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On the Initiation of Polymerization by Solid Potassium Amide and by an Alkoxide in Dimethoxyethane

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It is well known that, by changing the reaction medium, it is possible to influence the reactivity of substances and even the direction of chemical processes. Vivid examples of this are provided by the study of isotopic exchange of hydrogen (^{1}). The reactions of hydrogen exchange, metallation, isomerization with migration of a multiple bond, alkylation, and anionic polymerization, induced by electron donors—bases—in the limiting case of which carbanions arise, belong to the general field of organic anionochemistry (^{2}). Reactions leading to the formation of anion-radicals have some similarity with these reactions. In analyzing results established in the study of certain reactions, it is often possible to predict the influence of particular factors or conditions on other reactions whose direction is determined by similar regularities. In the present work we attempted, from these positions, to approach anionic polymerization. The methods described below for initiating polymerization by solid potassium amide and by an alkoxide in dimethoxyethane were suggested by work devoted to the study of hydrogen exchange of hydrocarbons with bases and to the investigation of the conditions for formation of anion-radicals.

It was shown earlier (^{3}) that hydrogen exchange and isomerization, which proceed in an ammoniacal solution of potassium amide, can be carried out on the surface of solid potassium amide without solvent. We decided to apply heterogeneous catalysis by potassium amide to polymerization, calculating that the absence of ammonia, which causes termination of the polymer chain, would make it possible to obtain polymers of considerably higher molecular weight than in ammoniacal solution. This prediction was justified: on solid potassium amide, in the present work, polymers of styrene with molecular weights of several millions were obtained, whereas according to literature data (^{4,5}), confirmed in our laboratory, in the polymerization of styrene catalyzed by potassium or sodium

Fig. 1

Figure 1: Fig. 1

amides in liquid ammonia, only low-molecular polymers are formed (mol. wt. 2000–4000).

The idea of initiating polymerization by an alkoxide in dimethoxyethane arose from a comparison of observations on the influence of solvents on the catalytic activity of alkoxides in hydrogen exchange and on the stability of anion-radicals. A sharp increase in the catalytic activity of C_2H_5OK (or $NH_2CH_2CH_2OK$) in isotopic hydrogen exchange in triphenylmethane was observed (6) if ethylenediamine was used as solvent instead of ethanol (or ethanolamine). This effect may be regarded as a consequence of an increase in the electron-donor ability of the alkoxide, caused by more energetic solvation of the cation in ethylenediamine than in alcohol. Formation of a strong solvate of the cation with the solvent disrupts the interionic interaction, in which non-Coulomb forces of donor–acceptor character participate (1), and the anion becomes a stronger base. One of the indications of a good solvating ability of a solvent with respect to alkali-metal cations is the solubility of po-

the latter with the formation of blue solutions that conduct electric current (7 8). Ethylenediamine belongs to the number of such solvents (6). The role of solvation of the metal cation in the formation of the anion-radicals of benzene and toluene is considered in (9). The solvents are arranged in a series according to the characteristic of the relative concentration of anion-radicals, determined by measurement of electron paramagnetic resonance spectra. At the beginning of the series is 1,2-dimethoxyethane, in which, as is known (7 8), potassium is soluble.

Taking into account the facts and considerations set forth, we expected that, upon dissolution in dimethoxyethane, alkoxides would possess considerable electron-donor activity. We confirmed this supposition by the fact that, under the action of $CH_3OCH_2CH_2OK$ in this solvent on fluorene, the latter ionizes with formation of carbanions, as may be judged from the spectrum of the solution. Figure 1 gives the light-absorption curves at several concentrations of the solution. The positions of the maxima on the curves (λ: 365, 465, 480 mμ) correspond to those found in the reaction of fluorene with caustic potash in liquid ammonia (10). The less acidic hydrocarbon—triphenylmethane—does not ionize under these conditions. Alkoxide in dimethoxyethane is also capable of initiating the polymerization of vinyl monomers. For example, $CH_3OCH_2CH_2OK$ causes rapid polymerization of methyl methacrylate. Polymerization is also observed when styrene is mixed with a solution and suspension of $CH_3OCH_2CH_2OK$ or CH_3OK.

Fig. 1

According to literature data (11–13), alkoxides initiate the anionic polymeriza-

Fig. 2

Figure 2: Fig. 2

tion of the most reactive monomers (acrylonitrile, β-nitrostyrene). Recently (^{14}), polymerization of methyl methacrylate by sodium methoxide in liquid ammonia—a solvent that vigorously solvates cations and readily dissolves alkali metals—has been noted.

Let us proceed to a description of the experiments. The monomers, purified by the usual method, were additionally purified before the experiment. Styrene was partially polymerized over metallic potassium and redistilled in high vacuum, while methyl methacrylate was distilled in high vacuum, collecting the middle fraction. Potassium amide was obtained by reaction with liquid ammonia, using the apparatus described in (^{15}), and was deposited on the surface of a glass packing used for packing rectification columns. After removal of the ammonia, the system was evacuated for 1-2 h with heating on a water bath, and the monomer was added under vacuum. On contact with solid potassium amide, styrene rather rapidly becomes colored red. Measurement of the absorption spectrum showed the presence of a broad band with an absorption maximum at $\lambda = 520$ mμ (Fig. 2, 1). The intensity of the coloration gradually increases and then falls. After 2-3 days at room temperature, the styrene polymerizes completely and a solid polymer is obtained,

Fig. 2

slowly soluble in benzene. From the benzene solution it was precipitated with methanol, dried in vacuum at 80°, and the viscosity of the solution in toluene at 25° was determined. For the polymer samples obtained, the following values of the intrinsic viscosity (without allowance for the pressure gradient) $[\eta]$ were established: 6.0; 6.8; 5.4; 8.8; 7.3; 5.1; 7.5. Thus, the polymers are distinguished by a very high molecular weight. When the surface area of the potassium amide is decreased, the general picture remains the same, but the solid polymer is formed more slowly. In a control experiment carried out in the absence of potassium amide, styrene, even after three weeks, had the appearance of a viscous liquid. Upon addition of methanol, a polymer precipitated in an amount of several percent.

In one of the experiments, part of the colored styrene was separated under vacuum from the styrene located over the potassium amide, and the vessel was sealed off. The styrene remaining over the potassium amide became almost completely decolorized after 2 days and then turned into a solid polymer, whereas the separated portion of monomer retained an intense red-violet color and full mobility for a month, while observation was being conducted. Therefore, it is probable that the bright coloration of styrene arising under the action of bases on it and determining the absorption of light with a maximum in the wavelength region $\lambda > 500$ mμ (Fig. 2) is not due to carbanions that conduct the polymerization process. The observations described below on the reaction of styrene with alcoholates in dimethoxyethane, as well as the facts presented in work (16), devoted to discussion of the mechanism of initiation of styrene polymerization by potassium amide in liquid ammonia, agree with this supposition. This question is intended for additional study*.

Methyl methacrylate is a more reactive monomer than styrene with respect to anionic polymerization, and on potassium amide within several minutes it turned into a solid polymer with considerable evolution of heat. The polymer was dissolved in chloroform and precipitated with methanol. The intrinsic viscosity of the chloroform solution at 25° $[\eta]$: 3.2; 2.2.

Experiments with alcoholates were carried out using high-vacuum technique, and individual stages were performed in an atmosphere of purified nitrogen. Special attention was paid to thorough purification of the dimethoxyethane and to complete removal of alcohol from the alcoholate. For this purpose the solvent was distilled several times onto the surface of a mirror of metallic potassium, and it was ensured that the solution of potassium in dimethoxyethane had a stable blue color. For the experiments, about 2 ml of dimethoxyethane were taken, containing 0.02 or more milliliters of alcohol, from 0.01 to 0.1 g of metallic potassium for preparation of the alcoholate, and 0.5-3 ml of monomer. Upon mixing the solution and suspension of the alcoholate in dimethoxyethane with styrene, a red coloration rapidly appears and the solid alcoholate dissolves. In the reaction of styrene with $CH_3OCH_2CH_2OK$ and with CH_3OK, the coloration differs in shade, but the maximum of light absorption lies in one and the same wavelength region, $\lambda = 520$–530 mμ (Fig. 2, 2, 3). It should be noted that the coloration persists, but only weakens, when the solution comes into contact with air and even when alcohol is added. The yield of styrene polymer, depending on the conditions of the experiment, was 3-30%. The intrinsic viscosity of solutions in toluene of polymers formed in the presence of $CH_3OCH_2CH_2OK$ proved to be $[\eta]$: 1.3; 0.3; 0.3; 0.3; 0.9; 0.6; 0.5; 1.2; 1.3; 0.6, and under the action of CH_3OK, $[\eta]$: 0.2. In control experiments carried out without alcoholate, polymer was absent.

When methyl methacrylate was mixed with a solution and suspension of $CH_3OCH_2CH_2OK$ in dimethoxyethane, rapid polymerization was observed, accompanied by heating of the mixture. The yield of polymer was greater than in the case of styrene. Cha–

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* *Note added in proof.* If colored styrene is distilled in high vacuum onto a new portion of KNH_2, the styrene remains colorless and its polymerization can occur rapidly with heating.

characteristic viscosity of the chloroform solutions of the polymers $[\eta]$: 0.13; 0.20; 0.25; 0.53.

We intend to continue the work in the direction of a more detailed study of the process of anionic polymerization on solid metal amides and on other solid bases, and of studying the properties of the polymers obtained; we also propose to compare the influence of solvents on the chemical activity of alcoholates of different alcohols and metals.

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