Primary Reactions during the Free Anionic Polymerization of β Nitrostyrene

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β-Nitrostyrene (βNS) was irradiated at r. t. in solutions of hexamethylphosph. triamide (HMPT) with 50 ns pulses of 15 MeV electrons. It was found that βNS reacts with solvated electrons almost encounter controlled ($k(e^-_{solv} + \beta NS) = (9 \pm 3) \cdot 10^9$ l/mol s) forming the radical anion $\cdot\beta NS^-$. The optical absorption spectrum of the latter was recorded in dilute solutions ($[\beta NS] < 5 \times 10^{-3}$ mol/l). At higher βNS concentrations the formation of an additional optical absorption after the pulse in the wavelength range between 460 nm and 570 nm was detected, which is attributed to the reaction of βNS with $\cdot\beta NS^-$ yielding the dimeric radical anion ($\cdot\beta NS\text{-}\beta NS^-$). The rate constant for this process is 4×10^7 l/mol s. At low βNS concentrations ($< 5 \times 10^{-3}$ mol/l) the transient spectrum decayed by a second order process ($k_2 = (2.2 \pm 0.5) \cdot 10^9$ l/mol s). This process is correlated to the neutralization of radical anions by cations formed initially. At $[\beta NS] > 5 \times 10^{-3}$ mol/l only the band at 630 nm decays according to second order kinetics. This band is correlated to the part of the anions with the highest electron density, the nitro groups. At wavelengths below 570 nm the absorptions of various species overlap. These species decay by different rate laws.

Introduction

Upon irradiation with ^{60}Co-γ-rays β-nitrostyrene (βNS) polymerizes in aprotic solvents forming an insoluble polymer [1]. The highest polymerization yields were obtained in hexamethylphosphoric triamide (HMPT). From copolymerization experiments it was inferred that the polymerization proceeds via an ionic mechanism. Scavenger experiments did show that the mechanism is anionic. In this paper we report on experiments which were carried out in order to elucidate the kinetics of the initiation of the polymerization of βNS. Upon irradiation of HMPT with ionizing radiation solvated electrons are generated [2—5] which react rapidly with βNS:

$$e^-_{solv} + \beta NS \rightarrow \cdot\beta NS^- . \quad (1)$$

$\cdot\beta NS^-$ particles are supposed to react with βNS-molecules to form a dimer:

$$\cdot\beta NS^- + \beta NS \rightarrow \cdot\beta NS\text{-}\beta NS^- . \quad (2)$$

We have irradiated HMPT solutions of various βNS-concentrations with 50 ns pulses of 15 MeV electrons and, by following the optical absorption as a function of time, were able to observe the kinetics of reactions (1) and (2).

Experimental

a) *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. Hexamethylphosphoric triamide (Merck, 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 (b.p. 85°, 2.3 Torr).

b) *Irradiation of the Solutions*

Solutions of βNS in HMPT were irradiated at room temperature in rectangular quartz cells with 50 ns pulses of 15 MeV electrons from an L-band linear accelerator (Vikkers). The solutions were bubbled beforehand with purified argon ($[O_2] <$ 1ppm). The optical absorption detection method was applied throughout. Two detectors were used (a 1P28 photomultiplier for the wavelength range between 400 nm and 800 nm, and a SGD 100 A, EG & G, photodiode for $\lambda > 800$ nm). The absorbed dose rate was determined by Fricke dosimetry with O_2 saturated solutions ($G(Fe^{3+}) = 13.0$).

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Results and Discussion

a) The Formation of the Transient Optical Absorption in Very Dilute Solutions of βNS

At low concentrations ($< 5 \times 10^{-3}$ mol/l) an optical absorption was observed in the wavelength range above ca. 800 nm immediately after the irradiation with a 50 ns pulse. With respect to results of other authors [4, 5] this absorption was ascribed to solvated electrons (e^-_{solv}) formed during the pulse. As reported before [1], simultaneously with the decay of the absorption of e^-_{solv} (Fig. 1 (a)) a new absorption arises the wavelength range between 400 nm and 700 nm. The resulting spectrum (Fig. 3, full circles) is identical with the spectrum observed immediately after the pulse at higher βNS concentrations. Figure 1 shows typical oscillograms obtained at $[\beta\text{NS}] = 1.0 \times 10^{-3}$ mol/l for the absorption at 1000, 420 and 645 nm. At the latter wavelengths the formation of the absorption occurs according to a first order process. It was found that the same rate law holds for the decay of the absorption at $\lambda > 800$ nm and the formation of the absorption between 400 nm and 700 nm. Rate constants k_1 were evaluated according to Equation (3):

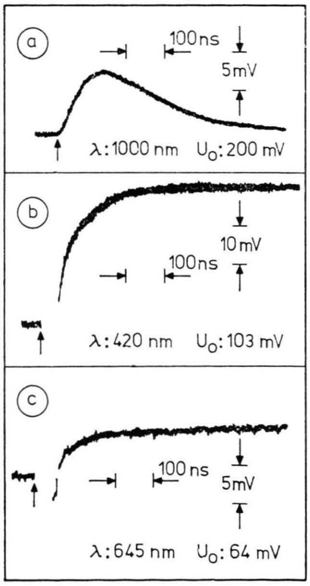

Fig. 1. Oscillograms demonstrating changes of the optical absorption of βNS solutions in HMPT (1×10^{-3} mol/l) caused by irradiation with a 50 ns pulse of 15 MeV electrons. Absorbed dose per pulse: 1×10^3 rad. (a) λ: 1000 nm, (b) λ: 420 nm, (c) λ: 645 nm.

$$\ln \frac{[e^-_{\text{solv}}]_t}{[e^-_{\text{solv}}]_0} = \ln \frac{[\cdot\beta\text{NS}^-]_\infty - [\cdot\beta\text{NS}^-]_t}{[\cdot\beta\text{NS}^-]_\infty} = \ln \frac{E_\infty - E_t}{E_\infty} = -k_1 t, \tag{3}$$

$$[\cdot\beta\text{NS}^-]_\infty = [e^-_{\text{solv}}]_0 \propto E_\infty \quad \text{and}$$

$$[e^-_{\text{solv}}]_t = [\cdot\beta\text{NS}^-]_\infty - [\cdot\beta\text{NS}^-]_t \propto (E_\infty - E_t).$$

E_∞ and E_t denote the optical densities a long time after the pulse and at the time t after the pulse, respectively.

Typical data are shown in Figure 2. A plot according to Eq. (3) demonstrating the increase of the optical density at 420 nm is shown in Figure 2(a). Figure 2(b) depicts the linear dependence of the reciprocal lifetime of the increase of the O.D. on the βNS concentration. From these results it is inferred that pseudo-first-order kinetics hold in this case. By following the increase of the absorption between 400 and 700 nm and the decay of the absorption of solvated electrons it was concluded that

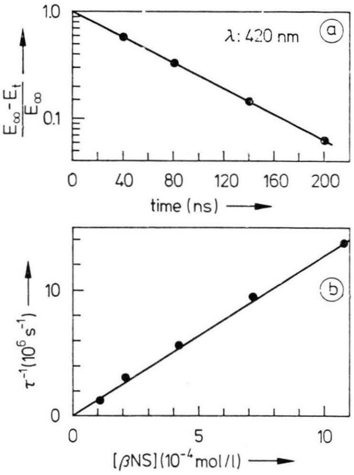

Fig. 2 The formation of the optical absorption at 420 nm. (a) Plot according to Eq. (3) demonstrating the increase of the optical density E with time. E_t: O.D. at time t and E_∞: O.D. a long time after the pulse. (b) The reciprocal lifetime of the formation of the optical density at 420 nm as a function of βNS concentration.

$$k(e^-_{\text{solv}} + \beta\text{NS}) = (9 \pm 3) \cdot 10^9 \text{ l/mol s}.$$

b) The Formation of the Optical Absorption in Moderately Concentrated Solutions of βNS

Figure 3 shows the changes of the transient spectrum observed with a HMPT solution of a βNS

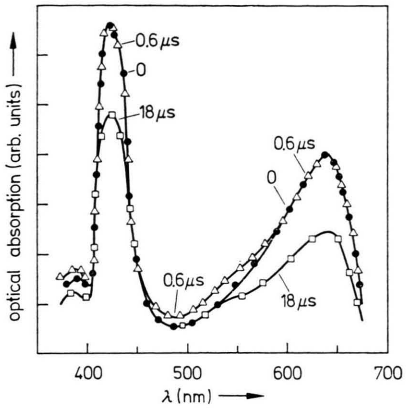

Fig. 3. Transient spectra obtained with βNS in HMPT (0.09 mol/l). Pulse length: 50 ns. Absorbed dose per pulse 6×10^3 rad.

concentration of 0.09 mol/l. It is seen that in the range between 460 and 570 nm the absorption increases significantly until about 0.6 µs after the pulse. During that time the absorption remains constant at 420 nm and 640 nm. At later times a decrease of the absorption at all wavelengths takes place, as is seen from the spectrum monitored 18 µs after the pulse. A typical oscilloscope trace demonstrating the increase of the absorption at 470 nm is shown in Figure 4(a). It may be emphasized that at βNS concentrations above about 2×10^{-2} mol/l all solvated electrons react with βNS within the pulse. The formation of an additional absorption after the pulse indicates, therefore, a reaction of the radical anions $\cdot\beta\mathrm{NS}^-$ with intact βNS molecules, according to reaction (2).

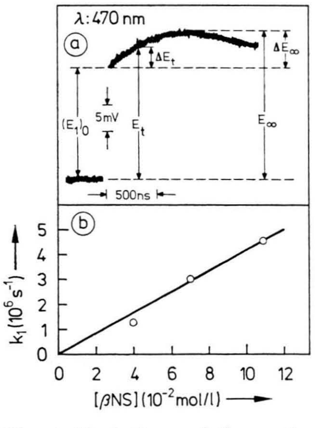

Fig. 4. Variations of the optical absorption at 470 nm at relatively high βNS concentrations. Duration of pulse: 50 ns. Absorbed dose per pulse: 500 rad. (a) Oscilloscope trace demonstrating the formation of an additional absorption after the pulse and its decay. $U_0 = 200$ mV. [βNS]: 1.1×10^{-1} mol/l. (b) Plot of the first order rate constant pertaining to the increase of the optical absorption after the pulse at 470 nm vs. [βNS] (Formation of $\cdot$M–M$^-$).

Based on the assumptions that dimeric radical anions $\cdot\mathrm{M\text{-}M}^-$ are formed and that the pseudo-first order law holds:

$$\frac{-\mathrm{d}[\cdot\mathrm{M}^-]}{\mathrm{d}t} = k_2[\cdot\mathrm{M}^-][\mathrm{M}] = k_1[\cdot\mathrm{M}^-] \qquad (4)$$

with

$$k_2[\mathrm{M}] = k_1 \qquad (5)$$

one obtains:

$$\ln\frac{[\cdot\mathrm{M}^-]_t}{[\cdot\mathrm{M}^-]_0} = \ln\frac{[\cdot\mathrm{M\text{-}M}^-]_\infty - [\cdot\mathrm{M\text{-}M}^-]_t}{[\cdot\mathrm{M\text{-}M}^-]_\infty} = -\,k_1 t\,. \qquad (6)$$

At a given wavelength the measured optical density E is the sum of the optical densities of both species $E = E_1 + E_2$ (E_1: O.D. of $\cdot\mathrm{M}^-$; E_2: O.D. of $\cdot\mathrm{M\text{-}M}^-$). Thus, E varies with time according to

$$E_t = (E_1)_0\, e^{-k_1 t} + E_\infty(1 - e^{-k_1 t})\,. \qquad (7)$$

From Eq. (7) it is derived that

$$\Delta E_t = \Delta E_\infty(1 - e^{-k_1 t})\,. \qquad (8)$$

ΔE_t and ΔE_∞ designate the amount of increased optical density after the time t and a long time after the pulse. For the definition of E and ΔE see also Figure 4(a). Values of rate constants k_1 were obtained at various βNS concentrations according to Equation (8). As can be seen in Fig. 4(b), k_1 is proportional to the βNS concentration. The slope of the straight line yields $k_2 = 4.2 \times 10^7$ l/mol s.

c) The Decay of the Optical Absorption

At low βNS concentrations ($< 5 \times 10^{-3}$ mol/l) the transient absorption decayed according to a second order law in the wavelength range investigated. Figure 5(a) shows a typical oscilloscope trace obtained with a solution of $[\beta\mathrm{NS}] = 3.7 \times 10^{-3}$ mol/l at 440 nm. Figure 5(b) shows a plot of the reciprocal optical density vs. time. It is assumed that the observed decay of the optical absorption corresponds to the neutralization of the radical anions $\cdot\beta\mathrm{NS}^-$ by the positive ions:

$$\cdot\beta\mathrm{NS}^- + \mathrm{X}^+ \xrightarrow{k_2} \text{products}\,. \qquad (9)$$

The validity of this assumption was corroborated by the fact that the first half life of the decay is

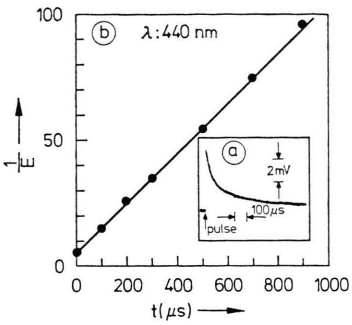

Fig. 5. The decay of the transient absorption at 440 nm. [βNS]: 3.7×10^{-3} mol/l. Absorbed dose per pulse: 3.8×10^3 rad. (a) Oscilloscope trace, $U_0 = 32$ mV. (b) Plot of the reciprocal optical density vs. time.

proportional to the reciprocal absorbed dose as shown in Fig. 6, where typical results are presented. Actually, such a dependence is expected for a second order process ($\tau_{1/2} = (k_2 c_0)^{-1}$). The initial concentration $[\cdot\beta NS^-]_0$ is proportional to the absorbed dose. Since the 100 eV yield for solvated electrons is known [5] ($G(e^-_{solv}) = 2.3$), $[\cdot\beta NS^-]_0$ could be calculated based on the assumption that all solvated electrons are scavenged by βNS. From plots of the kind shown in Fig. 6, it was inferred that the rate constant for the neutralization (Eq. 9) is $k_2 = (2.2 \pm 0.5) \cdot 10^9$ l/mol s.

At βNS concentrations above 5×10^{-3} mol/l a second order decay of the absorption was observed only at 630 nm. At lower wavelengths, plots of the reciprocal optical density vs. time did not yield straight lines and the first halflife did not depend linearly on the reciprocal absorbed dose.

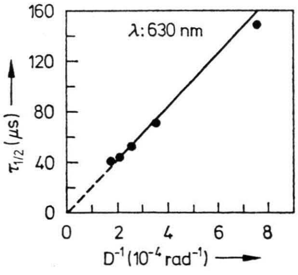

Fig. 6. The first halflife of the decay of the optical absorption at 630 nm vs. the reciprocal absorbed dose. [βNS]: 3.7×10^{-3} mol/l.

It has been pointed out above that at βNS concentrations greater than 5×10^{-3} mol/l the formation of dimeric radical anions becomes important. It thus appears to be feasible that under these conditions reactions such as (10) and (11) occur,

$$2 \cdot \text{M-M}^- \rightarrow {}^-\text{M-M-M-M}^- , \qquad (10)$$

$$\cdot\text{M-M}^- + \text{M} \rightarrow \cdot\text{M-M-M}^- . \qquad (11)$$

which lead to the formation of oligomeric species and cause changes of the absorption spectrum at wavelengths below 570 nm. The spectra of various species then overlap in that wavelength range and it is not possible anymore to follow the fate of a single species by monitoring the rate of decay of the absorption. On the other hand, the kinetics of the decay of the band at 630 nm are not affected by the extent of the conversion (formation of monomeric or oligomeric anions). If it is assumed that this decay is still due to the neutralization reaction, it may be inferred that the absorption at 630 nm pertains essentially to the part of the molecule with the highest electron density, and that the negative charge is essentially located at the nitro group.

Concluding Remarks

It has been shown that hexamethylphosphoric triamide is an appropriate solvent for the investigation of the initial steps of the polymerization via free anions at room temperature. In the case reported spectroscopic evidence could be obtained for the formation of monomeric and dimeric radical anions, the kinetic of the formation of these species could be followed and the rate of the neutralization of the anionic species with the cations could be measured.

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