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# CHEMISTRY

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## Abstract

## Full Text

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# LOW-TEMPERATURE RADIATION POLYMERIZATION OF ACROLEIN

*(Presented by Academician S. S. Medvedev, October 24, 1964)*

As is known ([1,2]), at 0° and above, acrolein in the presence of various initiators polymerizes through the vinyl bond, with simultaneous or subsequent ([3]) cyclization through the carbonyl group to form infusible polymers whose solubility depends on the method of preparation. Under the action of gamma radiation, acrolein polymerizes in bulk and in various solvents at 20°. In bulk polymerization an insoluble polymer is formed ([4]). It has also been shown that acrolein and its $\alpha$-alkyl-substituted derivatives polymerize under the action of various catalysts over a wide temperature range (from −60 to 100°), forming low-molecular-weight products with a high content of double bonds ([5–9]). It is assumed that in this case polymerization proceeds predominantly (and in some cases exclusively) through the $C{=}O$ bond of the aldehyde group. Recently it was shown ([10,11]) that in the radiation polymerization of diketene both carbocyclic and heterocyclic polymers can be obtained, the structure of the polymer chain depending on the conditions under which the process is carried out (liquid or solid state of the monomer).

**Fig. 1.** IR absorption spectrum of polyacrolein obtained in bulk at −78° (in a KBr pellet)

In view of the foregoing, it is of interest to study the low-temperature polymerization of acrolein under the action of gamma radiation and to determine the possibility of obtaining carbocyclic or heterocyclic polyacrolein. This article presents preliminary results.

Acrolein of chemically pure grade was freed from stabilizer by vacuum distillation on a column 60 cm high packed with Wilson spirals. The distilled monomer was filtered through a glass filter at −78°, and then dried in vacuum over calcium hydride for several days at room temperature. The monomer purified in

Fig. 2. IR absorption spectra of polyacrolein obtained by gamma irradiation of solid acrolein at −196°: a, b —the monomer was removed by repeated dissolution of the irradiated system in acetone followed by evacuation; c —the monomer was removed in vacuum after thawing the sample

Figure 2: Fig. 2. IR absorption spectra of polyacrolein obtained by gamma irradiation of solid acrolein at −196°: a, b —the monomer was removed by repeated dissolution of the irradiated system in acetone followed by evacuation; c —the monomer was removed in vacuum after thawing the sample

this way contained impurities of acetaldehyde and propionaldehyde.

Before the ampoules were filled, the monomer was degassed to $10^{-3}$–$10^{-4}$ mm Hg. Polymerization was carried out in bulk and in various solvents at −78 and −196° (the melting point of the monomer is −87.7° ([12])). The radiation source was $Co^{60}$. The dose rate was about 200 r/sec.

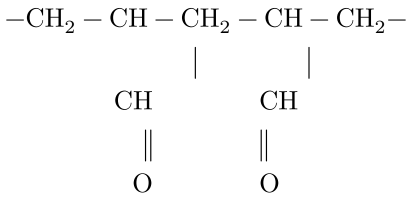
As a result of irradiation at −78°, acrolein and its solutions in methanol, ethanol, ethyl chloride, and acetone form a polymer soluble in the monomer or in the initial solution at low temperature. However, after

after some time (approximately after 10-30 min, depending on the nature of the solvent) after it has warmed to room temperature, the transparent solution becomes turbid and a flocculent insoluble polymer precipitates.

The polymer obtained is a white powder, soluble in dimethylformamide and pyridine and insoluble in other organic solvents. The IR spectrum of this polymer (Fig. 1) coincides with the spectrum of polyacrolein obtained in the polymerization of acrolein under the action of various initiators at room temperature ([2]).

**Fig. 2.** IR absorption spectra of polyacrolein obtained by gamma irradiation of solid acrolein at −196°:
*a*, *b* —the monomer was removed by repeated dissolution of the irradiated system in acetone followed by evacuation;
*c* —the monomer was removed in vacuum after thawing the sample

On the basis of the available literature data ([2], [3]), the formation at −78° of polyacrolein of the structure



$$-CH_2-CH-CH_2-CH-CH_2- \quad \text{with } -CH{=}O \text{ on each } CH \qquad (I)$$

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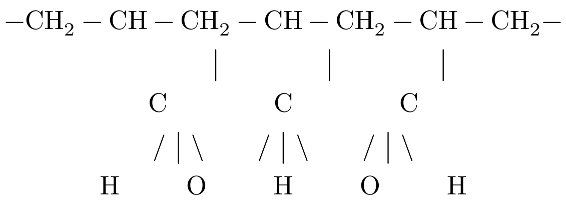
may be considered sufficiently probable, with subsequent cyclization upon raising the temperature, leading to the structure



$$\begin{array}{c} -\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH_2}- \\ \quad | \qquad\qquad | \qquad\qquad | \\ \mathrm{C} \qquad\qquad \mathrm{C} \qquad\qquad \mathrm{C} \\ / \mid \backslash \qquad / \mid \backslash \qquad / \mid \backslash \\ \mathrm{H} \qquad \mathrm{O} \qquad \mathrm{H} \qquad \mathrm{O} \qquad \mathrm{H} \end{array} \tag{II}$$

The energetic possibility of such cyclization has been shown in work (3).

Gamma irradiation of solid acrolein at $-196^\circ$ was carried out with doses on the order of 7-14 Mrad. Thawing was performed either by rapidly (1-2 min) heating the irradiated ampoule to room temperature (in this case the acrolein was immediately removed in vacuum), or by dissolving the irradiated monomer in solvents cooled to $-78 \div -90^\circ$ (acetone, methanol) containing hydroquinone.

The polymer obtained under these conditions is a viscous white mass with a strong odor. It is soluble in acrolein, acetone, carbon tetrachloride, petroleum ether, acetonitrile, benzene, toluene, glacial acetic acid, butyl alcohol, and ether. It is partially precipitated by methanol and ethanol. It is precipitated by water.

The polymer is unstable and undergoes degradation both in air and in vacuum. On storage in air, the viscous polymer turns into a liquid containing appreciable amounts of acrolein (several percent). When polymer samples are stored in vacuum, a continuous loss in weight is observed. In water, rapid degradation of the polymer also occurs, proceeding completely within several hours.

The yield of polymer at doses on the order of 10 Mrad is approximately 10-15%.

IR spectra of polymers obtained by gamma irradiation of solid acrolein indicate that polymerization proceeds predominantly via the $C{=}O$ bond (Fig. 2). In samples obtained by repeated dissolution of the polymer in acetone and evaporation of the solvent followed by evacuation, the absorption band of the unconjugated carbonyl group at 1740 $\mathrm{cm}^{-1}$ is absent (Fig. 2a) or almost absent (Fig. 2,b). In the spectra of samples obtained when the monomer is removed in vacuum, an absorption band of the unconjugated carbonyl group is present (Fig. 2c).

The weak absorption band at 1685 $\mathrm{cm}^{-1}$ (carbonyl group conjugated with a carbon-carbon double bond ($^{13}$)) is apparently due to the presence of free acrolein in the polymer (as a result of polymer degradation).

Intense absorption in the region 930-990 $\mathrm{cm}^{-1}$ is associated with deformation vibrations of hydrogen atoms in the $-CH{=}$ group of the vinyl group and out-of-plane deformation vibrations of hydrogen atoms in the $=CH_2$ group of the vinyl group ($^{13,14}$), as well as with out-of-plane deformation vibrations of hydrogen atoms in the $-CH{=}CH-$ group ($^{13}$). The absorption band in the region

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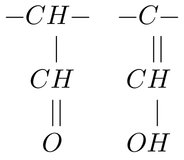
3090-3070 cm$^{-1}$ (stretching vibrations of $=C-H$) also indicates the presence of the $=CH_2$ group in the polymer.

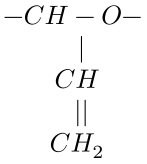
The absorption band in the interval 1060-1150 cm$^{-1}$ is due to stretching vibrations of $C-O$ groupings $-C-O-C-O-C-$ ($^{13}$).

It is interesting that in the spectra of polyacrolein containing the absorption band of the $C{=}O$ aldehyde group, there is an absorption band corresponding to stretching vibrations of the $O-H$ bond of the hydroxyl group (at 3450 cm$^{-1}$) (Figs. 1 and 2c), whereas when the carbonyl-group absorption band is absent from the spectrum, the absorption band of the OH group is also absent. This fact indicates the existence of keto-enol tautomerism



$$\begin{array}{c} -CH- \\ | \\ CH \\ \| \\ O \end{array} \qquad \begin{array}{c} -C- \\ \| \\ CH \\ | \\ OH \end{array}$$

From the data presented it follows that the polymer obtained upon irradiation of solid acrolein contains the groupings

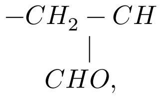


$$\begin{array}{l} -CH-O- \\ \;\;\;| \\ \;\;CH \\ \;\;\;\| \\ \;\;CH_2 \end{array}$$

I

$$-CH_2-CH=CH-O-$$

II



$$\begin{array}{l} -CH_2-CH \\ \qquad\;\;| \\ \qquad CHO, \end{array}$$

III

with structural element I probably being predominant.

As a result of gamma irradiation at −196° of acrolein containing no impurities of acetaldehyde or propionaldehyde (the monomer was purified by rectification on a column with an efficiency of 100 theoretical plates), we obtained a solid, soluble polymer that does not change during storage.

Thus, the polymers formed as a result of gamma irradiation of solid acrolein at −196° are, in their structure, analogous to the products obtained from this monomer under the action of ionic catalysts (9).

The results obtained indicate the possibility of obtaining polymers of different structures in the low-temperature radiation polymerization of acrolein.

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