

REACTIONS OF METHACRYLALDEHYDE-STYRENE COPOLYMER. III.* THERMAL DEGRADATION OF LINEAR AND CROSSLINKED COPOLYMERS IN THE SOLID STATE

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The changes in the limiting viscosity number of a series of copolymers methacrylaldehyde-styrene and 2-ethylacrylaldehyde-styrene during heating to 80–120°C were investigated. Basing on the difference in the aldehyde content determined by the oximation method and elemental analysis and on the knowledge of the copolymer structure it is assumed that thermal instability is due to the crosslinks of the hemiacetal type which readily undergo thermal and chemical cleavage. Degradation in the presence of radical scavengers confirmed the assumption of an ionic reaction mechanism.

We have shown in earlier communications^{1,2} that the copolymer of styrene and methacrylaldehyde obtained by radical bulk and emulsion polymerization very readily undergoes degradation when heated to comparatively low temperatures; degradation was shown to occur both in benzene solutions and in the solid state. This paper is dealing in more detail with the degradation process due to heating of a solid polymer in an inert medium. Degradation is caused by the presence of thermally unstable bonds. From this viewpoint we also investigated copolymers of styrene and 2-ethylacrylaldehyde. The introduction of readily splitting bonds into polymers becomes important in practice in connection with the plastics waste disposal.

EXPERIMENTAL

Chemicals. Methacrylaldehyde (Spolana, Neratovice) was cooled to -72°C (ethyl alcohol-solid carbon dioxide), freed from water by filtration and rectified on a column 0.5 m long and filled with stainless steel coils, b.p. 40.7°C/300 Torr; the purity of the products was better than 99.5% according to GLC. 2-Ethylacrylaldehyde (Spolana, Neratovice) was purified in the same way; b.p. 92–92.5°C/760 Torr, purity better than 98.5%. The purification of styrene has been described earlier³. 2,2'-Azobis(isobutyronitrile) (Porofor, Lachema Brno) was used after having been twice recrystallized in ether.

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Copolymerization and degradation. A mixture of monomers and 2,2'-azobis(isobutyronitrile) (0.062 mol%) in an ampoule was freed from oxygen by repeated evacuation with freezing and washing with an oxygen-free nitrogen; on sealing, the ampoule was heated to 60°C. The copolymers were dissolved in benzene, precipitated into petroleum ether (b.p. 60–90°C) and dried *in vacuo* at room temperature to constant weight; the characteristic data are summarized in Table I (determination of the limiting viscosity number and the oximation determination of the content of free aldehyde groups had been described earlier^{3,4}). The aldehyde content in the copolymer from the elemental analysis data was determined by recalculation from the oxygen content determined differentially. The thermal degradation of copolymers took place in an oxygen-free nitrogen in sealed glass ampoules (initial pressure $5 \cdot 10^{-3}$ Torr) placed in a thermostated block. The samples designated for degradation in the presence of radical scavengers were dissolved beforehand in chloroform, the solution was homogenized with the respective scavenger, and the solvent was distilled off.

RESULTS AND DISCUSSION

Stability of Copolymers

The thermal stability estimated according to the change in the limiting viscosity number during heating of the copolymer methacrylaldehyde–styrene is much lower

TABLE I
Copolymerization of Styrene (S) with Aldehydes (A)

Co-polymer	[S] ₀ /[A] ₀ mol/mol	Conversion weight %	[η] dl/g	Content of aldehyde groups, %	
				oximation	elemental analysis
Poly(styrene-co-methacrylaldehyde)					
M 1	6.12	46.0	2.81	13.3	23.6
M 2	6.12	2.5	0.424	22.7	25.5
M 3	32.3	3.1	0.681	8.3	9.5
M 4	32.3	70.0	1.381	2.5	2.8
Poly(styrene-co-2-ethylacrylaldehyde)					
E 1	30.3	50.33	0.801	0.67	1.79
E 2	32.3	5.81	0.494	1.19	10.70
E 3	11.5	41.74	0.571	1.02	10.30
E 4	11.5	5.48	0.334	1.83	17.03
E 5	5.67	27.35	0.257	4.58	18.97
E 6	5.67	6.88	0.211	6.73	28.07

compared to pure polystyrene. Already heating to relatively low temperatures in an inert medium leads to a considerable decrease in the limiting viscosity number (Tables I and II). The samples M2–M4 heated to 120°C for 24 hours have their limiting viscosity number lower by 29–35% than the original material. The decrease in the limiting viscosity number for M1 is even deeper, although the original value of 2.81 dl/g proves a considerable branching near the point of gelation. In the case of polystyrene (a reference sample) the limiting viscosity number decreases by less than 1% under the same conditions (from 2.68 to 2.66 dl/g).

The copolymer M 1, which was completely insoluble in common solvents already after standing for 20 days, could be transformed into a low-molecular weight soluble product by mere

TABLE II

Limiting Viscosity Numbers (dl/g) of Copolymers after Degradation for 24 h
Samples M are defined in Table I.

Temperature, °C	M 1	M 2	M 3	M 4
80	0.564	—	—	—
90	0.216	0.388	0.627	1.288
100	0.181	0.331	0.567	1.095
110	0.161	0.275	0.490	0.965
120	0.162	0.275	0.484	0.890

TABLE III

Changes in the Limiting Viscosity Number of the Styrene-Methacrylaldehyde Copolymer (sample M 4) in the Presence of Radical Scavengers

Degradation conditions: 120°C, 24 h.

Scavenger	Limiting viscosity number, dl/g	
	before degradation	after degradation
—	1.381	0.890
Topanol CA	1.457 ^a	0.780
Alizarin	1.382	0.836
Anthraquinone	1.387	0.817
Chloranil	1.380	0.730

^a Cf. in Table I and Experimental — chloroform obviously forms an addition compound with the copolymer: it cannot be removed even by drying at $5 \cdot 10^{-3}$ Torr at room temperature for 2 days.

heating. Its thermal degradation at various temperatures ranging from 90 to 120°C leads to a constant reduced limiting viscosity number (Fig. 1a); at 80°C a similar tendency can be observed (Fig. 1b), but the time interval under investigation is not sufficient for a constant final value to be attained.

The analysis of products after the degradation of polymers by GPC in two different stages of the process showed that the copolymers exhibit a broad molecular weight distribution. An example is shown in Fig. 2 for the copolymer M 1: while on the first curve ($\bar{M}_w = 88\,600$) fractions having a molecular weight higher than 500 000 and also fractions lower than 3 200 can be seen, the sample after 8 hours of degradation ($\bar{M}_w = 31\,000$) contains only a small portion of fractions having a molecular weight higher than 10 000 and a major number of fractions whose molecular weights are lower than 3 200. Both distribution curves obtained for different times of degradation have practically the same shape and are only shifted with respect to each other, which is due to the different average molecular weight. It can be derived therefrom that from the very onset of degradation the decomposition of the polymer molecules proceeds statistically and not according to the size of the polymer molecules or by gradual splitting-off.

Measurements of the limiting viscosity number of the copolymers of styrene and 2-ethylacrylaldehyde (designated by E) differing by their molecular weights and the content of the aldehyde groups (Table I) show that these copolymers — similarly to the styrene-methacrylaldehyde copolymers — undergo degradation already at comparatively low temperature. After 24 hours of degradation of the copolymers at 100 and 120°C the limiting viscosity numbers were as follows:

Copolymer:	E 1	E 2	E 3	E 4	E 5	E 6
$[\eta]$, dl/g (100°C):	0.637	0.344	0.492	0.292	0.186	0.163
$[\eta]$, dl/g (120°C):	0.592	0.339	0.318	0.268	0.183	0.149

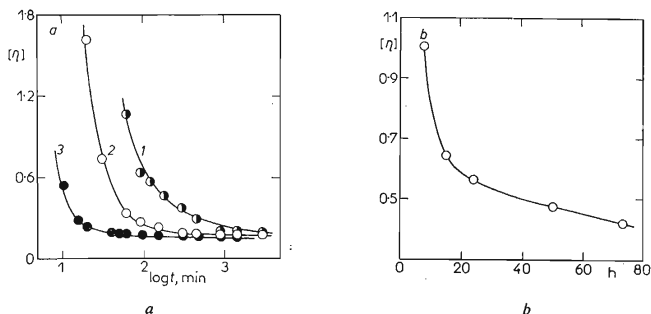


FIG. 1

Dependence of Limiting Viscosity Number (in dl/g) of Copolymer M 1 on Time of Degradation at 90–120 (a) and 80°C (b)

Temperature: 1 90, 2 100, 3 120°C.

The degradation too proceeded in an analogous way (example for the sample E 3 is given in Fig. 3); the limiting viscosity number decreases with increasing time of degradation while an increase in temperature above 120°C almost does not allow a higher degree of degradation to be achieved.

Mechanism of the Degradation Reaction

To elucidate the mechanism one has to start with the existing knowledge about the structure of the styrene-methacrylaldehyde copolymers. Generally, the structure of these copolymers can be described by Scheme 1, where OY can be the OH group.

It has been shown⁵ that the copolymers involved here have a statistical distribution of the monomer repeat units in the chain. As long as the methacrylaldehyde fraction in the copolymer does not exceed 40 mol.%, the majority of the aldehyde units at low conversions are bound in the triads styrene-methacrylaldehyde-styrene, as follows from the calculations and has also been proved experimentally. Thus, the presence of only an insignificant portion of structures A and B given in Scheme 1 can be taken into consideration. On the other hand, it has been found^{3,6} that acidobasic

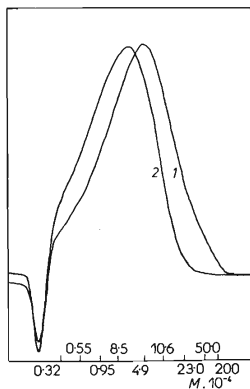


FIG. 2

Distribution Curves (GPC) of Copolymer M 1 after Degradation at 120°C

Time of degradation: 1 15 min ($[\eta] = 0.29$ dl/g, $\bar{M}_w = 88600$), 2 8 h ($[\eta] = 0.16$ dl/g, $\bar{M}_w = 31800$).

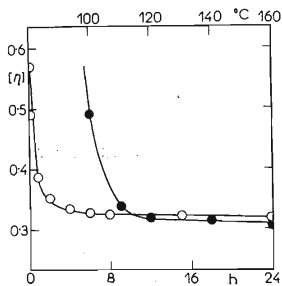
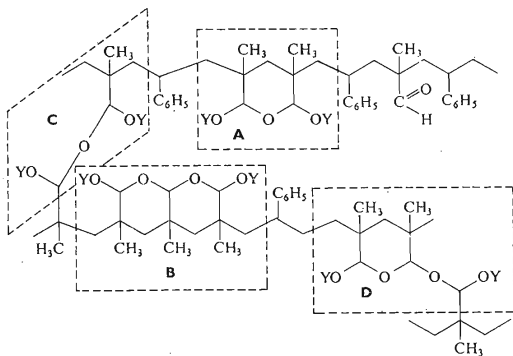


FIG. 3

Dependence of Limiting Viscosity Number (in dl/g) of Copolymer E 3 on the Time (○) (at 120°C) and Temperature (●) (after 24 h) of Degradation



SCHEME 1

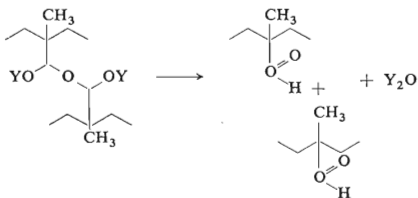
catalysts readily lead to the formation of polymer networks having a structure similar to D and particularly to C, for which a homopolymeric sequence of the aldehyde is not strictly necessary. Table I exemplifies the difference between the aldehyde content in the copolymer determined by different methods, namely, by the oximation method and by elemental analysis. In most cases, this difference is accounted for by the above structures and has been observed earlier². The ether bonds mentioned here are relatively weak and unstable both chemically and thermally.

If the copolymer molecules are considered to be steric formations, the crosslinks of the C and D type can be both intermolecular and intramolecular, and their formation can involve two stages in the process of preparation of the polymer. They can arise during the polymerization itself. At a low conversion the macromolecular coils are isolated in the monomer solution, they are strongly swollen, and the loops of the twisted chain are relatively far from each other. As a consequence, only intramolecular crosslinks can be formed here to a small extent. After a certain critical polymer concentration has been reached in solution, the polymerization mixture does not contain free solvent any more, and the coils touch each other. During a further increase in conversion, assuming a mutual impenetrability of the coils⁷ the chains become concentrated in the coils while at the same time the contact "areas" of the individual molecules increase owing to permeation in the surface zones. In this stage the probability of formation of both inter- and intramolecular crosslinks increases, the intermolecular bonds being more likely with respect to the coil surface-coil volume ratio.

An operation where also crosslinks of both types, that is, inter- and intramolecular can be formed, is separation of the polymer after completed polymerization, *i.e.*

during precipitation and drying. If the solvent quality becomes impaired, processes similar to those outlined above take place, that is, contraction of coils and their concentration in the separated concentrated phase. According to some results, this way of formation of the crosslinks is more likely, since in this stage the presence of a relatively sufficient amount of compound supporting the formation of hemiacetal bonds (water, alcohol) cannot be ruled out.

The thermally unstable hemiacetal bonds present in the styrene-methacrylaldehyde copolymer split again with a comparative ease. Since the degradation occurs under inert conditions, the splitting can be regarded as a purely thermal process which may be catalyzed by a trace amount of unremovable "impurities", obeying the following scheme:



Owing to the chemical identity of the inter- and intramolecular crosslinks the likelihood of their splitting is the same; it is given by their concentration in the polymer used and is reflected, in the first place, in a change in the limiting viscosity number. The splitting of an intramolecular bond or of the tetrahydrofuran ring (structures A and B, Scheme 1) will lead in a good solvent to a certain increase in the limiting viscosity number, since it will make possible a better solvation and an increase in the size of the coil. On the contrary, breaking of the intermolecular bonds will reduce the molecular weight considerably, thus also markedly decreasing the limiting viscosity number. Consequently, the limiting viscosity number determined in this fashion is a superposition of both processes described above. An example is provided by the sample M1 where the difference between the determination of the concentrations of the aldehyde groups (oximation and elemental, *cf.* Table I) shows that almost 45% of methacrylaldehyde is bonded in hemiacetal bonds and the degradation leads to a considerable reduction in the limiting viscosity number. An opposite case is represented by the other copolymers, where the hemiacetal bonds include 11% on the average of the total aldehyde content.

The assumed degradation mechanism, *i.e.* the decomposition of the ionic type, was confirmed by the results of degradation in the presence of compounds acting

as inhibitors of radical reactions (radical scavengers of the R• and RO• type) (Table III). A similar mechanism also holds for the copolymers styrene–2-ethylacrylaldehyde. However, the difference between the aldehyde content determined by the oximation method and that determined by elemental analysis cannot be assigned to the expense of the hemiacetal bonds only, since the oximation determination in the case of the copolymers of 2-ethylacrylaldehyde is not quite precise owing to the weak reactivity of the carbonyl group⁴.

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