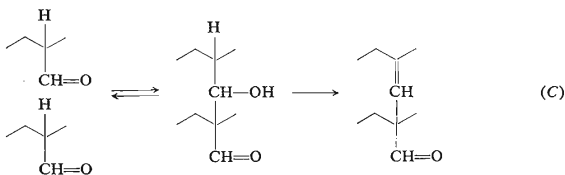


The instability of gels obtained by the crosslinking of the originally soluble copolymer with hexamethylenediamine can be explained on the basis of the mechanism

of network formation of the styrene-methacrylaldehyde copolymers by the action of the salt of a primary amine and carboxylic acid⁸⁻¹⁰, and also by a spontaneous process, bearing in mind that the —C—O—C— structures are formed in the copolymers of acrylaldehyde. Consequently, two parallel reactions are likely to occur during the process of crosslinking:



The oxygen bonds formed by reaction (B) are the cause of the relative thermal instability of the samples. On the other hand, thermally and hydrolytically stable bonds are obviously formed with the participation of the hydrogen atom at the α -position to the carbonyl group:



The reaction may occur both inside the molecule itself (intramolecular cyclization) and between different molecules (intermolecular crosslinking). No similar reaction is possible for the α -alkyl homologs of acrylaldehyde.

On heating of a spontaneously crosslinked copolymer, first the breaking of the crosslinks of the C—O—C type occurs; if the aldehyde concentration in the copolymer is not too high, the stage can be recorded in which the polymer is soluble. At the same time, the reaction (C) leads to branching, and eventually to the formation of gel. If the initial spontaneously crosslinked copolymer contains a major amount of the aldehyde component, then new bonds of the C—C type are formed already when not all C—O—C bonds have been split yet, and the stage of soluble products cannot be perceived. The splitting stage of the relatively unstable gel preceding the reaction (C) is its indispensable prerequisite. Splitting leads to a loosening of the chains which were originally firmly bonded in the polymer network. This will make possible larger motions of the chains and collisions between the reaction partners, which is immediately feasible in the case of soluble copolymers. The crosslinks of the C—C

type thus formed are thermally and hydrolytically very stable, and the final gel cannot be split.

Infrared spectroscopy did not yield any data on the structures arising during the above reactions because of the insignificant concentration of bonds needed for the network formation.

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