Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR
M. M. Koton, I. V. Andreeva

1962

SovietRxiv

Abstract

Full Text

Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR M. M. Koton,
I. V. Andreeva
and Yu. P. Getmanchuk

Emulsion Polymerization of α-Methacrolein in the Presence of Various Oxidation-Reduction Systems

The polymerization of α-substituted acroleins has been studied insufficiently. It is known that, under the action of dilute alkali on α-methacrolein, tri-, tetra-, and pentamers are formed (^{1}). In the cationic polymerization of α-methacrolein in the presence of boron trifluoride etherate, polymers with reactive aldehyde groups are formed; the same polymers are formed when polymerization is carried out in an aqueous medium with potassium persulfate. Despite the different polymerization conditions, polymers of low molecular weight are obtained, apparently owing to the particular behavior of the monomer itself, which acts as a chain-transfer agent (^{2}). The highest intrinsic viscosity attained for α-methacrolein was $[\eta] = 0.04$—0.06 (pyridine).

We have carried out the polymerization of α-methacrolein with various oxidation–reduction systems in the presence of a new specific emulsifier—an aqueous solution of sulfurous-acid polyacrolein—used for the first time to achieve a substantial increase in the molecular weight of vinyl polymers (^{3}).

The conditions for carrying out the polymerization are presented in Table 1. When this emulsifier is used, a stable emulsion is formed, and polymerization proceeds not in the aqueous medium but in the micelles of the emulsifier.

Table 1

No. of polymers	Oxidizing agent	Reducing agent	Oxid., mol. %	Red., mol. %	Oxid.:red.	Polymer yield, %
1	$K_2S_2O_8$	without red.	1.3	–	–	80
2	$K_2S_2O_8$	$AgNO_3$	1.3	1.3	1 : 1	85
3	$K_2S_2O_8$	$AgNO_3$	1.3	0.13	1 : 0.1	100
4	$K_2S_2O_8$	$Fe(NH_4)_2(SO_4)_2$	2.6	2.6	2 : 2	63
5	$K_2S_2O_8$	$Na_2S_2O_3$	2.6	2.6	2 : 2	25
6	$K_2S_2O_8$	$Na_2S_2O_3$	3.3	3.3	2.5 : 2.5	84

Polymerization is carried out in a tenfold amount of water with the addition of a double amount of a 2% aqueous solution of emulsifier relative to the monomer. As is evident from the data in Table 1, the concentrations of initiators in experiments 4, 5, and 6 had to be increased in order to raise the polymer yield.

The properties of the polymers obtained are given in Table 2.

As is evident from the data in Table 2, irrespective of the nature of the oxidation-reduction system, the polymers of α-methacrolein obtained contain aldehyde groups within the range of 65–70% (determined by oximation), whereas for polyacrolein obtained in the same oxidation-reduction systems, the content of aldehyde groups varies from 20 to 70% (^{4}).

This difference is apparently associated with the presence of a side methyl group in the α-methylacrolein molecule, which hinders secondary cyclization reactions of the aldehyde groups, as occurs in the acrolein molecule. Although, with all oxidation-reduction systems, poly-α-methylacroleins are obtained that have approximately the same percentage of aldehyde groups, the most convenient system for polymerizing α-methylacrolein, as well as acrolein, is the system consisting of persulfate and silver nitrate, since it makes it possible to obtain polymers with the highest molecular weight and good yields.

Table 2

Polymer Nos.	Aldeh. groups by the oxime method, mol. %	Pyridine	Softening point, °C
1	71	0.24	191
2	69	0.42	215
3	66	0.38	211
4	65	0.26	189
5	63	0.27	192

The polymers obtained are soluble in pyridine. The intrinsic viscosity of the α-methylacrolein polymers, measured in pyridine, varies within the range from 0.19 to 0.43. The molecular weight of these polymers, determined by the translational-diffusion coefficient method and by intrinsic viscosity, had values from 70,000 to 195,000.

The α-methylacrolein polymers obtained in emulsion are white powders capable of being pressed (temperature 200° and pressure 75 atm) into light-yellow transparent plates with a softening temperature from 190 to 215° (on the IFP instrument).

Experimental Part

Preparation of the emulsifier (^{3}). 10 g of polyacrolein obtained by oxidation-reduction polymerization (potassium persulfate—silver nitrate) is dissolved in

50 ml of an aqueous solution of sulfurous acid (approximately a 7% solution). The gel that forms, depending on the molecular weight of the acrolein taken, gradually passes into solution over the course of 24–100 h. Dissolution can be achieved more rapidly if, after gel formation, about 50 ml of water is added and the mixture is shaken. After the polymer has dissolved, the solution is dialyzed to remove completely the excess sulfurous anhydride. Dialysis is usually carried out for 3–4 days. The process of removing sulfurous anhydride can be accelerated by passing nitrogen through the solution or with the aid of a suitable anion exchanger. The solution of sulfurous-acid polyacrolein is then transferred to a 500-ml volumetric flask and brought up to the mark with oxygen-free water. Without access of air, the solution can be stored for a long time.

Carrying out the polymerization. Into a three-necked flask equipped with a centrifugal stirrer, reflux condenser, dropping funnel, and nitrogen inlet, 300 parts by weight of water are poured and, while pure nitrogen is passed through, boiled for 3–4 h. After removal of air and cooling, 100 ml of emulsifier solution is added to the water. Calculated on the monomer, 5% emulsifier is taken. Then the reducing agent and 40 parts by weight of monomer are introduced into the reaction flask. After a stable emulsion has formed and after heating to 40° for 10 min, a solution of potassium persulfate is introduced, and during this time the temperature rises to 60°. The reaction is conducted for 5–6 h under nitrogen at a temperature of 60–65°.

To break the emulsion, 1–2 ml of hydrochloric acid is added to the reaction flask; the polymer is filtered off, washed with water and dry methyl alcohol, and dried to constant weight under vacuum.

Reprecipitation of the polymer is carried out by dissolving it in pyridine and precipitating it into ether or methyl alcohol. Experiments to determine the viscosity of the polymers and the diffusion coefficient, and the calculation of the molecular weight of the polymers, were carried out by V. E. Eskin and S. I. Klenin, to whom the authors express their gratitude.

Institute of High-Molecular-Weight Compounds
Academy of Sciences of the USSR

Received
23 III 1962

REFERENCES

1. E. Cilbert, J. Donleavy, *J. Am. Chem. Soc.*, **60**, 1737 (1938).
2. W. Kern, R. Schulz, *Angew. Chem.*, **69**, No. 5, 158 (1957).
3. H. Cherdron, *Kunststoffe*, **50**, 10, 568 (1960).

4. M. M. Koton, I. V. Andreeva, P. F. Andreev, E. M. Rogozina, *DAN*, **139**, No. 6, 1371 (1961).

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