Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, K. S. MINSKER,

1962

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, K. S. MINSKER,
R. P. CHERNOVSKAYA

THE INFLUENCE OF ORGANIC COMPOUNDS WITH A CLOSED π-CONJUGATED SYSTEM OF BONDS ON THE STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

The totality of results published in the literature on the study of heterogeneous catalytic polymerization proceeding in the presence of a binary stereospecific Ziegler-type system (a halide of a transition metal of groups IVA–VIA; VIII in a mixture with a metal, a metal hydride, or a hydrocarbon compound of a metal of groups I–III of the periodic table) permits the conclusion that the reaction cannot be assigned either to purely ionic or to purely radical processes. The direction and character of the course of the reaction process depend in many respects on the properties and state of the solid surface. It is important that the homogeneous component of the binary catalyst also plays a major role in determining the direction and course of polymerization. Naturally, the presence in the reaction medium of various compounds capable of interacting with at least one of the components of the binary Ziegler catalyst may exert a significant influence on the polymerization process. This is clearly seen in the example of introducing into the reaction system nucleophilic compounds of the polar type ([1–5]) and unsaturated hydrocarbons (comonomers) possessing conjugated bonds ([6,7]).

In contrast to the work (polymerization of ethylene) ([6]), in attempting to obtain a copolymer of propylene with styrene (the concentration of styrene was 10–100 times higher than in work ([6])) we found that propylene was bound with formation of a solid polymer product at an anomalously high rate.

Moreover, when the aliphatic solvent was replaced by aromatic hydrocarbons (in particular, benzene), an effect of an additional increase in the rate of binding of propylene was observed ([8]). Developing these studies, it was shown that styrene does not behave identically over the entire range of its concentrations in the reaction medium (Fig. 1, 1). Small additions (up to 0.2 mole/l) to the heptane fraction of gasoline (b.p. 96–102°), taken as solvent, slowed the rate of binding of propylene ($k_g/k_0 = 0.5$—0.6)*. At the same time the comonomer styrene did not enter into the composition of the polymer product formed. Elemental analysis, differential-thermal analysis, and thermomechanical investigations of

Fig. 1. Dependence of the rate of polymerization of propylene on the concentration of the aromatic additive

Figure 1: Fig. 1. Dependence of the rate of polymerization of propylene on the concentration of the aromatic additive

the polymer product showed the absence in it of styrene units. In this part our results agree satisfactorily with the data of work ([8]).

Increasing the styrene content in the reaction mixture (concentration range 0.2 —0.4 mole/l) led to an increase in the rate of polymerization of propylene. The latter, as a function of styrene concentration, reached a maximum when its content in the aliphatic solvent was 3.0—4.0 mole/l (the ratio k_g/k_0 corresponded to $2 \div 2.2$).

The slowing of the rate of propylene binding with an increase in the concentration of styrene in the reaction volume above 3.5-4.0 mole/liter was due to the binding of styrene, which was confirmed by elemental and differential-thermal analyses of the polymer product formed.

These new experimental facts prompted us to study in greater detail the influence on stereospecific polymerization of the Ziegler type of several other organic compounds possessing a closed π-conjugated system of bonds (benzene, biphenyl, naphthalene, anthracene), also using propylene as the model monomer. The indicated additives are characterized by enhanced electron-donor and electron-acceptor properties of the molecules.

Fig. 1. Dependence of the rate of polymerization of propylene on the concentration of the aromatic additive at 45°; $C_{\mathrm{TiCl_3}} = 0.0265$ mole/liter; $C_{\mathrm{Al(C_2H_5)_3}} = 0.26$ mole/liter. Reactor volume 4 liters; volume of the liquid mixture 1 liter; initial propylene pressure 4.5-5 atm. 1 —styrene; 2 —benzene; 3 —naphthalene; 4 —biphenyl; 5 —anthracene. 3a —experiments carried out with an addition of naphthalene exceeding its solubility in benzine at the temperature of the experiment.

The aromatic compounds listed above were introduced into the reaction volume immediately before the feed of propylene. The concentration of the additive in different experiments was varied by replacing part of the aliphatic solvent with the corresponding amount of the aromatic compound used, calculated so that the total volume of the liquid phase remained constant in all experiments.* The experiments were carried out at 45° under static conditions in a special 4-liter steel reactor and at an initial propylene pressure of 4.5-5 atm. The kinetic data were treated according to equations (20) and (33), proposed in work ([9]).

---

* k_0 and k_g are the rate constants for the binding of propylene in the medium of the aliphatic solvent without additives and in the presence of an additive, respectively (in l per 1 g of $\mathrm{TiCl_3}$ in 1 min.).

Typical dependences of the change in the rate of propylene binding in the presence of introduced additives of aromatic character are shown in Fig. 1. From consideration of the experimental results it follows that, as in the case of nucleophilic polar additives, a complex dependence was observed for the process of stereospecific polymerization on the aromatic compounds investigated that were introduced into the reaction medium. However, this dependence has a different character than in the case where nucleophilic compounds of the polar type are used as additives.

Small amounts of aromatic compounds (of the order of up to 0.3 mole/liter) slowed the overall reaction rate. Increasing the content of aromatic hydrocarbon above 0.2-0.3 mole/liter led to a noticeable increase in the overall rate of propylene binding. Thus, when conducting reaction in a medium of the heptane fraction of gasoline with additions of up to 0.3 mole/liter benzene, a slowing of the rate of polymerization of propylene by a factor of 1.5-2.0 was observed ($k_g/k_0 = 0.5 \div 0.6$).

A further increase in the benzene content in the reaction mass led to an increase in the overall rate of binding of propylene ($k_g/k_0 = 2.6$ at a benzene concentration in the reaction medium above 10 mole/liter).

A similar character of the dependence of k_g/k_0 on the additives introduced into the reaction mixture was also observed for the other aromatic hydrocarbons studied. Moreover, the rate of change of k_g/k_0 with the concentration of the aromatic additive depended on the nature of the latter; the greatest rate of increase was observed for naphthalene.

The low solubility of anthracene in gasoline did not permit analogous studies to be carried out over a wide range of its concentrations. Therefore the experimental data are limited to the introduction of only small amounts of it (up to 0.1 mole/liter).

Analysis of the experimental data obtained suggests that, in the systems studied, complex formation occurs between the aromatic hydrocarbon, which possesses enhanced electron-donor and electron-acceptor properties, and at least one of the components of the binary complex catalyst. The formation of a molecular compound with the titanium component may occur through electrophilic attack by the positively charged metal, exposed at defects of the ionic crystal $TiCl_3$, on the aromatic π-electron system, which stabilizes the complex. In this case, naturally, one should assume a back dative bond from the metal to the unoccupied π- and σ-orbitals of the cyclic ligands.

It is also quite probable that interaction takes place between the aromatic compounds and the aluminum-alkyl component of the complex catalyst, analogous to the well-known complexes of $AlCl_3$ with benzene, toluene, etc. ([10]).

---

* The maximum amount of solid additives introduced into the reaction zone depended on their solubility in the aliphatic solvent.

The equilibrium state of the indicated interaction depends on the chemical structure and concentration of the additives, which undoubtedly should also affect the electronic state of the active centers and, consequently, their polymerizing ability.

Received
29 VIII 1962

CITED LITERATURE

1. G. A. Razuvayev, K. S. Minsker et al., *Vysokomolek. soed.*, **1**, 1691 (1959).
2. G. A. Razuvayev, K. S. Minsker et al., *Vysokomolek. soed.*, **2**, 404 (1960).
3. K. Vesely, *J. Polymer Sci.*, **34**, 46 (1959).
4. K. Vesely, J. Ambroz et al., *J. Polymer Sci.*, **55**, 25 (1261).
5. K. Kodama, Yu. Atarasi, *J. Chem. Soc. Japan, Industr. Chem. Sec.*, **64**, 1140 (1961); *RZhKhim.*, 7P122 (1962).
6. L. M. Lanovskaya, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **2**, 1391 (1960).
7. L. M. Lanovskaya, A. R. Gantmakher, S. S. Medvedev, *Vysokomolek. soed.*, **2**, 1655 (1960).
8. G. A. Razuvayev, K. S. Minsker, I. Z. Shapiro, *Vysokomolek. soed.*, **4**, No. 12 (1962).
9. V. I. Tsvetkova, O. N. Pirogova et al., *Vysokomolek. soed.*, **3**, 585 (1961).
10. Ch. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry*, IL, 1949, p. 55.

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

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