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Controlled/"living" atom transfer radical polymerization of styrene in the synthesis of amphiphilic diblock copolymers from a poly(ethylene glycol) macroinitiator

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Summary

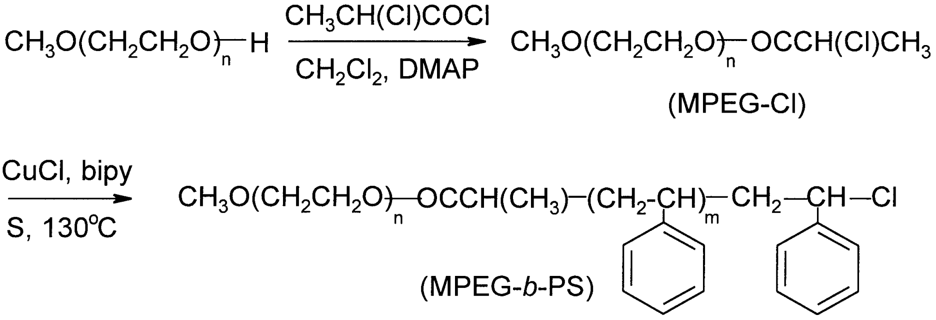
Atom transfer radical polymerization (ATRP) of styrene was initiated by a poly(ethylene glycol) macroinitiator prepared by quantitative esterification of MPEG2000 with 2-chloropropionyl chloride. The polymerization carried out at 130°C catalyzed by addition of cuprous chloride and 2,2'-bipyridine has been found to comply to the criteria for a "living" polymerization, since a linear $\overline{M}_n$ versus monomer conversion plot was found in accordance with the theoretical line indicating essentially 100% initiating efficiency. Also the polymerization is first order with respect to monomer concentration determined in two independent ways. The polydispersity index remained around 1.3 throughout the polymerization and no formation of homopolystyrene could be detected.

Introduction

Poly(ethylene glycol), PEG is of wide interest for a variety of applications and often in covalent attachment to other materials(1). Recently, we reported the synthesis of amphiphilic PS-*b*-PEG-*b*-PS by atom transfer radical polymerization(2). This polymerization technique(3) has been found versatile and useful in the synthesis of various polymers with well-defined structure(4). The PS-*b*-PEG-*b*-PS cannot be prepared directly from PEG by anionic living polymerization of styrene since the alkoxy anion is not basic enough to initiate the polymerization of this monomer. However, by functionalizing the PEG with 2-bromo- or 2-chloropropionic ester endgroups, the macroinitiator thus obtained could in our reported preparation be converted into the desired triblock copolymer by ATRP by being heated in bulk or in xylene solution in the presence of cuprous halide and the complexing ligand 2,2'-bipyridine (bipy). This polymerization by ATRP has now been studied in detail in bulk with styrene by using a synthesized monofunctional PEG macroinitiator to asses the control and living nature of the macroinitiator systems.

Amphiphilic block copolymers with PEG may be used e.g. as dispersion agents and compatibilizers. When dispersed in selective solvents diblock copolymers MPEG-*b*-PS synthesized by anionic technique form aggregates of various morphologies(5,6). Such polymers were also synthesized for studies of colloidal behavior in water and use as stabilizers in emulsion polymerization(7,8). We previously have synthesized this diblock copolymer by using a MPEG-TEMPO macroinitiator(9), however, a large amount of homopolystyrene was also formed. Structural properties in aqueous phase were previously also studied for the triblock copolymer with the hydrophobic block polyisobutylene, PEG-*b*-PIB-*b*-PEG(10) prepared by coupling reaction of suitably functionalized telechelic block(11).

Scheme 1



Experimental

Materials

Styrene (Riedel-de Haen) was passed through a column filled with activated Al2O3 (Aldrich, neutral, Brockmann I, standard grade, ~150 mesh, 58 Å) to remove the inhibitor, stored over CaH2 and then vacuum distilled before polymerization. MPEG 2000 (Aldrich) was dried by aceotropic distillation with toluene. Traces of residual toluene was removed under vacuum. All other chemicals purified as described before(2) or used as received.

The preparation of the PEG macroinitiator (MPEG-Cl) from poly(ethylene glycol) methylether MPEG2000 (Aldrich) was carried out by a procedure similar to that published previously(2) for the preparation of the corresponding difunctional initiator, using 2-chloropropionyl chloride and 4-(dimethylamino)pyridine (DMAP) as base.

General Procedure for the ATRP of styrene using the PEG macroinitiator

ATRP of styrene using the PEG macroinitiator and the copper coordination complex CuCl/bipy was performed as periously described(2). For typical ATRP with CuCl, a glass tube was charged with 1,0 g (0.5 mmol) of the macroinitiator MPEG-Cl, 0.0498 g (0.5 mmol) CuCl and 0,2349 (1.5 mmol) bipy. 10 ml, (87.4 mmol) styrene was added, and the system was degassed 3 times and then heated at 130°C under nitrogen. At time intervals an appropriate volume of the mixture was taken out with a degassed syringe, diluted with solvent for NMR and SEC and analysed for conversion, M_n and M_w/M_n.

Purification of the Block Copolymers

The separation of the diblock copolymers from possible homo PS and PEG macroinitiator was carried out as previously described(2). Thus, the crude product was extracted with cyclohexane at room temperature three times for 3 days, for possible removal of PS. In case of block copolymers with long PS blocks the residue after drying and weighing was purified by extraction twice with distilled water at room temperature in order to remove possible unreacted PEG macroinitiator. The purified product was dried in vacuum and weighed. SEC traces, molecular weights, molecular weight distributions as well as the PS content calculated by NMR were compared.

Measurements

The structure of reactants, macroinitiator, and block copolymers was characterized by ^1H NMR, using a Bruker 250 MHz spectrometer and DMSO-d_6, $CDCl_3$ or CD_2Cl_2 as solvents. Molecular weights and molecular weight distributions of the withdrawn samples were measured using a Viscotek 200 instrument (USA) with 2 mixed D colums, filled with PS-PDVB from Polymer Laboratories (England). Measurements were performed in THF solvent at room temperature with a 1 mL/min flow and molecular weights were calculated using universal calibration, PEG or PS standards.

The degree of functionalization of MPEG2000 in the esterification process was determined by ^{1}H NMR in DMSO-d_6 solution by the disappearance of the OH signal around 4,56 ppm and appearance of a new signal at 4,24 ppm due to the chloro substituted propionic ester.

For the calculation of monomer conversion during ATRP samples of the solution were withdrawn at regular time intervals under nitrogen atmosphere, diluted with $CDCl_3$ and analysed by NMR or SEC. The conversion from the ^{1}H-NMR data was calculated using the integrated and normalized area for the olefinic $-C\underline{H}=\underline{CH}_2$ protons (5.1-5.9 ppm) for styrene as compared to the sum of the aliphatic $-C\underline{H}-\underline{CH}_2-$ protons (1.3-2.0 ppm) for PS. The content of S as well as PS was determined also by SEC in the withdrawn samples and on this basis the conversion in mass % could also be calculated.

The block copolymer composition was determined by either the M_n or the ratio of the NMR signal intensity of the phenyl peak region (6.4-7.3 ppm) to that of the PEG region (3.4-3.8 ppm).

Results and Discusssion

A macroinitiator (MPEG-Cl) was prepared by esterification of MPEG 2000 (M_w/M_n = 1.05) with 2-chloropropionyl chloride and quantitative substitution was accomplished as determined by ^{1}H-NMR. The polymerization in bulk was initiated by heating to 130°C after addition of monomer, cuprous halide and bipy. The progress of the polymerization was followed by withdrawing samples from the polymerizing mixture at intervals over a 6 hour period and cooling to stop the reaction. The samples were analysed in two ways, by SEC and by ^{1}H-NMR after dilution of the samples with the appropriate solvent. In Figure 1 is seen how the experimental points fall in close accord with the theoretical line for the increase of the molecular weight (M_n) with conversion calculated on the basis of the converted styrene and the amount of initiator added. The points based on the NMR measurements show some deviation at the higher conversions. The molecular weights develop from a starting value corresponding to the molecular weight of the PEG macroinitiator. The molecular weight distribution remains relatively low with M_w/M_n close to 1.3.

The kinetic plot in Figure 2 is strictly linear based on measurements based both by NMR and SEC. It may therefore be concluded that essentially no termination takes place in the macroinitiated ATRP of styrene up to a conversion of around 55 %.

In Figure 3 is presented the overlay of the actual SEC traces in the samples withdrawn from the polymerizing mixture. It is obvious that the initiation is not very fast under the selected polymerization conditions, since in the first sample withdrawn after 1 h and 10 % conversion a shoulder amounting to about 4% clearly indicates the presence of unreacted macroinitiator. However, at higher conversions the macroinitiator is eventually consumed and at 55% conversion only very little remains. The calculated M_w/M_n values, however, remain as already indicated close to 1.3 and with a slight decreasing trend. In these polymerizations there was no indication of formation of homopolystyrene. Extraction of the diblock copolymer with cyclohexane yielded an extracted material with unchanged composition and therefore no enrichment with homopolystyrene. This is in contrast to our previous attempts to synthesize this diblock copolymer by TEMPO mediated controlled radical polymerization, where large amounts of homopolystyrene was formed(9).

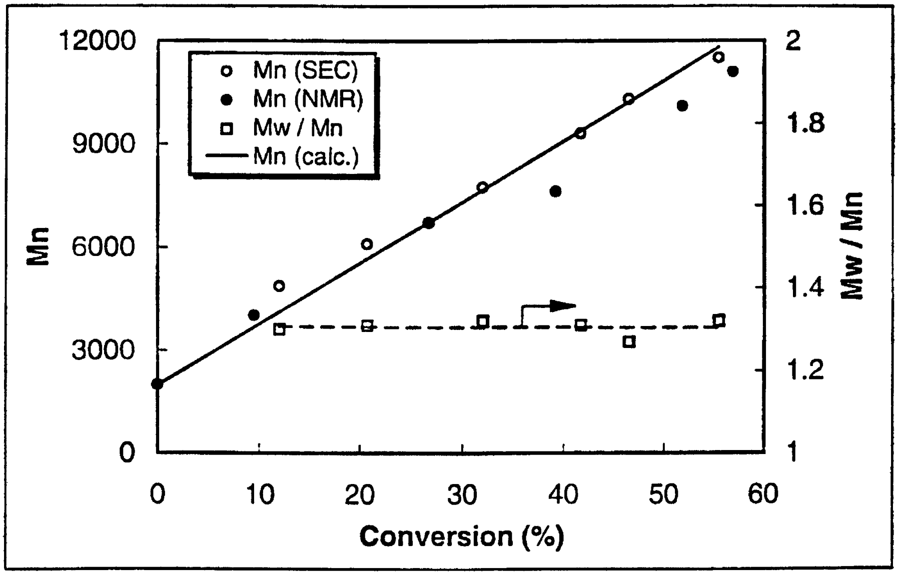


Fig. 1. $\overline{M}_n$ and $\overline{M}_w$/ $\overline{M}_n$ for diblock copolymer as a function of conversion of styrene as determined by SEC og ^{1}H-NMR.

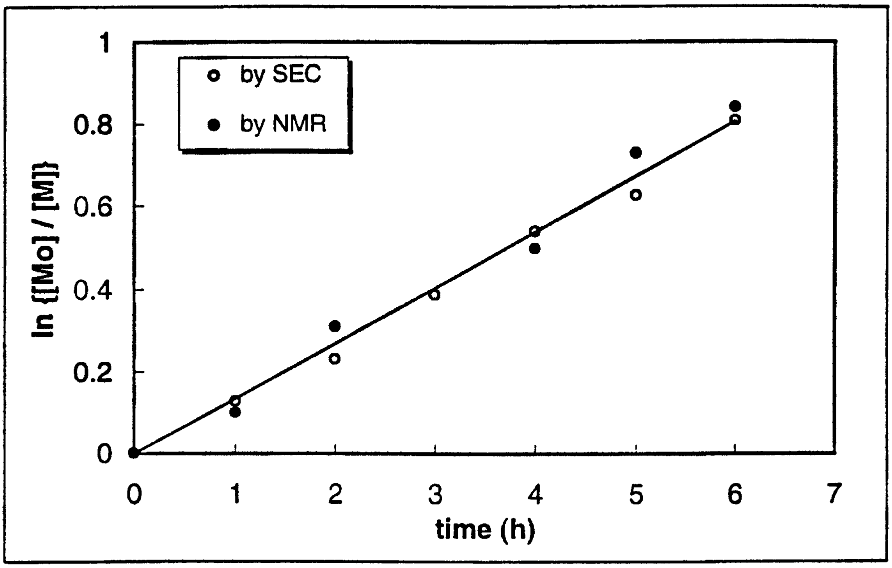


Fig. 2. First order plot for ATRP of styren and macroinitiator with residual monomer concentration determined by SEC and ^{1}H-NMR.

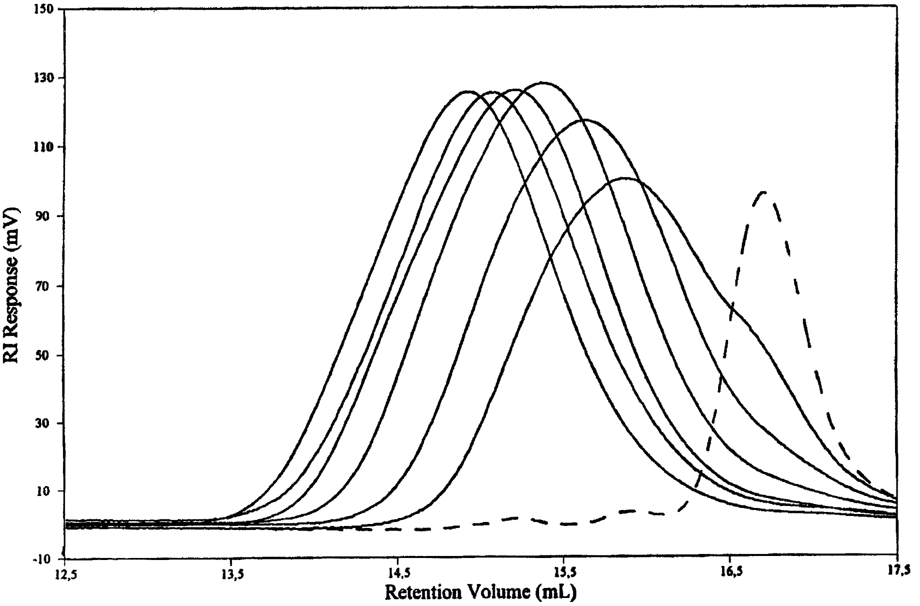


Fig. 3. Overlay of SEC curves for diblock copolymers with increasing styrene conversion.

Conclusions

ATRP with a α-chloropropionic ester macroinitiator of MPEG 2000 proceeds in a controlled/"living" manner and diblock copolymers PEG-*b*-PS may be synthesized with predetermined molecular weights and polydispersity indices of around 1.3. No detectable amount of homopolystyrene is formed.

Acknowledgment

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