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Abstract

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ON THE POLYMERIZATION OF IMIDES OF UNSATURATED DICARBOXYLIC ACIDS

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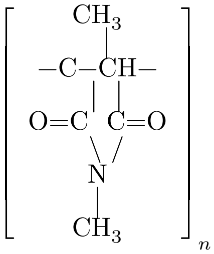
Establishing the relationship between the structure of monomers and their behavior in polymerization reactions is one of the central problems of macromolecular chemistry. The synthesis, carried out earlier by the authors ([1]), of N-substituted imides of citraconic acid made it possible to obtain the first quantitative and semiquantitative characteristics of the polymerization processes of this little-studied class of compounds.

Comparison of the experimental data with certain information that has appeared in the literature in recent years on the polymerization and copolymerization of maleic acid imides ([2,3]), as well as of cyclic anhydrides of citraconic ([3]) and maleic acids ([4]), made it possible to draw conclusions about the influence of the structure of this group of monomers on their ability to polymerize.

The most thoroughly investigated compound was N-methylimide of citraconic acid. It has been shown that it polymerizes by a radical mechanism with various initiators, and also upon prolonged standing at room temperature in an atmosphere of air, forming linear macromolecules consisting of cyclic imide units:



The structure of the polymer has been proven by chemical and spectral analyses. The elemental composition corresponds to the elemental composition of the monomer; the polymer is not hydrogenated over palladium; the infrared spectrum of the monomer differs from that of the polymer by the presence of an absorption band at 1650 cm^{-1}, assigned to stretching vibrations of the C=C bond; the bands at 1703-1725 and 1780 cm^{-1} are assigned to stretching vibrations of C=O in the five-membered ring, which is observed both in the polymer and in the monomer; the absorption band at 2962 cm^{-1}, assigned to deformation vibrations of the CH_3 group, is observed both in the polymer and in the monomer.

The rate of polymerization of N-methylimide of citraconic acid in the presence of DINIZ at 60, 70, and 80° is presented in Fig. 1. In the presence of various amounts of benzoyl peroxide at 70°—in Fig. 2.

As can be seen from Figs. 1 and 2, the absolute values of the polymerization rates are extremely small. The activation energy, calculated on the basis of the temperature dependence of the rate of the process, is ordinary for vinyl monomers. The polymerization rate in the initial period is proportional

to the square root of the initiator concentration, which is shown in Fig. 3.

The molecular weights of the polymers, judging from the intrinsic viscosity, are small. Only after prolonged standing of N-methylcitraconimide at room temperature (in an air atmosphere) was a polymer with a rather high molecular weight isolated. The data are presented in Table 1.

The low rate of polymerization and the small molecular weights can be explained by the peculiar structure of the monomer, which is a cyclic derivative of 1,2,2-substituted ethylene. Along with steric hindrance, the character of the polymerization is determined by the presence in the monomer of a methyl group at the carbon-carbon double bond. The mobile hydrogen atoms of this group make chain transfer to the monomer the most probable termination of the growing polymer chain. When chain transfer to the monomer occurs, a low-activity radical is formed

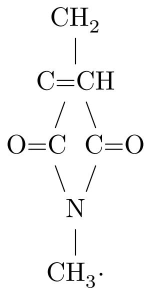


Fig. 1. Dependence of the polymerization rate of N-methylcitraconimide on temperature in the presence of $0.102 \cdot 10^{-3}$ mol/l of azobisisobutyric acid dinitrile in a nitrogen atmosphere.
$E_p = 21.2$ kcal/mol, $A_p = 5.3 \cdot 10^7$

As can be seen from the formula given, the activity of such a radical should be lower than that of an allylic radical owing to stabilization by two electron-withdrawing carbonyl groups. Initiation of polymerization by such a stable radical is improbable. If stable radicals can appear during the entire process, the active centers should slow down both initiation and chain growth, and the termination constants should increase, which leads to low molecular weights. Complete confirmation of such an interpretation can, of course, be obtained only by a detailed kinetic study. However, it seems to us that the data presented provide grounds for the proposed interpretation, in favor of which the comparison of the activity—

Fig. 2. Polymerization rate of N-methylcitraconimide at 70° in the presence of benzoyl peroxide:
1 —0.3% benzoyl peroxide, 2 —5.4%

Fig. 3. Dependence of the polymerization rate of N-methylcitraconimide on the concentration of azobisisobutyric acid dinitrile.

of imides and anhydrides of citraconic and maleic acids with respect to the styrene radical (see Table 2).

As can be seen from the data in Table 2, the activity toward styrene of the maleic acid derivatives is several times greater than that of the corresponding citraconic acid derivatives. Consequently, the growth constants of maleimides and maleic anhydride are significantly greater than those of citraconimides and citraconic anhydride, since for maleic acid derivatives the possibility of the appearance of stable radicals of the above-mentioned type is excluded owing to the absence of a methyl group at the double bond.

Table 1

Polymerization of N-methylcitraconimide under various conditions

Polymerization temperature	Benzoyl peroxide, %	Duration	Conversion, %	Intrinsic viscosity	Molecular weight (osmometrically)	Molecular weight (by light scattering)
60°	0.3	72 hours	23	0.12		
60°	5.4	72 hours	64	0.07		
20–25°	–	2 years	–	0.56	$250 \cdot 10^3$	$600 \cdot 10^3$

Experimental part

Synthesis of monomers

Citraconic anhydride was obtained by pyrolysis of citric acid. It was purified by two- or threefold vacuum distillation. The constants corresponded to those reported in the literature.

Citraconic acid imides were obtained from citraconic anhydride and the corresponding amines, by a one-stage or two-stage method, as described by us earlier.

The purity of the products was checked by refraction, elemental analysis, IR spectra, and chromatographically.

Table 2

Copolymerization constants of monomers M_1 with styrene M_2 (r_1 and r_2) and their activity with respect to the styrene radical

Monomer M_1	r_1	r_2	$r_1 \cdot r$	$1/r_2$
Maleic anhydride	0.01	0.041	0.0004	29.4
N-Butylmaleimide	0.06	0.025	0.0015	40
Citraconic anhydride	0.01	0.15	0.0015	6.7
N-Methylcitraconimide	0.24	0.135	0.032	7.4
N-Butylcitraconimide	0.206	0.14	0.029	7.2
N-Phenylcitraconimide	0.196	0.145	0.028	6.9

Polymerization was carried out in sealed ampoules in a nitrogen atmosphere. The polymer was isolated by reprecipitation from chloroform or dimethylformamide into methyl alcohol, filtered through a Schott funnel No. 4, and dried to constant weight in a thermostat or vacuum dryer at 70–80°. The polymerization rate was determined dilatometrically.

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