European Polymer Journal, Vol. 16, pp. 425 to 429

0014-3057/80/0501-0425$02.00/0

INVESTIGATION OF THE MACROMOLECULAR STABLE FREE NITROXIDE RADICAL—II

POLYSTYRENE WITH tert.-BUTYL NITROXIDE GROUPS AT THE *meta*-POSITION

M. AZORI[1] and F. TÜDŐS[2]

[1]Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1025 Budapest and [2]Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1025 Budapest, Hungary; Eötvös Loránd University, Department of Chemical Technology, Budapest, Hungary.

(*Received* 8 *October* 1979)

Abstract—Polystyrene containing *t*-butyl nitroxide groups at the *meta*-position was prepared from styrene-(*m*-bromostyrene) copolymer. The structure of the radical was identified by ESR measurements. Polymerization of styrene initiated by AIBN at 50° has been studied dialatometrically in the presence of the polymeric radical; a strong inhibiting effect was observed. A linear relationship was found between the concentration of the polymeric inhibitor and the length of the inhibition period. Radical contents of the samples were determined by ascorbic acid titration. The concentration of the reactive groups (10^{-5}–10^{-4} mol-equiv/g) was identical with radical concentration determined by kinetic measurements.

INTRODUCTION

In the first paper of this series [1] a study was made on the macromolecular polyradical of styrene with *t*-butyl nitroxide groups at the *para*-position. This compound was prepared from polystyrene via polymer-analogous reactions of iodination, iodine–lithium exchange and the reaction of the lithiated polymer with 2-methyl-2-nitrosopropane (MNP) by the method of Bullock *et al.* [2]. The polymeric nitroxide was found to be an efficient inhibitor of radical polymerization of vinyl monomers [1]. In the present work a more convenient method [3] was used for the preparation of the polyradical. By application of the complexed *n*-butyllithium (BuLi) with tetramethylethylenediamine (TMEDA), the halogenation step could be eliminated. The BuLi/TMEDA complex had been earlier used for direct lithiation of polystyrene and other polymers by Platé *et al.* [4] who found mainly *meta*-substitution of the aromatic ring by i.r. spectroscopy. For regulation of the radical content, we favour the approach [3] in which styrene-(*m*-bromostyrene) copolymer was used as starting material.

EXPERIMENTAL

Materials

The monomers styrene and *m*-bromostyrene (Fluka) were washed free of inhibitor and distilled under reduced pressure. TMEDA (Fluka, purum) and *n*-butyllithium (Merck, 20% in hexane) were used as received. L-Ascorbic acid (Reanal, analt. grade) and azo-bis-isobutyronitrile (Fluka, purum) recrystallized twice [1] were used.

Solvents

Benzene was Na dried and distilled and, in addition, refluxed with DPPH for several hours and redistilled for titrations. Methanol analt. or spectr. grade was used.

Copolymers

Monomer mixtures containing 10 or 5 mol % of *m*-bromostyrene and 0.02 mol·l^{-1} AIBN were degassed and sealed in ampoules, polymerized at 60° for 6 hr (conversion 22–23%). Reaction mixtures were diluted with chloroform before precipitation. For purification, copolymers were repeatedly precipitated.

Preparation of polynitroxide

1–2% solution of copolymer in dry benzene was added dropwise to the BuLi/TMEDA 1:1 complex (20–25-fold excess to bromine). The reaction was conducted at room temperature in argon stream, with intensive stirring. To the resulting orange solution, MNP in benzene was added and stirred for an additional 30 min. A brownish-yellow polymer was separated on pouring the reaction mixture into methanol. The product was then dissolved in chloroform and filtered into methanol. The procedure was repeated and the yellow flakes obtained were dried *in vacuo* at room temperature.

Additional oxidation of the product was carried out in 2% benzene solution with AgO or PbO_2. The mixture was shaken at 25° for several hours, and then allowed to stand overnight. After filtration, the orange-red solution was precipitated in methanol (spectr. gr.) or evaporated on a water surface until a thin polymer film was formed.

Analysis and characteristics

Elemental analysis: bromine wt % sample *m*-BuNOPSt-3 5.0, precursor copolymer 9.4; *m*-BuNOPSt-4 2.8, precursor 4.9.

Intrinsic viscosity (benzene, 30°) 100 cm^3/g: *m*-BuNOPSt-3 0.71, precursor 0.57; *m*-BuNOPSt-4 0.61, precursor 0.63.

The ESR spectra were recorded at 80° in 1% toluene solution on a JEOL JES-ME 3X spectrometer. Spectrum simulation was carried out on a JRA-5 spectrum-computer. Ultraviolet-visible spectra were recorded on a Unicam SP 8000 spectro-photometer in benzene solution.

Ascorbinometry: 5 cm^3 of 1–0.5% benzene solutions of the polyradical were titrated with 5 mmol·l^{-1} ascorbic acid in

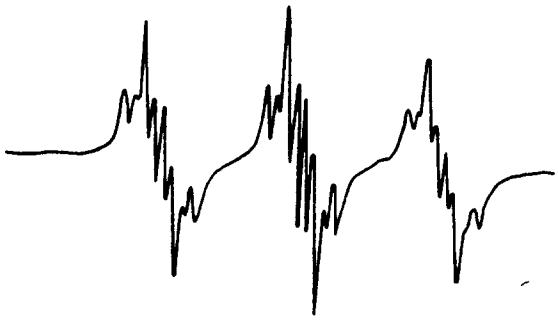

Fig. 1. ESR spectrum of *m*-BuNOPSt in toluene solution (1%) taken at 80°.

acetone, using a 2 cm^3 (1/100)microburette. The measurements were carried out by means of a Specol type spectrophotometer at 400 nm.

RESULTS

The ESR spectrum of the polynitroxide is shown in Fig. 1. It yields a nitrogen coupling constant a_N = 12.87 G and an isotropic g-factor = 2.0060. Hyperfine coupling constants obtained by computer simulation are $a_{H(o,p)} = 1.88 \pm 0.02$ G, $a_{H(m)} = 0.90 \pm 0.02$ G. These data indicate that the nitroxide groups occur only at the *meta*-position of styrene ring, and are practically identical to published data [5].

No gel formation was observed during the polymer-analogous reactions; intrinsic viscosity of the polynitroxide (*m*-BuNOPSt-4) was nearly identical with that of the starting copolymer when dilute ($\leq$ 1%) copolymer solution was used in the reaction.

Kinetic curves of styrene polymerization in Fig. 2 exhibit inhibition periods (t_i), increasing with the amount of polyradical (*m*-BuNOPSt-3) added to the monomer. As can be seen, no polymerization takes place during the inhibition period. After complete consumption of the inhibitor, at the moment t_i, polymerization starts at the rate of the uninhibited process (curve 1 in Fig. 2). The overall rate constants (K) determined from the slopes of the curves have the same average value ($= 3.05 \times 10^{-5}$ $dm^{3/2}$ $mol^{-1/2}$ sec^{-1}) thus no retardation has occurred. Similar results were obtained for the *para*-substituted analogue [1]. In the case of the *m*-BuNOPSt-4 sample, however, we found some slight systematic decrease in the K values with the concentration of the polymeric inhibitor (Table 1). An explanation to this phenomenon was found as a result of oxidation experiments, which were aimed at complete conversion of the —NOH groups to —NO·. Figure 3

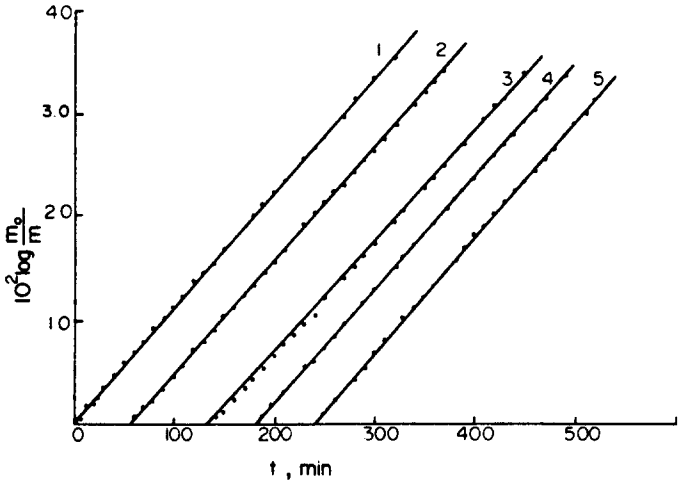

Fig. 2. Kinetic curves of styrene polymerization at 50°, AIBN 0.02 $mol \cdot l^{-1}$. Inhibitor *m*-BuNOPSt-3: (1) no inhibitor, (2) 3.9, (3) 8.3, (4) 12.1 and (5) 16.2 g/dm^3.

Table 1. Polymerization of styrene initiated by AIBN in the presence of polymeric inhibitor *m*-BuNOPSt (sample 4 and ox. 4)

Inhibitor concentration (g/dm^3)		Inhibition period (min)		$10^5 \cdot K$ ($dm^{3/2}$ $mol^{-1/2}$ sec^{-1})	
m-4	ox·*m*-4	*m*-4	ox·*m*-4	*m*-4	ox·*m*-4
0	0	0	0	3.0	3.0
5.9	6.0	52	220	2.8	3.0
12.6	12.8	104	434	2.6	2.9
19.2	19.1	150	664	2.2	2.8
26.3	—	202	—	2.0	—

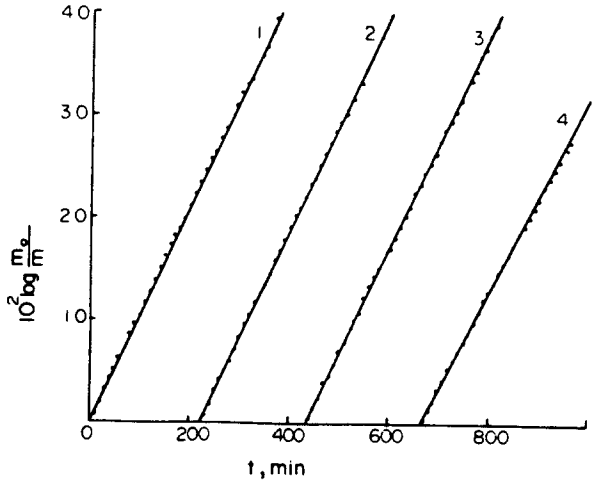

Fig. 3. As for Fig. 2 but inhibitor ox.*m*-BuNOPSt-4: (1) no inhibitor, (2) 6.0, (3) 12.8 and (4) 19.1 g/dm^3.

shows kinetic curves of polymerization in the presence of sample ox.*m*-BuNOPSt-4, oxidized with PbO_2. Concentrations of the polymeric inhibitor used, as well as, measured values of t_i and calculated K values for both original and oxidized samples are listed in Table 1. It is evident that the additional oxidation caused more than 4-fold increase in the length of the inhibition period. Comparison of K values shows that retardation has meanwhile ceased.

A linear relationship was found between the length of the inhibition period and the inhibitor/initiator ($z_0'/\bar{x}$) ratio, as for the *para*-analogue [1]. This dependence is shown in Fig. 4 for all *m*-BuNOPSt samples examined. The linearity of this function means that nitroxide groups attached to the polymer chains react predominantly with the growing radicals induced by the initiator, and side-reactions can be excluded. In this case we may use a simple relation (Ref. 5 in [1])

$$t_i = (z_0/2k_1 f \bar{x})$$

where k_1 is the rate constant of initiation, $\bar{x}$ is the average concentration of the initiator during the inhibition period, and $z_0(=cz_0')$ is the appropriate value of the initial inhibitor concentration (in mol/dm^3). Since for this system, the $2k_1 f$ value is known (2.92 10^{-6} sec^{-1}, Ref. 6 in [1]), the actual radical content (c) of the polynitroxide can be calculated, assuming that one nitroxide reacts with one propagating styryl radical. Evaluated data are included in Table 2 and will be discussed later.

Table 2. Radical content in *m*-BuNOPSt samples determined by kinetic and titrimetric methods

Sample	Radical concentration (mol-equiv/g polymer) 10^5 Kinetic	Titrimetric
m-3	5.3	5.2
ox·*m*-3	—	5.4
m-4	2.9	2.9
ox·*m*-4	11.5	11.9

Solutions of polynitroxide are orange coloured and show characteristic absorption between 350–500 nm (spectrum 1 in Fig. 5). The corresponding copolymer solutions being colourless do not absorb in this region.

The polyradical can be reduced with ascorbic acid as for low molecular nitroxides, e.g. Banfield's radical

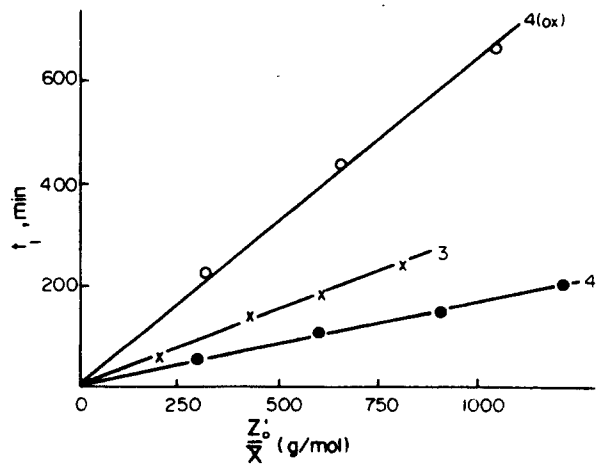

Fig. 4. Dependence of the length of inhibition period (t_i) upon the *m*-BuNOPSt/AIBN ratio ($z_0'/\bar{x}$) in styrene polymerization at 50 for samples Nos 3, 4 and 4(ox.).

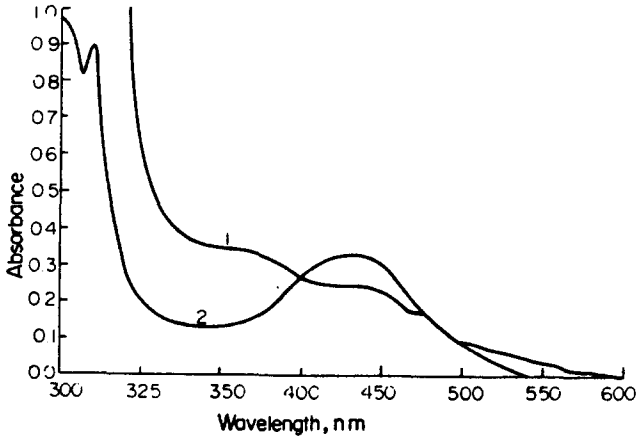

Fig. 5. Absorption spectra of *m*-BuNOPSt in benzene after oxidation (1) with PbO_2 (c = 7.5 g/dm^3) and (2) with AgO (c = 10.3 g/dm^3).

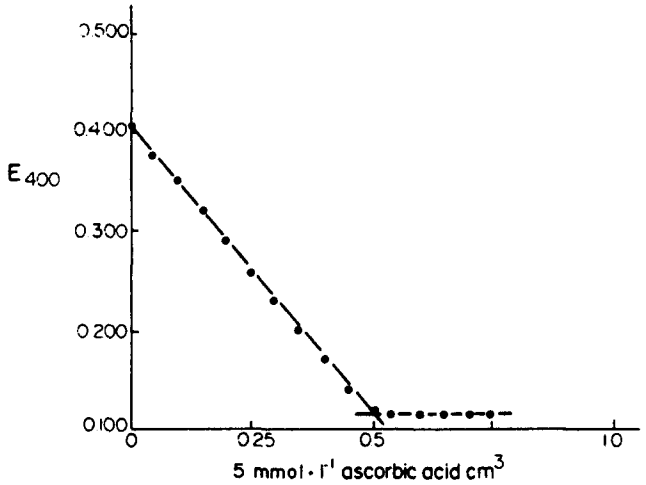

Fig. 6. Titration curve of sample ox.*m*-BuNOPSt-4 8.24 g/dm^3 in benzene taken at wavelength 400 nm.

(ref. 5 in [1]), and [6]. This reaction proved to be convenient for analysis of the polynitroxide also. Thus we found that silver oxide (AgO) leads to the formation of a by-product which is also orange-red but unreducible with ascorbic acid, and hinders titration. Further on, significant difference was found between the absorption spectra of the PbO_2 and AgO treated polynitroxide (spectra 1 and 2 resp in Fig. 5).

In order to eliminate precipitation of the polymer during titration, an appropriate solvent pair (benzene/acetone was chosen. Consumption of —NO$^\cdot$ in the reaction with ascorbic acid was measured spectrophotometrically; the solutions of polynitroxide obeyed Beer–Lambert's law. Optical density of the polymer solution decreased linearly with the amount of ascorbic acid to a limiting value of about 0.100. The end-point was therefore determined graphically. A typical titration curve is shown in Fig. 6. Reproducibility of the titrations was within 1%. Radical content of various samples ranged between 10^{-5}–10^{-4} mol-equiv/g polymer. Analysis of the oxidized samples shows that impurities in the methanol used for precipitation may cause decrease in radical concentration. Thus, the radical content of the sample could be reproduced only if polymer separation was carried out by the evaporating technique or with spectroscopic grade methanol.

Data listed in Table 2 show good agreement between the average values of radical concentration obtained by two independent methods. Additional oxidation with PbO_2, resulting in 4-fold increase in radical concentration of sample 4, caused practically no change in that of sample 3 where no retardation was observed. These facts confirm our suggestion that the polymerization of styrene is retarded by —NOH groups which are present due to incomplete oxidation.

The polymeric inhibitor studied was successfully employed in heterogeneous grafting as a phase selective inhibitor for the suppression of homopolymerization [7]. These results will be published in a subsequent paper.

Acknowledgements—We are grateful to Dr A. Rockenbauer and Dr P. Simon for ESR measurements, and to Mrs E. Löke and Mrs E. Winkler for technical assistance.

REFERENCES

1. M. Azori, F. Tüdős, A. Rockenbauer and P. Simon, *Eur. Polym. J.* **14**, 173 (1978).
2. A. T. Bullock, G. G. Cameron and P. Smith, *Polymer* **13**, 89 (1972).
3. A. T. Bullock, G. G. Cameron and J. M. Elsom, *Polymer* **18**, 930 (1977).
4. M. A. Jampolskaya, O. Yu. Okhlobustin, S. L. Davidova and N. A. Platé, *Vysokomolek. Soedin.* **8**, 771 (1966); N. A. Platé, M. A. Jampolskaya, S. L. Davidova and V. A. Kargin, *J. Polym. Sci., C* **22**, 547 (1969).
5. A. T. Bullock, G. G. Cameron and P. M. Smith, *Polymer* **14**, 525 (1973).
6. F. Tüdős, J. Heidt and J. Erőné, *Magy. kém. Foly.* **70**, 329 (1964).
7. F. Tüdős, M. Azori and A. Rockenbauer, MA2891.