Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 155, No. 4

PHYSICAL CHEMISTRY

I. M. BARKALOV, Corresponding Member of the Academy of Sciences of the USSR V. I. GOLDANSKII,
and MING-TAO GUO

KINETICS OF THE POLYMERIZATION OF ACETYLENIC HYDROCARBONS INITIATED BY AZOISOBUTYRIC ACID DINITRILE

The kinetic features of the polymerization of acetylenic hydrocarbons appear under various types of initiation and are apparently associated with the formation, during polymerization, of macromolecules with a system of conjugated bonds ($^{1-4}$). We have considered various possible explanations of these features (cyclization, restoration of the triple bond, transfer of the chain to the monomer (^{3}), etc.), but only on the basis of the assumption of attenuation of the activity of the growing macroradical was a kinetic scheme constructed that is in satisfactory agreement with the experimental data, including (^{4}), and that explains such anomalies as the independence of the molecular weight of the polymer formed from temperature, the absence of an activation energy for chain growth, etc. (^{4}). In the initiation of acetylenic polymerization by benzoyl peroxide (BP), intense chain decomposition of the initiator was observed; the chain development in this decomposition is due, on the one hand, to the reaction of the benzoyl radical with the monomer with abstraction of labile acetylenic hydrogen and, on the other hand, to decomposition of BP by weakly active polymer radicals with a comparatively high stationary concentration, which do not continue the polymer chain but are capable of decomposing BP. In the present work it has been established that azoisobutyric acid dinitrile (DN) effectively initiates the polymerization of phenylacetylene (PA), without, however, undergoing chain decomposition in the process. Thus, radical polymerization of PA in the presence of DN is observed here, uncomplicated by simultaneously occurring processes.

The experimental procedure was analogous to that described in (^{4}). The rate of decomposition of DN was determined volumetrically from the evolution of nitrogen. It was established that, in contrast to BP, the rate constant of decomposition of DN in benzene, PA, and methylphenylacetylene is the same and equal to $\sim 8.6 \cdot 10^{-3}$ min^{-1} at 80°C, which agrees well with the literature data (^{5}). The activation energy of the decomposition rate of DN in PA is 31 ± 1

Fig. 1

Figure 1: Fig. 1

kcal/mole, which also agrees well with the literature data (^{6}). Evidently, the presence of an acetylenic monomer does not affect the rate of decomposition of DN, in contrast to the decomposition of BP. At the same time, the previously established kinetic features of acetylenic polymerization—the effective abstraction of labile acetylenic hydrogen by initiating radicals and the attenuation of the activity of the growing polymer radical—are retained. As in the case of peroxide initiation (^{4}), the rate of polymerization upon initiation of deuterated PA by DN is one and a half times lower than that of PA, and polymerization of methylphenylacetylene is not observed at all. Thus, the polymerization of acetylenic hydrocarbons initiated by DN may be represented by the following scheme:

$$\begin{aligned} \mathrm{DN} &\to 2\mathrm{R}', && (0)\\ \mathrm{R}' + \mathrm{M} &\to \mathrm{R}'\mathrm{H} + \mathrm{R}\cdot, && (1)\\ \mathrm{R}' &\to \text{termination}, && (2)\\ \mathrm{R}\cdot + \mathrm{M} &\to \mathrm{R}\cdot, && (3)\\ \mathrm{R}\cdot + \mathrm{M} &\to \text{polymer}, && (4) \end{aligned}$$

where DN is azoisobutyric acid dinitrile, M is the acetylenic monomer, R' is the radical $(\mathrm{CH_3})_2\mathrm{CN}\cdot$, $\mathrm{R}\bullet$ is the radical $\mathrm{C_6H_5C \equiv C}\cdot$, and also the growing polymer radical. In the interaction of the radical R' with the monomer, abstraction of labile hydrogen occurs (reaction 1), as in the case of peroxide initiation. This reaction is somewhat slowed in deuterated PA and is absent under the given experimental conditions in methylphenylacetylene. The termination reaction (2) should be regarded as the entry of primary radicals into various side processes, for example into reaction with solvent molecules with the formation of inactive radicals or termination on the wall of the reaction vessel. The acetylenic radical $\mathrm{R}\bullet$ formed in reaction (1) conducts the polymer chain; moreover, the activity of the growing polymer radical decreases with increasing chain length, which ultimately leads to termination (reaction 4). The possible reasons for such damping of the activity of the polymer radical were considered by us earlier $^{(1-4)}$. Starting from this scheme, we obtain for the polymerization rate the relation:

Fig. 1. Dependence of the polymerization rate of PA on the monomer concentration in benzene and xylene (1) and on the DN concentration (2) during polymerization in bulk at 80°

$$W = 2k_0[\mathrm{DN}]\left(2 + \frac{k_3}{k_4}\right)\frac{k_1[\mathrm{M}]}{k_2 + k_1[\mathrm{M}]},$$

which agrees well with the experimental dependences obtained. Indeed, the rate of DN-initiated polymerization of PA is proportional to the first power of the initiator concentration, whereas the reaction order with respect to monomer varies from zero to first—in accordance with the relation:

$$\frac{1}{W} = A + \frac{B}{[\mathrm{M}]},$$

where

$$A = \frac{1}{2k_0[\mathrm{DN}]\left(2 + \frac{k_3}{k_4}\right)}, \qquad B = \frac{k_2}{k_1}A.$$

The experimentally observed dependence of the reciprocal rate of DN-initiated polymerization of PA in benzene and xylene on the reciprocal concentrations of initiator and monomer is presented in Fig. 1. The dependence $1/W$ on $1/M$ (straight line 1) was obtained at $[\mathrm{DN}]_0 = 0.061$ mol/l. From the magnitudes of the intercepts cut off by straight line 1 on the abscissa and ordinate, we obtain $A = 140$ l • min/mol, $A/B = 0.6$ l/mol, i.e. $2k_0[\mathrm{DN}]\left(2 + \frac{k_3}{k_4}\right) \simeq 7 \cdot 10^{-3}$ and $k_1/k_2 = 0.6$ l/mol. Knowing the decomposition rate of the DN polymerization initiator: $k_0[\mathrm{DN}] \simeq 0.5 \cdot 10^{-3}$, we obtain $k_3/k_4 \simeq 5$. The same ratio of the rate constants of polymer-chain growth with retention and with disappearance of the activity of the polymer radical, determining the "damping" of the chain, was obtained earlier (4) for PA polymerization initiated by benzoyl peroxide. From the ratio k_1/k_2 it is easy to conclude that, during PA polymerization in bulk ($[\mathrm{M}] = 9.8$ mol/l), the rate of reaction (1) exceeds the rate of reaction (2) by approximately 6 times. A similar efficiency of initiation of polymerization chains is close to that established in (7) for vinyl monomers. The dependence of W on the initiator concentration (DN), presented in Fig. 1 by straight line 2 in the form $1/W = C \cdot 1/[\mathrm{DN}]$, was obtained at $[\mathrm{M}] = M_0 = 9.8$ mol/l. The proportionality coefficient

$$C = \frac{1 + \dfrac{k_2}{k_1[M]}}{2k_0\left(2 + \dfrac{k_3}{k_4}\right)}$$

is obviously related to A and B by the relation $C = [A + B/M_0]\,D_0$, i.e., at the above values of M_0 and D_0 it should be equal to ~ 10. Since the initiation rate in the present scheme is equal to

$$W_{\mathrm{in}} = k_1 RM = 2k_0 D \frac{k_1 M}{k_1 M + k_2},$$

Fig. 2. Kinetic curves of PA polymerization at 80°, initiated by DN (0.061 mole/liter): 1—without benzoquinone, 2—with addition of 0.047 mole/liter benzoquinone

Figure 2: Fig. 2. Kinetic curves of PA polymerization at 80°, initiated by DN (0.061 mole/liter): 1—without benzoquinone, 2—with addition of 0.047 mole/liter benzoquinone

the average degree of polymerization is, obviously, $\bar{p} = 2 + \frac{k_3}{k_4} \simeq 7$, which agrees well with the experimentally found length of the polymer chain (molecular weight of the reprecipitated polymer 680—750). Let us recall that close values of the degree of polymerization were obtained by us for phenylacetylene ($^{1-4}$) with other types of initiation. Thus, the length of the polymer chain of PA and other acetylene derivatives is practically independent not only of the temperature and monomer concentration, but also of the type of initiation.

The activation energy of the polymerization reaction of PA initiated by DN is 31 ± 1 kcal/mole of initiator. Under the assumption of attenuation of the activity of polymer radicals as they grow, this means practical equality of the activation energies of reactions (3) and (4), as was also assumed earlier ($^{1-4}$). Finally, we note that in the case considered of initiation of PA polymerization by dinitrile of azoisobutyric acid (in contrast to benzoyl peroxide), additions of benzoquinone only slightly retard the rate of polymerization: a fourfold increase in the concentration of benzoquinone—from 0.05 to 0.2 mole/liter—decreases the reaction rate by 10% (from $4.86 \cdot 10^{-3}$ mole/liter • min to $4.42 \cdot 10^{-3}$ mole/liter • min). Apparently, the radicals formed here in the reaction of growing polymer radicals with benzoquinone are, in their activity, comparable with the activity of the polymer radicals themselves, and therefore the role of benzoquinone is reduced only to a weak decrease in the effectiveness of initiation.

Fig. 2. Kinetic curves of PA polymerization at 80°, initiated by DN (0.061 mole/liter): **1**—in the absence of benzoquinone, **2**—with addition of 0.047 mole/liter benzoquinone.

Thus, in the polymerization of PA in the presence of DN, not complicated by chain decomposition of the initiator, as in radiation polymerization, the characteristic features of acetylene polymerization are most clearly manifested, namely—the important role of the reaction of abstraction of mobile acetylenic hydrogen and the decrease in the activity of the polymer radical as it grows.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
28 XI 1963

REFERENCES

1. I. M. Barkalov, A. A. Berlin et al., *Vysokomolek. soed.*, **2**, 1103 (1960).
2. I. M. Barkalov, V. I. Goldanskii et al., *Vysokomolek. soed.*, **5**, 373 (1963).
3. I. M. Barkalov, A. A. Berlin et al., *Vysokomolek. soed.*, **5**, 377 (1963).
4. I. M. Barkalov, V. I. Goldanskii, Go Min' -gao, *DAN*, **151**, 1123 (1963).
5. L. M. Arnett, *J. Am. Chem. Soc.*, **74**, 2027 (1952).
6. M. Jalât-Erben, S. Bywater, *J. Am. Chem. Soc.*, **77**, 3712 (1955).
7. L. M. Arnett, J. H. Peterson, *J. Am. Chem. Soc.*, **74**, 2031 (1952).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.