PHYSICAL CHEMISTRY

G. P. GLADYSHEV and S. R. RAFIKOV

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

G. P. GLADYSHEV and S. R. RAFIKOV

INITIATION OF POLYMERIZATION BY ELECTRIC CHARGES ARISING AT PHASE BOUNDARIES

(Presented by Academician N. N. Semenov, 15 X 1960)

The course of many chemical reactions is associated with the presence in the system of interfaces (in the simplest case, the wall of a vessel—the reaction medium), with the formation of new phases, and with phase transitions.

Phenomena of polymerization during the melting of solid monomers (MMA, styrene, etc.) have been described (^{1,2,3}). An increase in the rate of polymerization of isobutylene at low temperature in the presence of solids is known (^{4}). When powders are used, the reaction rate depends strongly on the size of the solid particles, but only slightly on the nature of the powders (^{1}). Recently Adler, Ballantyne, and others reported (^{5}) that they observed a polymerization reaction in a liquid on the surface of lumps of polymer. Abkin (^{6}) notes the role of the wall in the radiation polymerization of styrene in ethyl chloride solution at $-78°$. Of interest are the studies of Kargin, Kabanov, Plate, and others (^{7}) on polymerization caused by freshly comminuted solids and using the method of molecular beams. In studying the polymerization of sodium acrylate in the presence of certain salts, these authors found a substantial influence of the solid crystalline phase on the reaction rate.

Other examples can also be cited of the initiating influence of phase transformations on the course of chemical reactions. Thus, reactions of chlorination and hydrochlorination upon freezing of reaction mixtures have been described (^{1,8}), as have reactions of oxides of alkali and alkaline-earth metals with oxides and chlorides of elements of group 4 at the temperatures of the polymorphic transformation of one of the components (^{1,9}), and a number of others. Medvedev notes the special role of the surface in the initiation and growth of the chain in the case of emulsion polymerization (^{10}).

It seems to us that in all the processes mentioned, an essential role belongs to electric charges arising at phase boundaries, during phase transitions, as a result of mechanical destruction, etc. The occurrence of charges in such cases has been observed by many investigators (^{11}). Alexander and Rideal (^{12}) believe that, in the case when the active complex acquires an electric charge, the reaction rate in monolayers changes in proportion to the factor $e^{-E\varphi/RT}$, where φ is the potential jump. In this connection, Danieli and Davies (^{13}) note that the value PH_s (in the surface layer) is related to PH_b (in the bulk):

$$PH_s = PH_b + \frac{\varphi_s}{0.058}.$$

Some authors indicate that the electric potential affects the activation energy of chemical reactions (^{12}), whereas others suppose that this influence occurs only in the case of solid surfaces (heterogeneous catalysis) (^{14}). It is quite natural to assume that the existence of a potential difference at phase boundaries will promote the orientation of molecules near the interface, which, according to

Semenov' s views (^{1}), is necessary for polymerization processes to proceed at low temperatures.

In our opinion, the potential jump should affect not only the pre-exponential factor in the Arrhenius equation, but in all cases when the active complex acquires an electric charge, the activation energy of the chemical reaction must also change.

If the reaction rate in the bulk is represented in the usual form:

$$V = A_1 e^{-E_1/RT}, \tag{1}$$

then the rate of the same reaction in the presence of a potential jump (i.e., at the interface) is written as:

$$V = A_2 e^{-E_2/RT}, \tag{2}$$

where A_2 is different from A_1, $E_2 = E_1 - E_\varphi$, $E_\varphi = n\,23060\left(\varphi - T\frac{d\varphi}{dT}\right)$ (the sign of E_φ depends on the system under consideration).

Consequently, it may be expected that under certain conditions the polymerization reaction will proceed at a considerable rate owing to a decrease in the activation energy and an increase in the pre-exponential factor caused by the presence of a potential jump.

In order to determine the possibility of initiating polymerization processes by means of surface electric potentials, we studied the polymerization of certain unsaturated compounds at phase boundaries at relatively low temperatures and in the absence of generally known initiators and catalysts of this reaction. The influence of certain impurities on the rate of the polymerization process in the boundary layer monomer—surface (surface-active substances, inhibitors) was also studied. In the work, monomers purified of stabilizer and peroxides and distilled under vacuum were used. Other reagents were purified by ordinary methods; the constants of the substances used were in agreement with literature data. In all the cases studied, the absence of peroxides in the substances taken was checked, and control experiments on polymerization in a homogeneous system were carried out in the presence of benzoyl peroxide, as well as of certain additives that had a positive effect on polymerization in the presence of two phases.

Experiments on the polymerization of acrylonitrile (AN) and methyl methacrylate (MMA) at 20–22° at phase boundaries (liquid–liquid, liquid–solid) showed the possibility of initiating polymerization processes in the absence of ordinary initiators and catalysts due to the jump of the surface potential.

Thus, for example, after holding for 10–12 hours a layer of AN 1–2 cm thick on the surface of glycerin containing 1–2% water, at 20–22° the formation of noticeable amounts of polymer in the form of white flakes is observed. The molecular weight of the polymer obtained is 100000–200000 (from solution viscosity). At the same time, atmospheric oxygen, which is an inhibitor in the radical polymerization of AN, does not exert a substantial effect on the course of the process.

Polymerization of AN at the AN–water interface (more precisely, their mutually saturated solutions) proceeds at a measurable rate only in an atmosphere of CO_2. In the case of MMA polymerization at the boundary with water and with mercury in an air atmosphere, noticeable polymer films form after 30–40 hours; at the MMA–paraffin and MMA–glycerin interfaces, film formation was observed after 4–5 hours. Carrying out the experiments in an atmosphere of carbon dioxide leads to a more rapid conversion of the monomer into polymer, and noticeable amounts of the polymer formed can in some cases be observed immediately after oxygen has been removed from the system.

It is well known that the introduction of many substances has a strong effect on the potential jump between phases, which undoubtedly must be reflected in the reaction rate. Indeed, when acids (CH_3COOH, $CH_2ClCOOH$, HCl) are added in amounts of about 0.01% in the case of polymerization in the AN–glycerin system with 1% water (20°), after 15-20 hours of standing the degree of conversion reaches 25-30%, while oxygen does not exert any noticeable inhibiting effect. In the AN–water system (1 : 1) with addition of acids (0.01 mole/l) in a nitrogen atmosphere, after 100 hours following mixing of the liquids the degree of conversion is only 1.5%, and the molecular weight of the polymer is about 6,000,000 (from viscosity).

The rate of polymer formation in the AN–glycerin–acid system increases greatly in the presence of water. In this case polymerization proceeds both in the upper and in the lower layers. In the AN layer, polymer formation begins at the interface, and further polymerization occurs directly on particles of polyacrylonitrile. The occurrence of the reaction throughout the entire volume of the lower layer (AN–glycerin–water–HCl, AN–water–HCl) is apparently associated with initiation on microscopic surfaces of separation or during mixing of the components, which is confirmed by the dependence of the reaction rate on the order of mixing of the substances composing the system, on the presence in the system of finely divided solid bodies, and by other facts.

Another example showing the influence of the electric potential on the course of the polymerization reaction is provided by experiments on the polymerization of MMA during its electrization. Thus, when a thoroughly degassed monomer is shaken (electrized) in glass ampoules (400–600 oscillations/min) at 20° in the absence of any other reaction initiators, a rapid increase in the viscosity of the monomer is observed owing to the formation of polymer. The degree of conversion under these conditions reaches 5–10% in 3 hours. Thus, the investigations carried out show that the polymerization of acrylonitrile and methyl methacrylate can undoubtedly be initiated by electric charges arising at phase boundaries in the absence of the usual reaction initiators. There are grounds to believe that the polymerization of many other unsaturated compounds can be accomplished in an analogous manner. The data available at present do not permit a definite judgment to be made about the mechanism of the reaction; however, the fact that it is inhibited by inhibitors indicates the radical character of the process.

Institute of Chemical Sciences
Academy of Sciences of the Kazakh SSR

Received
15 X 1960

CITED LITERATURE

1. N. N. Semenov, *Khim. i tekhnol. polimerov*, No. 7–8, 196 (1960).
2. J. C. Bevington, R. G. W. Norrish, *Proc. Roy. Soc.*, A **196**, 363 (1949).
3. H. A. Rigby, C. J. Danby, C. W. Hinshelwood, *J. Chem. Soc.*, 1948, 234.
4. R. Worrall, S. H. Pinner, *J. Polym. Sci.*, **34**, 229 (1959).
5. J. Adler, D. Ballantyne, B. Baeyzal, International Symposium on Macromolecular Chemistry, reports and abstracts, Section II, Moscow, 1960, p. 396.
6. A. D. Abkin, A. L. Sheinker et al., International Symposium on Macromolecular Chemistry, reports and abstracts, Section II, Moscow, 1960, p. 410.
7. V. A. Kargin, V. A. Kabanov et al., *Vysokomolek. soed.*, **1**, 264 (1959); **1**, 301 (1959); **1**, 330 (1959); **1**, 1853 (1959); **1**, 1859 (1959); **2**, 765 (1960); V. A. Kargin, N. A. Platé, International Symposium on Macromolecular Chemistry, reports and abstracts, Section II, Moscow, 1960, p. 460.

8. V. A. Lishnevskii, G. B. Sergeev, *DAN*, **128**, 767 (1959).

9. V. I. Evdokimov, *ZhNKh*, **3**, 1232 (1958).

10. S. S. Medvedev, *Collection Czechoslovak Chem. Comm.*, **22**, Suppl. 174 (1957).

11. H. K. Adam, *Fizika i khimiya poverkhnostei*, Moscow-Leningrad, 1947; A. Nikuradze, *Liquid Dielectrics*, NKTP USSR, 1936; N. Saito, K. Tanaka, *Proc. 7th Japan Nat. Congr. Appl. Mech.*, 1957, Tokyo, 1958, p. 35; *Proc. 6th Japan Nat. Congr. Appl. Mech.*, 1956, Tokyo, 1957, p. 205; G. S. Rose, S. G. Ward, *Brit. J. Appl. Phys.*, **8**, 121 (1957); J. Kobatake, J. Inone, *Koll. Zs.*, **159**, 168 (1957); L. G. Kuchurin, V. I. Bekryaev, *DAN*, **130**, 57 (1960).

12. E. Hsiao, *Monomolecular Layers*, IL, 1956, p. 222.

13. J. F. Danielli, J. T. Davies, *Adv. in Enzymol.*, **11**, 35 (1951).

14. D. Davies, *Catalysis, Study of Heterogeneous Processes*, IL, 1956, p. 241.

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

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