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Use of the phenanthrene-based lithium initiator in the anionic polymerization of methyl methacrylate

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Summary

A series of poly(methyl methacrylate) PMMA polymers with low polydispersity was synthesized anionically using sterically hindered (1-(9-phenanthryl)-1-phenyl-3-methylpentyl)lithium as an initiator. Results of absorption spectroscopy and gel-permeation chromatography (GPC) analyses were used to discuss the initiator efficiency.

Introduction

In (meth)acrylate anionic polymerization, the reaction conditions (initiator, temperature, solvent) affect dramatically the polymer yield, tacticity and distribution of molecular weights. In the initiation and propagation process, the carbanions can attack not only vinyl groups but also the ester groups or alpha-acidic hydrogens. This leads to limited monomer conversion and metal alkoxide formation, and broadening of the molecular weight distribution of the resulting polymer is observed (1,2). It has been shown that side reactions can be limited if sterically hindered and less basic initiators having 1,1-diarylalkyl structures (e.g. (diphenylhexyl)lithium) are used and if the polymerization proceeds in the presence of lithium salts (3-5). The use of 1,1-diarylethylene derivatives provides an excellent method for the synthesis of functionalized and spectroscopically labelled (co)polymers (6). 1,1-diarylethylenes do not homopolymerize and react quantitatively and rapidly with polymeric or simple alkyllithium compounds to produce corresponding 1,1-

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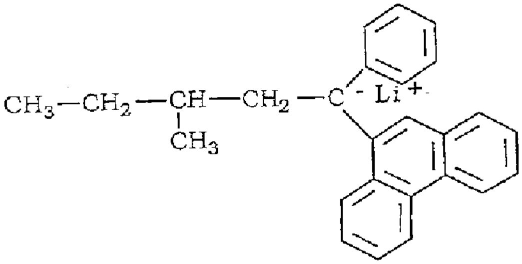
diarylalkyllithium species. For example, 1-Phenyl-1-(1-pyrenyl)ethylene and 1-phenyl-1-(1-naphthyl)ethylene were used to label polystyrene or polystyrene-poly(ethylene oxide) copolymers (7). Similarly, (1-(1-naphthyl)-1-phenylhexyl)lithium was used as an initiator to prepare chain-end labelled methyl methacrylate (8). Molecular characteristics of the labelled polymers can be easily studied by taking advantage of the spectroscopic (absorption or fluorescence) properties of the diaryl structures covalently attached to the polymer chains.

Our first objective was to investigate the effect of (1-(9-phenanthryl)-1-phenyl-3-methylpentyl)lithium initiator on the anionic polymerization of methyl methacrylate (MMA). The second objective of our work was to use the absorption properties of the phenanthrene chromophore to further characterize the prepared polymers.

Experimental

Materials. The initiator (1-(9-phenanthryl)-1-phenyl-3-methylpentyl)lithium was prepared under inert atmosphere by the reaction of 1-(9-phenanthryl)-1-phenylethylene with *sec*-butyl lithium at -78°C (Scheme I). The details of the 1-(9-phenanthryl)-1-phenylethylene preparation have been described recently (9). *Sec*-butyl lithium - 1.4 M solution in cyclohexane/hexane mixture (Janssen) was used as received from the new bottle. According to our experience, in this case the initiator concentration given by the producer does not differ by more than 10 % from the real value. MMA monomer (Norsolor) was purified according to Allen (10).

Scheme I



Polymerization. The usual high vacuum technique was used during the polymerization. All equipment was carefully flamed and flushed with nitrogen just prior to use. Into the reactor containing LiCl and THF at -78°C the calculated amount of *sec*-butyl lithium was introduced (mole ratio *sec*-BuLi/LiCl = 1/10). The 1-(9-phenanthryl)-1-phenylethylene monomer (M), which had been sublimed in the vacuum line just before use, was dissolved in a small amount of THF and added (mole ratio M/sec-BuLi = 1.2). The dark green colour of the (1-(9-phenanthryl)-1-phenyl-3-methylpentyl)lithium solution developed instantaneously. Calculated amounts of methyl methacrylate was then slowly added to the vigourously stirred solution. The polymerization was carried out for less than an hour and finally terminated by the addition of a small amount of methanol/acetic acid mixture (vol. ratio 2 : 1). The polymers were precipitated successively into an excess of methanol and heptane. Purified polymers did not contain any unreacted 1-(9-phenanthryl)-1-phenylethylene monomer as checked by the thin layer chromatography.

Instrumentation. The dependence of the experimental molecular weight (M_n(GPC) or M_n(UV)) on the initiator : monomer ratio (M_n(theory)) was examined by the gel permeation chromatography (GPC) or by the UV-absorption spectroscopy (UV). The GPC analyses were performed on an ALC/GPC 150C chromatograph (Milipore - Waters) equipped with four Microstyragel columns (10^4 A, 10^3 A, 500 A and 100 A) using both the refractive index and UV detectors. PMMA standards were used for the GPC calibration. For the UV detector, 298 nm wavelength was chosen to detect phenanthrene groups. The UV spectra were recorded on a Beckman DU-7 spectrophotometer. The M_n(UV) values were determined according to the Beer's law using THF as a solvent. 3-(9-phenanthryl)-3-phenyl-5-methyl-heptan-1-ol was used as a model compound (molar absorption coefficient was determined to be 11000 L mol^{-1} cm^{-1} at 298 nm in THF) (11).

Results and discussion

We have previously reported the synthesis of phenanthrene and anthracene end-labelled polystyrene polymers as well as polystyrene-poly(t-butyl acrylate) block copolymers labelled at the junction point between the two blocks (9). To accomplish the syntheses, the polystyryl anions reacted with either 1-(2-anthryl)-1-phenylethylene or 1-(9-phenanthryl)-1-phenylethylene monomers, and the resulting macroanions were either quenched by methanol or they initiated in the next step the polymerization of t-butyl acrylate. The chromophore monomers reacted quantitatively with polystyryl anions assuring complete labelling of the (co)polymer chains. Prepared (co)polymers had predetermined molecular weights and narrow polydispersities (M_w/M_n). In the case of phenanthrene labelled (co)polymers the M_n(GPC) and M_n(UV) values were in a good agreement. In the case of anthracene labelled (co)polymers these values differed significantly, probably because of the side reactions involving the athracene aromatic system.

In view of these facts we decided to investigate the behaviour of (1-(9-phenanthryl)-1-phenyl-3-methylpentyl) lithium initiator in the methyl methacrylate polymerization with the aim to prepare PMMA in a wider range of molecular weights. Strongly absorbing phenanthrene group covalently attached to the PMMA chain end facilitates the characterization of prepared polymers. Characteristic data of poly(methyl methacrylate) polymers are reported in Table I. In all cases, the initiator efficiency is higher than 0.8. This is consistent with the published data on efficient initiation systems for methyl methacrylate (3,4). Up to 20% of the initiator is lost because of various side reactions. The M_n(UV) values were found according to the Beer's law. For all the prepared polymers, the Beer's law is obeyed in the examined concentration range (from 0.04 g/l to 0.6 g/l). The molecular weights determined by the absorbance measurements are in a fairly good agreement with those obtained by the GPC analysis.

Table I. Characteristic data of synthesized PMMA polymers

N°	M_n a) (theory)	M_n b) (GPC)	M_n (UV)	M_w/M_n b) (GPC)	initiator eff. c)	labelling eff. d)
1	5000	5900	6300	1.11	0.85	0.94
2	6000	6800	6900	1.09	0.88	0.99
3	10000	12000	12300	1.08	0.83	0.98
4	40000	50000	56600	1.16	0.80	0.88
5	60000	74000	82400	1.21	0.81	0.90

a) Calculated from the monomer to initiator molar ratio.

b) Calculation of the number-average molecular weight (M_n) and the ratio of weight-average to number-average molecular weight (M_w/M_n) is based on the evaluation of GPC chromatograms using PMMA standards.

c) Initiator efficiency is determined by the ratio of M_n(theory) and M_n(GPC).

d) Labelling efficiency: fraction of labelled macromolecules [M_n(GPC)/M_n(UV)].

Within the experimental error, the labelling efficiency is very high, and almost constant. It is highly probable that all polymer chains are labelled by a phenanthrene group. Phenanthrene-based lithium initiator was also successfully used in the polymerization of *tert*-butyl acrylate. The relationship between M_n(GPC) and M_n(UV) in this case is not simple and requires further study.

Conclusion

(1-(9-phenanthryl)-1-phenyl-3-methylpentyl)lithium appears to be a highly efficient initiator for the anionic polymerization of methyl methacrylate. Resulting polymers are obtained in quantitative yields and they have narrow polydispersities as well as predicted molecular weights. The spectroscopic properties of the phenanthrene groups covalently attached to the polymer chains give the possibility to evaluate the molecular data of prepared polymers according to the Beer's law.

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