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POLYMERIZATION OF METHACROLEIN WITH ANIONIC CATALYSTS

Among the series of α-alkyl-substituted acroleins, methacrolein has recently been attracting increasing attention from researchers both in the field of synthesis [1,2] and in polymerization.

In work by foreign authors [3,4], as well as by the authors of the present article [5], the radical polymerization of methacrolein has been studied in recent years.

In 1961 we established that acrolein and a number of its α-alkyl-substituted derivatives, including methacrolein, form soluble (for acrolein, partially soluble) polymers containing units with double bonds of the 3,4 or 1,4 type

$$\left[\begin{array}{c} C{-}O \\ | \\ CR \\ \| \\ CH_2 \end{array}\right] \quad \text{and} \quad [CH_2{-}CR{=}CH{-}O]$$

where $R = -H;\ -CH_3;\ -C_2H_5;\ C_3H_7;$ iso-C_3H_7 and C_4H_9

during polymerization with metallic sodium [6].

Subsequently, Schulz and co-workers, carrying out the polymerization of acrolein with a number of anionic catalysts, found the same type of polyacrolein structure and, moreover, indicated that under similar conditions methacrolein does not polymerize [7].

Fig. 1. Kinetics of polymerization of acrolein and methacrolein under identical conditions: 1 –acrolein with sodium naphthalene, 2 –methacrolein with sodium trityl, 3 –methacrolein with sodium naphthalene. Catalyst concentration in all cases 0.1 mol.%. Monomer : solvent ratio = 4 : 3, temperature −10°.

Using methacrolein and solvent of a high degree of purity, we succeeded in obtaining its polymers in the presence of sodium naphthalene and triphenyl-

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methylsodium. Polymerization was carried out over a wide temperature range from −40 to +20° in tetrahydrofuran solution.

Soluble polymers were obtained with yields of 55-100% and molecular weights from 50 to 100 thousand. All polymers contained double bonds from 10 to 20%. The content of aldehyde groups ranged from 25 to 40%. The polymers obtained also contain cyclic units (from 50 to 30%) analogous in structure to that obtained by us in the cationic polymerization with gaseous boron trifluoride of methacrolein and α-ethylacrolein [8].

The structural study was carried out by the methods of ozonization, hydrogenation, oxidation with perbenzoic acid, as well as IR and NMR spectra, and is the subject of a separate communication. In studying the rate of polymerization of methacrolein, it was established that it polymerizes considerably more slowly than acrolein.

Comparison of the kinetic curves for the polymerization of methacrolein in the presence of triphenylmethylsodium and sodium naphthalene showed that with the first catalyst methacrolein polymerizes more rapidly. Figure 1 gives the polymerization curves for acrolein and α-methylacrolein under identical conditions.

In studying the rate of polymerization of methacrolein with sodium naphthalene and with sodium trityl, we encountered the interesting phenomenon of a decrease in the rate of polymerization when the temperature was raised from −10 to 0°. This can be seen in Figs. 2 and 3, where curves 2 correspond to polymerization at 0°.

In polymerization with sodium naphthalene, a considerable decrease in the rate was observed upon dilution with solvent by a factor of two (Fig. 2, 1, 3).

Fig. 2. Kinetics of polymerization of methacrolein with sodium naphthalene (0.3 mol.%). 1 —polymerization at −10°, 2 —polymerization at 0°, 3 —polymerization at −10° with dilution by a factor of two, 4 —polymerization at −20°.

Fig. 3. Kinetics of polymerization of methacrolein with sodium trityl (0.2 mol.%). 1 —polymerization at −10°, 2 —polymerization at 0°, 3 —polymerization

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The content of double bonds in methacrolein polymers obtained by ionic polymerization gradually decreases upon storage in air. Thus, after storage of methacrolein for 12 months, a decrease in unsaturation by approximately a factor of one and a half was observed.

Experimental Part

Purification of the monomer and solvent

The initial technical methacrolein, containing 95-96% of the main substance, was distilled on an efficient rectification column, collecting the 68-69° fraction. The distillate was inhibited with hydroquinone and, for 4 hours, was shaken with zeolite of grade 5A. Recently, purification of the monomer on molecular sieves has been carried out countercurrently to fresh portions of zeolite. After this, the monomer was again distilled on the column.

The methacrolein obtained in this way was distilled on a vacuum manifold at a vacuum of $1 \cdot 10^{-2}$-$5 \cdot 10^{-3}$. The ampoule and receiver were preliminarily baked at 300° to remove occluded oxygen. Before distillation, the methacrolein in the ampoule was degassed in vacuum by alternating cooling with liquid nitrogen and solid carbon dioxide. The receiver containing the monomer was stored at −80°. The purified methacrolein contained 99.9% of the main substance. The purity of the monomer was determined by gas chromatography; tetrahydrofuran was purified in the usual manner. After this, a dark-red solution of triphenylmethyl potassium was obtained directly in the calibrated burette. The tetrahydrofuran was distilled off from this solution.

The purity of tetrahydrofuran was also monitored on a gas chromatograph, and

the finally purified solvent contained 99.97% of the principal substance.

Catalysts. For polymerization, sodium naphthalene at a concentration of 0.1 mole and triphenylmethylsodium at a concentration of 0.05 mole were used. Sodium naphthalene was used only within 24 hours after its preparation, since on longer storage it noticeably changes its activity.

Polymerization. In the study of the polymerization of methacrolein, two-section ampoules with a partition and a graduated neck were used. The ampoules were filled on a manifold (for the filling technique, see (8)). The second part of the ampoule was prepared for filling in the same way as the first, on the manifold, and the catalyst was metered into it from a Schlenk vessel. All polymers were precipitated into methanol. In reprecipitation, benzene was used as the solvent.

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Note: Figure translations are in progress. See original paper for figures.