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Polymerization of styrene in the presence of oligo(ethylene glycol) alkoxides: a new route to amphiphilic polymers?

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Abstract

Polymerization of styrene occurs at ambient temperature in the presence of $H(OCH_2CH_2)_nO^-$, K^+, where $n = 1$–5. The reaction rate and molecular weight of polymer can be controlled by the number of ether oxygen atoms in the initiator molecule. These dependencies are related to the presence of aggregates of alkoxide molecules and to the formation of associates of oligo(ethylene oxide) chains with potassium cations. Chain transfer reactions are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene; Oligo(ethylene glycol) alkoxides; Anionic polymerization

1. Introduction

It is well known that alkali metal alkoxides generally do not initiate the polymerization of vinyl monomers. However, some exceptions can be found in the literature. Methacrylates and acrylates as polar monomers polymerize in the presence of several anionic systems. Trekoval [1] used lithium *tert*-butoxide for the polymerization of methyl methacrylate. Tomoi et al. [2] described the polymerization of this monomer by lithium, sodium and potassium alkoxides. The best results were obtained when $CH_3OCH_2CH_2OK$ was used as the initiator. It was explained by the presence of an additional oxygen atom in the vicinity of alkoxide group.

Lochmann and co-workers [3–5] showed that alkali metal alkoxides lowered the polydispersity of the polymer as well as the stability of active centres in the anionic polymerization of methacrylates. Kunkel [6] and Janata [7] demonstrated the existence of multiple equilibria between associated and non-associated ion pairs in the anionic polymerization of methyl methacrylate, *tert*-butyl methacrylate and *tert*-butyl acrylate. Lithium *tert*-butoxide exerted a beneficial effect on the stability of active centres, decreasing the rate of termination. Tsvetanov et al. [8,9] studied the polymerization of methyl methacrylate and 2-vinylpyridine in the presence of lithium *tert*-butoxide, and also used poly(ethylene oxide) to activate the anionic initiator. Teyssié and co-workers [10–13] applied alkoxyalkoxides, mainly polydentate lithium alkoxides, as very efficient μ/σ dual ligands in the anionic polymerization of (meth)acrylates. Nagasaki and co-workers [14,15] as well as Lascelles et al. [16] and Vamvakaki et al. [17] show that potassium alkoxides can polymerize various tertiary amine methacrylates and 2-(trialkylsiloxyethyl) methacrylate in tetrahydrofuran at room temperature. Moreover, these polymerizations can proceed in a living fashion to produce polymers with relatively narrow polydispersities ($M_w/M_n = 1.10$–1.40), with a good control over molecular weight. In particular, Vamvakaki et al. [17] demonstrate that well-defined poly(ethylene glycol)-based block copolymers can be obtained if the potassium salt of monohydroxy-capped poly(alkylene oxide)s are used as macroinitiators.

It might be assumed that alkali metal alkoxides are active predominantly in the polymerization of acrylates and methacrylates. Until now only two other vinyl monomers were found to polymerize by such initiators. The first one was mentioned above; that is 2-vinylpyridine [8,9]. The second was styrene. Boileau et al. [18] reported on its polymerization by sodium *tert*-amylate with cryptand [2.2.2]. However, in the absence of cryptand the reaction did not occur.

We have found that styrene can be polymerized by potassium alkoxides also without addition of a ligand. The reaction occurred when the alkoxide possesses one or more additional oxygen atoms in the molecule. The aim of the present work was to explain this phenomenon and to study the influence of ether oxygen atoms on the course of

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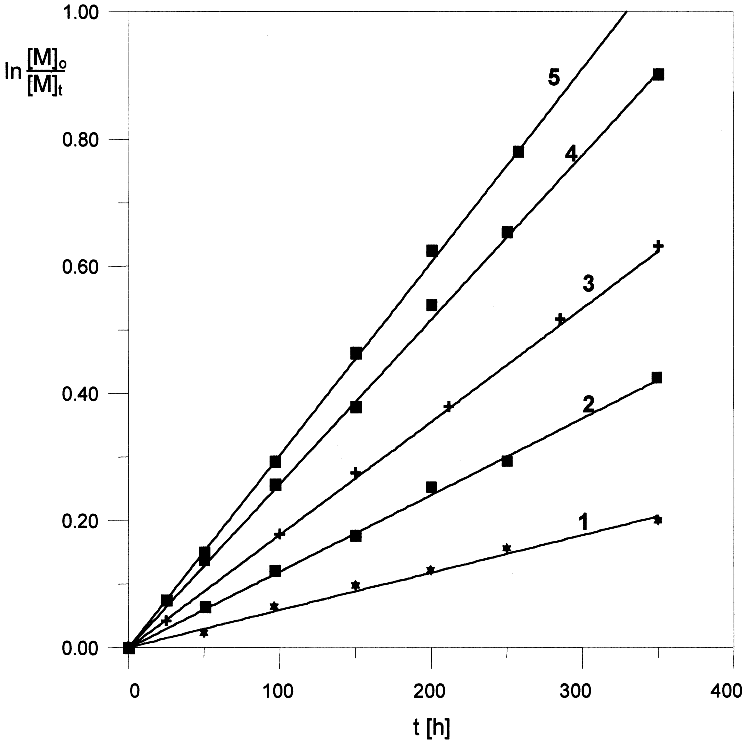


Fig. 1. Semilogarithmic plot of monomer concentration vs. time in the polymerization of styrene in the tetrahydrofuran solution with: $HOCH_2CH_2O^-$, K^+ (1), $H(OCH_2CH_2)_2O^-$, K^+ (2), $H(OCH_2CH_2)_3O^-$, K^+ (3), $H(OCH_2CH_2)_4O^-$, K^+ (4) and $H(OCH_2CH_2)_5O^-$, K^+ (5). $[\text{Alkoxide}]_0 = 0.036$, $[\text{styrene}]_0 = 4.0$ mol/dm^3. Polymerization temperature 25°C.

polymerization. The following oligo(ethylene glycol) alkoxides were selected for study: $HOCH_2CH_2O^-$, K^+ (**1**), $H(OCH_2CH_2)_2O^-$, K^+ (**2**), $H(OCH_2CH_2)_3O^-$, K^+ (**3**), $H(OCH_2CH_2)_4O^-$, K^+ (**4**) and $H(OCH_2CH_2)_5O^-$, K^+ (**5**). Tetrahydrofuran was used as a solvent.

The present work is closely connected with our earlier papers on the polymerization of butyl glycidyl ether and propylene oxide by potassium hydride [19,20]. We assumed in Ref. [20] that propylene presented in that system might be incorporated to the alkoxide active centre. The reaction was carried out at 25°C. Therefore, the same polymerization temperature was used in the present work. Styrene was selected as the model vinyl monomer.

2. Experimental

2.1. Materials and polymerization procedure

Styrene (Dwory, Poland) was extracted with 5% NaOH, and then dried over $CaSO_4$ and finally over CaH_2. Tetrahydrofuran was purified by the standard method, as in Ref. [21]. Oligo(ethylene glycol)s (all supplied by Aldrich) were dried over CaH_2. The preparation of potassium alkoxides and subsequent polymerizations were conducted at 25°C in a 50 cm^3 thermostatted reactor equipped with a magnetic stirrer and teflon valves, enabling substrates delivery and sampling under argon atmosphere. Into the reactor containing 0.5 mmol of potassium hydride a solution of 0.5 mmol of suitable glycol in 14 cm^3 of tetrahydrofuran was introduced while mixing. Alkoxides obtained after evolution of hydrogen contained about 95 mol% of mono- and 5 mol% of dipotassium derivatives as shown by gas chromatography–mass spectrometry (GC–MS). Then, 58 mmol of styrene was added to the reaction mixture. The polymerization was stopped after 14 days by the addition of methanol. The precipitated polymer was washed five times with methanol and dried under vacuum to a constant mass. The yield of reaction was below 36%, however, that was found to increase rapidly with the length of the initiator molecule.

2.2. Measurements

The number-average molecular weight, M_n, and polydispersity, M_w/M_n, were estimated by means of gel permeation chromatography (GPC) using a Spectra-Physics 8800 solvent delivery system with 10^4, 10^3 and 500 Å “Styragel” columns in series, and Shodex SF 61 refractive index detector. Polystyrene standards of low polydispersity (PL Lab) were used to generate a calibration curve.

GC–MS analyses were conducted on a 30 m-long fused silica capillary column coated with DB-1701, using Varian 3300 gas chromatograph equipped with a Finningan MAT 800 AT ion trap detector. In order to identify the

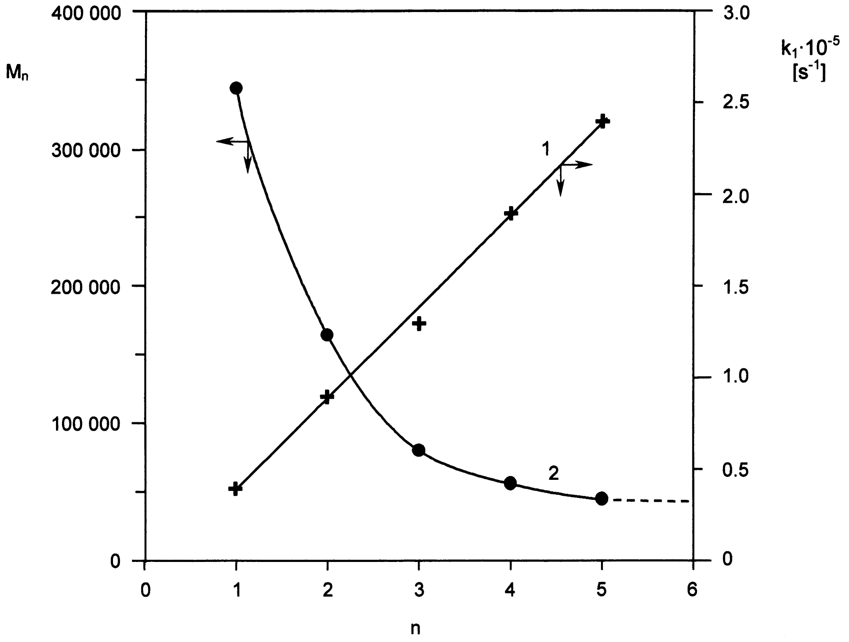


Fig. 2. Dependence of the rate constant k_1 (1), molecular weight of polystyrene (2) and the yield of polymer on the number of ether oxygen atoms, *n*, in the initiator molecule. $[\text{Alkoxide}]_0 = 0.036$, $[\text{styrene}]_0 = 4.0$ mol/dm^3. Tetrahydrofuran was used as the solvent. Polymerization temperature 25°C.

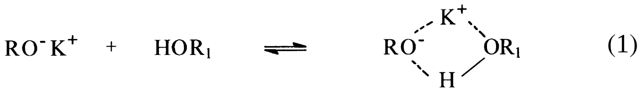
non-volatile potassium alkoxides, methyl iodide was added to the reaction mixture to form liquid products.

^{13}C NMR spectra of polymers in $CDCl_3$ were recorded at 20°C on a Varian VXR 300 multinuclear pulsed spectrometer operating at the ^{13}C resonance frequency of 75 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. IR spectra were taken on a FTS-40A BIO-RAD instrument.

3. Results and discussion

Preliminary results of this work showed that all alkoxides selected were active in the polymerization of styrene. However, the reaction rate was low at ambient temperature, and the molecular weight of polymers reached its final value within several days. Therefore, in the detailed study of polymerization the reactions were stopped after 14 days.

A semilogarithmic plot of monomer concentration vs. reaction time was linear for each system (Fig. 1) and enabled an estimate of the first order reaction rate constant k_1. The constant was found to increase linearly with the number of ether oxygen atoms in the alkoxide molecule, *n*, whereas the polymer molecular weight decreased rapidly (Fig. 2). It was assumed that this phenomenon is presumably related to differences in the concentration of active centres. Kazanski [16] found that alkali metal alkoxides form inactive associates with alcohols:



$$RO^-K^+ + HOR_1 \rightleftharpoons RO^- \cdots K^+ \cdots OR_1 \cdots H \quad (1)$$

The equilibrium constant for such a reaction ranged from 10^1 to 10^6 for various systems [22–24]. It influenced the rate of anionic polymerization of ethylene oxide [22] and other oxiranes [23,24]. Hydroxyl group-containing potassium alkoxides used in this work can form larger associates than those shown in reaction (1). The high molecular weight of polymer obtained with **1** suggests that the molecules of this initiator were strongly aggregated, only a small part of them being able to start the polymerization.

On the other hand, poly(ethylene glycol)s are known to form complexes with potassium cations [25–29]. Kazanskii and co-workers [27,28] studied carefully the solvation of metal cations by poly(ethylene oxide) chains in nitromethane solution. Complexes in which six ether oxygen atoms interact with one potassium cation were found to exist in such a system. The complexes were very stable, and their stabilities increased with the molecular weight of the polymer. Solvation of the cation by polyether chain occurred from the very early stages of the process. The role of polyether in the cation solvation was defined as a compromise between the donor nature of the heteroatom and the flexibility of the chain. This distinguishes the complexes discussed above from those formed by a crown ether or cryptand which possess the stable structure [30]. However, a linear polyether appears to be an efficient substitute for a cyclic ligand also in the present work.

The decrease in molecular weight of polystyrene when increasing the length of alkoxide molecules (Fig. 2) may be due to a gradual breaking up of their aggregates, because of a better complexation of the cation. Therefore, an increased number of active centres might be expected. Consequently, the use of five results in the highest reaction rate and the

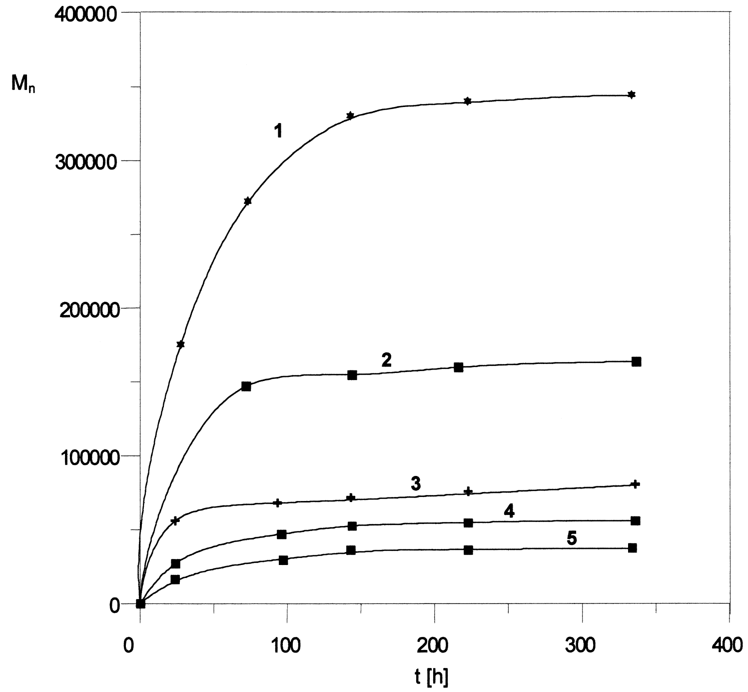


Fig. 3. Dependence between the molecular weight of polystyrene and the reaction time. Polymers were obtained in the presence of: $HOCH_2CH_2O^-$, K^+ (1), $H(OCH_2CH_2)_2O^-$, K^+ (2), $H(OCH_2CH_2)_3O^-$, K^+ (3), $H(OCH_2CH_2)_4O^-$, K^+ (4) and $H(OCH_2CH_2)_5O^-$, K^+ (5) in the tetrahydrofuran solution. $[\text{Alkoxide}]_0 = 0.036$, $[\text{styrene}]_0 = 4.0$ mol/dm^3. Polymerization temperature 25°C.

lowest molecular weight of polymer. However, the curvature of the plot of M_n vs. n shows to have a plateau for $n > 5$ (Fig. 2). The molecular weight equal to about 40,000 can be found by extrapolation of the curve for higher values of n, but it would be the M_n of a styrene–ethylene oxide block polymer rather than that of polystyrene with the incorporated initiator molecule. Jankova et al. [31] have recently prepared similar amphiphilic materials by atom transfer radical polymerization, although of low polydispersity.

In separate experiments conducted in the presence of simple alkoxides without any additional oxygen atoms, i.e. potassium methoxide and potassium ethoxide, no polymers were found in the reaction mixture. These alkoxides cannot activate the metal cation, and the polymerization of styrene does not occur.

As mentioned above, in the anionic polymerization of methacrylates and acrylates in tetrahydrofuran solutions both associated and non-associated chain ends were found to exist [6]. It was assumed that the rate of polymerization depends on the concentration of the latter because of the very low reactivity of aggregated, i.e. dormant, species. It may be assumed that the same types of ion pairs exist in the polymerization of styrene studied in the present work, influencing the course of the process. The low efficiency of initiation can also be connected with the presence of dormant species. The 100% initiation give $M_n < 10,000$ whereas values as high as 350,000 are found. One can calculate efficiency below 1% for the worst case.

A strong curvature of the plot of M_n vs. monomer conversion was found for each experiment (Fig. 3). It is typical for either a transfer reaction or slow initiation. Since no induction periods were observed (Fig. 1), transfer reactions are likely. That would account also for the high polydispersity indices, ranged from 2.0 to 3.0 independently of the kind of initiator used, as well as for the limiting yield of polymers. Chain transfer could occur with the participation of the unreacted initiator or polymer with the hydroxyl group. In this case the second active centre should be formed in the initiator or polymer molecule. Thus, polymers with central CH_2CH_2O units rather than terminal ones were expected. Infra-red spectroscopy studies confirmed such a hypothesis, since no signals of hydroxyl groups were observed. It is worth noting that dipotassium derivatives were present in small amounts in the selected alkoxides, as mentioned in Section 2. Therefore, a minor fraction of chains possessed CH_2CH_2O units in the central position independently of the chain transfer reactions.

NMR was used to determine the polymer tacticity. The analysis of ^{13}C NMR spectra showed the signals of aliphatic carbon atoms at 40.4 and 43.8 ppm and signals of *meta*, *ortho* and *para* carbon atoms of aromatic ring in the region between 125.5 and 128.0 ppm. The aromatic ipso carbon gave three signals at 145.3, 145.7 and 146.1 ppm. They were attributed to the (rr), (mr + rm) and (mm) diads, according to Ref. [32]. The polymers were found to be atactic as results from the comparison of their spectra with those observed for atactic polystyrene obtained via radical process [32].

4. Conclusions

Styrene is polymerized by various oligo(ethylene glycol) alkoxides. The presence of a cyclic ligand is not necessary in this case. It means that the non-polar vinyl monomer can be incorporated to the alkoxide active centre at room temperature. The polymerization rate, as well as the polymer molecular weight, are controlled by the number of oxygen atoms in the alkoxide molecule.

The results show that, firstly, the use of poly(ethylene glycol) alkoxides, i.e. possessing a longer chain, should result in the formation of amphiphilic ABA block polymers with the hydrophobic polyvinyl (A) and hydrophilic polyether (B) parts in the macromolecule. A likely reason for the poor livingness of the styrene polymerizations under study is that the rate of initiation by oxyanions at room temperature is too slow in comparison with the rate of propagation. Thus, secondly, taking into account the results of works of Nagasaki et al. [14,15], the polymerization should be attempted at 50–60°C. The study on such process will be the aim of our next work.

Acknowledgements

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