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Anionic Polymerization of β-Nitrostyrene under the Influence of High Energy Radiation

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ABSTRACT

β-Nitrostyrene (βNS) was polymerized in aprotic solvents. The rate of polymerization increased in the series dimethyl sulfoxide ≈ dimethylformamide < N-methylpyrrolidone < hexamethylphosphoric triamide (HMPT). From copolymerization experiments with α-methylstyrene and methacrylonitrile, evidence for an ionic mechanism was obtained. Electron scavengers inhibited the polymerization. Thus it was concluded that in dilute solution the initiation comprises the thermalization of electrons which become solvated and react with βNS to form the radical anion $\cdot\beta NS^-$. Pulse radiolysis experiments were carried out in HMPT. The spectrum of an intermediate (presumably $\cdot\beta NS^-$) was recorded. By measuring the rates of the formation of $\cdot\beta NS^-$ and of the decay of solvated electrons the rate constant $k_{e^-(solv + \beta NS)} = (9 \pm 3) \times 10^9$ liter/mole-sec was determined. At higher monomer concentrations the polymerization was autoinhibited which is probable due to the fact that direct absorption of radiation by the monomer becomes important.

INTRODUCTION

Ionizing radiation is capable of inducing ionic polymerization of various monomers. It was shown, for example, that styrene and isobutyl vinyl ether polymerize readily by a free cationic mechanism upon γ-irradiation of the carefully purified bulk monomer [1-3]. Most work devoted to radiation-induced ionic polymerization, however, has been concerned with the cationic mechanism. Only sparse information has been obtained so far on radiation-induced anionic polymerization. It was reported that the copolymerization of acrylonitrile (AN) and styrene (St) at -78°C proceeds by an anionic mechanism or that both anionic and radical mechanisms coexist during the copolymerization of these monomers [4-7]. A more recent publication [8] reports that upon the irradiation of AN/St mixtures in dimethylformamide (DMF) solution, radical anions are formed which grow simultaneously in two directions, adding AN units by an anionic mechanism on one end and forming a random copolymer at the other end by a radical mechanism.

Evidence for the radiation-induced anionic polymerization was obtained from irradiations of glassy systems containing AN. Solvents were DMF, triethylamine, or methyltetrahydrofuran [9, 10]. The radiation-induced polymerization of rigorously purified bulk AN at -78°C was shown to proceed by an anionic mechanism [11, 12].

Nitroethylene (NE) was found by Sokolov et al. [13] to polymerize upon γ-irradiation. Indications for a radical polymerization mechanism were obtained [13]. Later Yamaoka et al. investigated the radiation-induced polymerization of nitroethylene in tetrahydrofuran [14] solution at low temperature and the polymerization of nitroethylene at 10°C [15]. From the results of scavenger experiments it was inferred that the polymerization of NE proceeds via an anionic mechanism. It was reported that bulk 1-nitropropene-1 does not polymerize under the influence of γ-irradiation and that copolymers obtained by irradiating mixtures of AN and 1-nitropropene-1 in solution (DMF, THF, toluene) were formed by a radical mechanism [16].

The aim of this work was to extend the research on radiation-induced anionic polymerization to β-nitrostyrene (βNS), a compound which appeared to be appropriate in order to substantiate the capability of high energy radiation to initiate anionic polymerization. βNS is known to undergo anionic polymerization initiated by weak bases such as methoxide ions readily, but fails to undergo radical or cationic polymerization [17-20]. It has been reported that βNS may serve as an inhibitor or retarder for free-radical polymerizations [21, 22].

Besides the irradiation of βNS in the solid state at room temperature it was intended to irradiate βNS solutions. Solvents were selected which are known to stabilize positive ionic transients and to prevent thus the rapid combination of negative and positive ions. A relative long lifetime of primary negatively charged species is a prerequisite for the formation of anionic species which are capable of initiating anionic polymerization processes. Hexamethylphosphoric triamide (HMPT) appeared to be the most suitable solvent in this respect. Upon irradiation of HMPT, solvated electrons with a lifetime in the microsecond range are generated [23-25]. Actually, it was found that βNS polymerized quite effectively in HMPT solutions. Therefore, essential parts of this paper concern results obtained with the system βNS/HMPT. In order to elucidate the initiation mechanism some pulse radiolysis experiments were carried out.

EXPERIMENTAL

Materials

β-Nitrostyrene (Aldrich, 97%) was recrystallized three times from n-hexane solution and dried under high vacuum. The melting point was 57.5-58.0°C.

Methacrylonitrile (Merck-Schuchardt, p.a. 99%) was freed from stabilizer by washing with saturated $NaHSO_3$ solution and 1% NaOH solution saturated with NaCl. After washing with aqueous saturated NaCl solution it was dried over $CaCl_2$ and twice distilled under reduced pressure.

α-Methylstyrene (Ferak, Berlin, 99%) was washed with aqueous NaOH solution (20%) and with distilled water. It was dried with $CaCl_2$ and CaH_2. After having passed columns with activated Al_2O_3 and silicagel (Woelm) it was distilled from CaH_2 over a Vigreux column. The middle fraction was used.

Hexamethylphosphoric triamide (Merck-Schuchardt, p.a. 99%) was distilled from a flask containing metallic sodium via a Vigreux column into a flask containing Molecular Sieves (Merck, 4 Å and 10 Å). After two days it was distilled under reduced pressure (bp 85°C/2.3 Torr). N-Methylpyrrolidone (Merck-Schuchardt, p.a.) was distilled from BaO, dried over Molecular Sieves (4 Å) and distilled (bp 55°C/4 Torr). Dimethyl sulfoxide (Merck, p.a.) was dried with CaH_2 and Molecular Sieves (4 Å and 10 Å) and distilled under vacuum (bp 73°C/12 Torr).

Dimethylformamide (Riedel de Haën, p.a.) passed an Al_2O_3-column before it was dried with Molecular Sieves and distilled under vacuum (bp 76°C/39 Torr). Sodium methylate (Merck-Schuchardt, 98.5-99.5%) was dried at 1 Torr at 90°C for 2 days.

Preparation and Irradiation of Samples

In most cases samples were prepared by a high vacuum technique. Cells containing βNS were attached to a high vacuum line, to which flasks containing monomers and in some cases solvents were connected. The liquid compounds were degassed by several freeze-thaw-pump cycles and then condensed into the cells with βNS. Finally, the cells were separated from the vacuum line by sealing.

γ-Irradiations were carried out with a ^{60}Co source (ca. 16000 Ci). During pulse radiolysis experiments, solutions were irradiated with 50-nsec pulses of 15 MeV electrons from an L-band linear accelerator (Vickers). The absorbed dose rate was determined by Fricke dosimetry. $G(Fe^{3+}) = 15.5$ for γ-irradiations and $G(Fe^{3+}) = 13.0$ (O_2 saturated solution) for electron irradiations were used. For γ-irradiations the absorbed dose rate was 0.2 to 0.5 Mrad/hr.

During the scavenger experiments HMPT solutions containing βNS were saturated with SF_6 (Kalichemie AG), N_2O (Linde AG, 99.5%) or O_2 (Linde AG, 99.99%) by bubbling beforehand with one of the gases for about 30 min.

Analytical Procedures

For IR measurements a Perkin-Elmer apparatus (model 421) was used. UV absorption measurements were performed with a Carl Zeiss RPQ20 AV spectrophotometer. Elemental analyses were carried out with a Hewlett-Packard CHN Analyzer, model 185.

RESULTS

Irradiation of Bulk β-Nitrostyrene

Several samples of βNS were irradiated in the solid state at room temperature and at -80°C with doses up to 40 Mrad. Polymer was not formed. Also thermal post-irradiation treatment at a temperature slightly below the melting point of 58°C did not yield polymer.

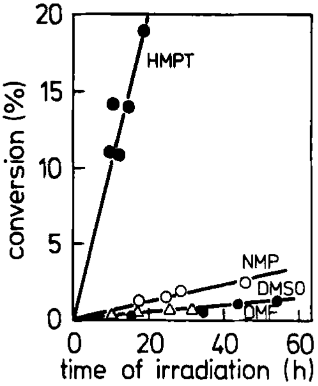

FIG. 1. Influence of solvent on the rate of polymerization of βNS at room temperature. ^{60}Co-γ-irradiation, absorbed dose rate: 0.3 Mrad/hr; [βNS] = 3.3 mole %.

Irradiation of β-Nitrostyrene in Solution

Polymer was formed in hexamethylphosphoric triamide, N-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF). In all cases insoluble polymer was generated which precipitated during the experiment. In tetrahydrofuran no polymerization took place. As is shown in Fig. 1, the polymerization rate decreased in the series HMPT > NMP > DMSO ≈ DMF. HMPT is the most appropriate solvent for the polymerization. The rate is in this case about 20 times greater than in NMP, as shown in Fig. 1. The rate of polymerization was found to depend on the βNS concentration. Figure 2 shows the rate of polymerization determined in HMPT as a function of βNS concentration. The rate possesses a maximum at about 4 mole %, indicating autoinhibition of βNS. A similar effect was observed recently by Chapiro et al. during the polymerization of acrylonitrile in DMF [26].

The poly-β-nitrostyrene obtained during these experiments has properties similar to those of poly-β-nitrostyrene generated by sodium methoxide initiation. The melting point under decomposition is about 285° C. The polymer did not dissolve. A great variety of solvents was tested. Swelling was observed with 1-chloronaphthalene and 2-chlorobenzothiazole. Piperidine and N-methylmorpholine decomposed the polymer totally at room temperature yielding colored solutions. A soluble fraction containing telomers could be extracted

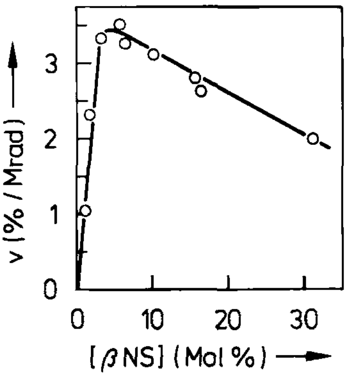

FIG. 2. Rate of polymerization vs. monomer concentration for polymerization of βNS in deaerated hexamethylphosphoric triamide at room temperature. Absorbed dose rate, 0.5 Mrad/hr; absorbed dose, 8 Mrad.

with methyl ethyl ketone at room temperature indicating the polymeric nature of the reaction product.

In order to elucidate the polymerization mechanism, βNS was irradiated in HMPT solutions containing additives. The βNS concentration was 3.64 mole %. In Fig. 3 the monomer conversion is plotted against the time of irradiation. The rate of polymerization is retarded by N_2O, SF_6, and O_2. The relative rates of polymerization evaluated from the slopes of the straight lines are 1.00 (Ar) : 0.55 (N_2O) : 0.10 (SF_6) : 0.025 (O_2). SF_6 and N_2O are known to scavenge electrons. O_2 may react both with electrons and carbanions. Since SF_6 and N_2O retard the polymerization effectively, it is assumed that solvated electrons are involved in the initiation step.

This was confirmed by the following experiments. βNS was polymerized in methanol solution using sodium methylate as an initiator. SF_6, N_2O, and O_2 did not exert any influence on the polymerization in this case. Since solvated electrons are not involved in this initiation process, the added compounds could, if at all, only interfere with the ionic propagation. From the fact that an inhibition effect was not detectable during the sodium methylate-initiated polymerization, it is concluded that during the radiation-induced polymerization SF_6, N_2O, and O_2 also do not influence the propagation but rather affect the initiation of the polymerization.

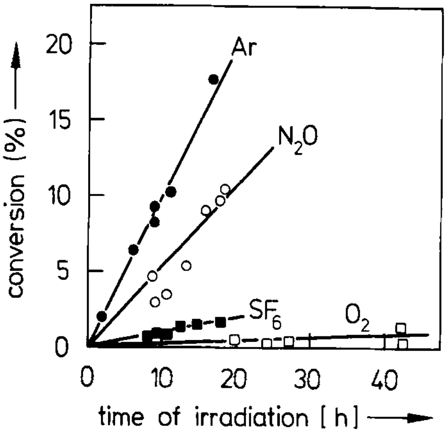

FIG. 3. Influence of scavengers on conversion vs. time of irradiation for the polymerization of βNS (3.64 mole %) in hexamethylphosphoric triamide solution at room temperature. Absorbed dose rate, 0.5 Mrad/hr. The solutions were saturated with the gases indicated prior to irradiation at a pressure of 1 atm.

Copolymerization Experiments

β-Nitrostyrene-α-Methylstyrene (αMS). αMS forms long chain polymers only by ionic mechanisms. Radical initiation leads only to oligomers. Therefore, αMS was selected as a monomer suitable for ionic copolymerization studies. Irradiation of a monomer mixture containing 10 mole % βNS at 25°C with a dose of about 10 Mrad yielded no polymer. In HMPT solution containing 35 mole % monomer, however, polymer was formed. Figure 4 shows the copolymer composition as a function of monomer composition. The shape of the curve is typical for an ionic copolymerization. The rate of monomer conversion was about one order of magnitude lower than in HMPT solutions containing no αMS. All copolymers were insoluble. The copolymerization parameters obtained according to the method of Fineman and Ross [27] are r_1(βNS) = 15.7; r_2 (αMS) = 0.09.

β-Nitrostyrene-Methacrylonitrile (MAN). The irradiation of mixtures of βNS and MAN in bulk at -20°C yielded copolymers. As shown in Fig. 5a, copolymers formed in mixtures with only small portions of βNS contain high fractions of βNS units, indicating an ionic polymerization mechanism. The addition of βNS

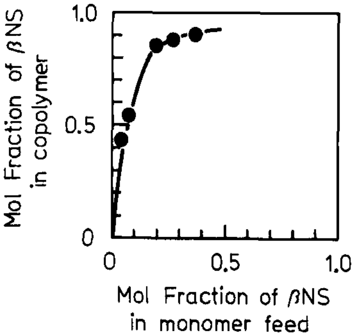

FIG. 4. Copolymer composition vs. composition of monomer mixture for copolymerization of α-methylstyrene and β-nitrostyrene in HMPT at room temperature. Concentration of monomers, 35 mole %; absorbed dose rate, 0.5 Mrad/hr; absorbed dose, 10 Mrad.

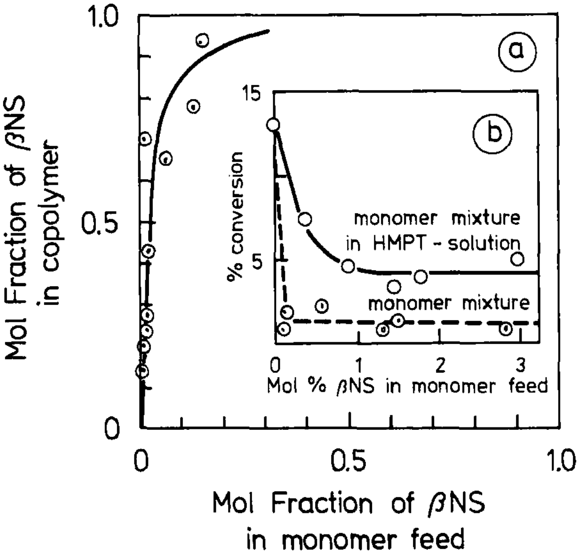

FIG. 5. Copolymerization of methacrylonitrile and β-nitrostyrene at -20°C in bulk and in HMPT solution containing 65 mole % monomer at room temperature: (a) copolymer composition vs. composition of monomer feed; (b) monomer conversion vs. composition of monomer feed. Absorbed dose rate, 0.5 Mrad/hr; absorbed dose, 10 Mrad.

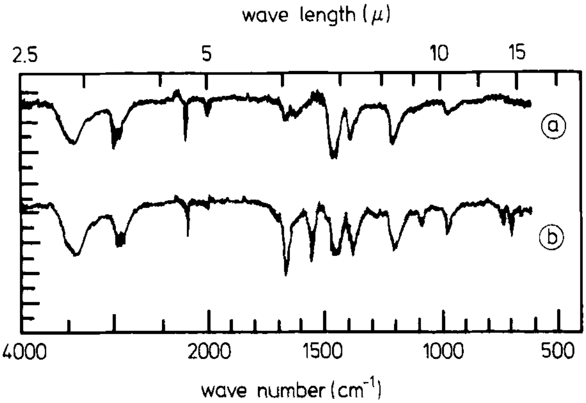

FIG. 6. Infrared spectra of (a) polymethacrylonitrile polymerized in bulk at room temperature by γ-irradiation; (b) poly(methacrylonitrile-co-β-nitrostyrene) containing 11 mole % βNS polymerized by γ-irradiation in HMPT at room temperature.

to MAN reduces the conversion of monomer appreciably, as shown in Fig. 5b. The polymerization of bulk MAN proceeds presumably via a radical mechanism, which is completely suppressed by the addition of small amounts of βNS.

Upon irradiation of monomer mixtures dissolved in HMPT at room temperature copolymers were generated whose composition corresponded exactly to the curve in Fig. 5a for copolymers formed by irradiation of the bulk monomer mixtures at -20°C. However, the conversion was about five times as high as in that case, indicating that the ionic copolymerization is favored in HMPT solutions. The copolymerization parameters obtained according to the method of Fineman and Ross [27] are r_1(βNS) = 54.4; r_2 (MAN) = 0.05.

Evidence for an anionic copolymerization mechanism was obtained from infrared absorption spectra. Figure 6b shows as a typical example an IR spectrum of a copolymer sample containing 11 mole % βNS. The rather strong band at 1670 cm^{-1} is due to imine groups (–N=C<). The latter are known to be formed during the anionic polymerization of acrylonitrile and MAN [28]. As demonstrated by the spectrum in Fig. 6a, no imine groups are contained in a PMAN sample obtained by a free radical mechanism during the γ-irradiation of bulk MAN at room temperature.

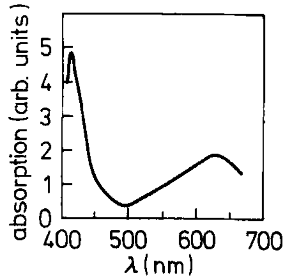

FIG. 7. Spectrum of the product of the reaction of the solvated electron with βNS in HMPT. Solution irradiated with a 50 nsec pulse of 15 MeV electrons; [βNS] = 3×10^{-2} mole/liter; absorbed dose, ca. 10^3 rad. Spectrum recorded 500 nsec after the pulse.

Pulse Radiolysis Experiments

O_2-free HMPT solutions containing βNS were irradiated with 50-nsec pulses of 15 MeV electrons. During the pulse solvated electrons were formed which absorb light at wave lengths longer than about 800 nm (absorption maximum at 2200 nm) as reported in the literature [23-25]. It was found that in the presence of βNS simultaneously with the decay of the absorption of e^-_{solv} an absorption in the wavelength range between 400 nm and 700 nm was formed. The spectrum, shown in Fig. 7, has maxima at 420 and 640 nm. Thus, it is concluded that the solvated electron reacts with βNS forming presumably the radical anion $\cdot\beta NS^-$. Following the rate of the decay of the absorption of e^-_{solv} and the rate of formation of the new absorption between 400 nm and 700 nm the rate constant $k_{e^-(solv} + \beta NS)} = (9 \pm 3) \times 10^9$ liter/mole-sec was determined.

DISCUSSION

From the results of the copolymerization experiments it is inferred that βNS polymerizes via an ionic mechanism in HMPT. The inhibitive action of SF_6, N_2O, and O_2 is considered evidence for an anionic mechanism. It has been shown by other authors [25] that solvated electrons are formed in HMPT with a relatively high yield [$G(e^-_{solv}) = 2.3$] and that the rate constant of the reaction of N_2O

with e^-_{solv} in HMPT is (1.4 ± 0.4) × 10^{10} liter/mole-sec. It could be shown in this work that solvated electrons react in a diffusion controlled reaction with βNS. It is, therefore, assumed that the initiation of the polymerization comprises the reactions

$$S \xrightarrow{\text{irradiation}} \cdot S^+ + e^-_k \tag{1}$$

$$e^-_k \longrightarrow e^-_{th} + \text{energy} \tag{2}$$

$$e^-_{th} \xrightarrow{S} e^-_{solv} \tag{3}$$

$$e^-_{solv} + \beta NS \longrightarrow \cdot\beta NS^- \tag{4}$$

Reaction (4) leads to anion radicals $\cdot\beta NS^-$ and might start the kinetic chain via reaction (5):

$$\cdot\beta NS^- + \beta NS \longrightarrow \cdot\beta NS\text{-}\beta NS^- \tag{5}$$

The other aprotic solvents used appeared to be much less effective than HMPT with respect to the polymerization of βNS. This might be due to the fact that solvated electrons are formed with a lower yield in these solvents. As is seen from Table 1, the rate of polymerization increases with increasing dipole moment of the solvent.

The dipole moment is correlated to the solvent power of the solvent towards cations, in other words to the basicity of the aprotic solvents or in the terminology of Gutmann [29] to the donor number. On this basis it becomes plausible that polymerization was also observed in mixtures of MAN and βNS. MAN has a dipole moment of 3.7 Debye [30]. The capability of the substances to solvate ions, especially cations, certainly is the determining factor with respect to the initiation of the polymerization of βNS.

The strong interaction of solvent molecules with ionic intermediates leads to a relatively long lasting stabilization of positive ions and enables electrons to become solvated after thermalization. Thus, solvated electrons can react with βNS. The lifetime of e^-_{solv} was about 4 μsec in HMPT in the absence of βNS. The stabilization of

TABLE 1. Dielectric Constants, Dipole Moments, and Rates of Polymerization with the Solvents Used in this Work

Solvent	Dielectric constant	Dipole moment (μ Debye)[a]	Rate of polymerization (% conversion/Mrad)[b]
THF	7.6	1.7	-
MAN		3.7	
DMF	36.1	3.8	0.1
DMSO	45.0	3.9	0.1
NMP	32.0	4.1	0.2
HMPT	30.0	5.4	3.7

[a] Value for MAN obtained in the gas phase between 120 and 200°C [30]; other values obtained in benzene solution at room temperature [31].
[b] Data from Fig. 1.

positive ions permits, of course, not only the formation of $\cdot\beta NS^-$ but also the growth of the chain, i.e., the propagation reaction. Besides the interaction between ions and solvent molecules steric effects can contribute to the stabilization of ions. Bulky substituents of solvent molecules might play an important role. Thus HMPT might be more appropriate than the other aprotic solvents used. The elucidation of the polymerization mechanism at higher monomer concentrations is rather difficult. This becomes obvious by considering the autoinhibition observed at concentrations above 4 mole % in HMPT (see Fig. 2). Certainly the direct action of the radiation on βNS becomes important as the monomer concentration is increased, i.e., in addition to positive solvent-ions, monomer-cations are formed which might be less stable than cations generated by the radiolysis of the solvent. Thus the neutralization rate is increased, which may cause a smaller yield of solvated electrons and/or shorter kinetic chains. Whereas a perfect explanation cannot be given yet, the maximum of the curve in Fig. 2 can be understood as an indication for the fact that by increasing the monomer concentration the polymerization mechanism is changed, or that at least certain additional reactions have to be considered due to the direct radiolysis of the monomer.

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