

Block copolymers of styrene and *p*-acetoxystyrene with polyisobutylene by combination of living carbocationic and atom transfer radical polymerizations

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SUMMARY: Successful combination of quasilinging carbocationic (QLCP) and atom transfer radical polymerizations (ATRP) was carried out by initiating ATRP with polyisobutylene (PIB) macroinitiators obtained by QLCP. It has been found that 1-chloro-1-phenylethyl-telechelic PIBs with \bar{M}_n of 7800 and 30700 are efficient macroinitiators for ATRP of styrene in bulk and in xylene solution and for *p*-acetoxystyrene (pAcOSt) in xylene. Size exclusion chromatography (SEC) traces clearly indicated quantitative initiation and the formation of the desired polystyrene-*block*-polyisobutylene-*block*-polystyrene (PSt-PIB-PSt) and PpAcOSt-PIB-PpAcOSt triblock copolymers. Experiments also revealed absence of thermal self-initiation of styrene under ATRP conditions.

Introduction

There have been rapid developments in the field of living polymerizations in recent years. In addition to living anionic polymerization, existing for more than four decades¹, these include evolution of living polymerizations by other mechanisms, such as group transfer², carbocationic^{3–5}, ring-opening^{6,7}, and free radical^{8–11} polymerizations, during the last decade. In all these polymerizations, there exist equilibria between active (propagating, living) and inactive (nonpropagating, nonliving) polymer chains^{12,13}. Usually the concentration of the propagating species is lower by orders of magnitude than that of the polymerization inactive chains. When the equilibrium occurs by reversible termination, the terminated chains bear reactive but nonpropagating (nonliving) endgroups^{2–11} which can be utilized in subsequent reactions.

Since the number of monomers, and thus the resulting polymer structures, are limited by any of the specific living polymerization techniques, precise combination of the different mechanisms can lead to a variety of new, otherwise unavailable polymeric materials. For instance, isobutylene can be homopolymerized only by carbocationic polymerization, and a large variety of different endgroups can be attached to the termini of polyisobutylene (PIB) obtained by quasilinging carbocationic polymerization (QLCP) (see Ref.⁵ and references therein). Due to the fully saturated structure, chemical, thermal and oxidative stability of PIB, only the reactive endgroups participate in many desired processes. Therefore, PIB prepared

by QLCP as building block in a variety of macromolecular systems have attracted wide interest both in academia and industry (see, e. g., Refs.^{5,14–22} and references therein).

Recently, we have developed a method for the preparation of 1-chloro-1-phenylethyl-telechelic PIB by QLCP²³. In this polymer (Cl-PSt-PIB-PSt-Cl), short polystyrene (PSt) segments with less than ten styrene units terminated with chlorine are attached to the PIB chain. Since 1-chloro-1-phenylethane is one of the most efficient initiators in living atom transfer radical polymerization (ATRP)¹⁰, Cl-PSt-PIB-PSt-Cl is a potential new macroinitiator for such polymerization processes. Several block copolymers obtained by ATRP induced with macroinitiators have been recently prepared by different techniques, such as free radical^{10,24}, cationic^{25–28}, ring-opening metathesis²⁹, and step growth³⁰ polymerizations. This study concerns the combination of QLCP with living ATRP, i. e., ATRP of styrene and *p*-acetoxystyrene by the Cl-PSt-PIB-PSt-Cl macroinitiator.

Experimental part

Materials

Styrene (Riedel-de Haen) and *p*-acetoxystyrene (Hoechst Celanese Co., 97.2%) were passed through a column filled with activated Al₂O₃ (Aldrich, neutral, Brockmann I, standard grade) to remove the inhibitor, then were vacuum distilled over CaH₂ before polymerization. CuCl (Aldrich, 98%), 2,2'-bipyridine (bpy) (Aldrich) and 1-chloro-1-phenyl-

ethane (Acros Organics, 99%) were used as received. The synthesis and characterization of 1-chloro-1-phenylethyl-telechelic polyisobutylene (Cl-PSt-PIB-PSt-Cl) by quasilinguistic carbocationic polymerization is described elsewhere²³. Two samples of PIB macroinitiators were used (sample 1: $\bar{M}_n = 7800$, $\bar{M}_w/\bar{M}_n = 1.19$, 13% styrene content; sample 2: $\bar{M}_n = 30700$, $\bar{M}_w/\bar{M}_n = 1.10$, 4.8% styrene content)²³.

Polymerizations

Predetermined amounts of monomer (styrene or *p*-acetoxy-styrene), macroinitiator, CuCl, bpy and, if used, solvent were mixed in a dry reaction tube equipped with a three-way stop-cock and a magnetic stirring bar. This mixture was degassed three times by freeze-pump-thaw cycles. Polymerizations were started by placing the reaction tubes into an oil bath (130 °C), and were stopped by removing the reaction vessels and cooling to room temperature at predetermined times. Then the solid reaction mixture was dissolved in THF, filtered on a filter paper, and the polymer was precipitated into methanol. Yields were determined gravimetrically. Further experimental details are given in Tab. 1 and in figure captions.

Size exclusion chromatography (SEC)

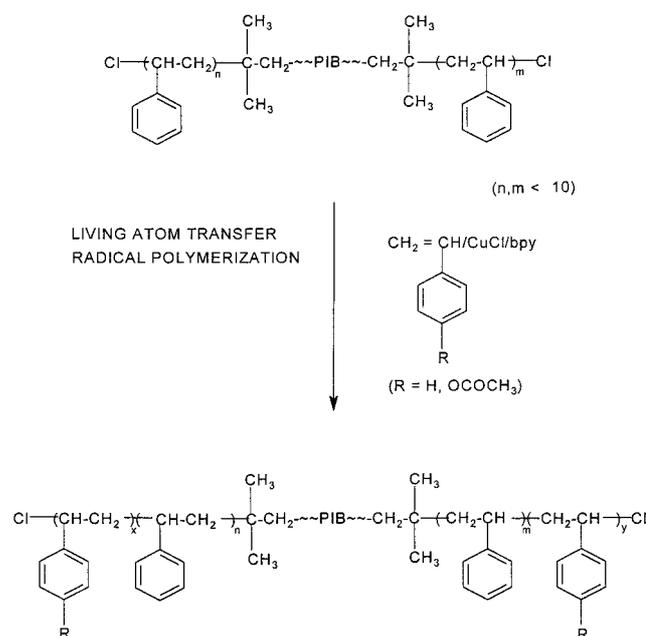
Size exclusion chromatography (SEC) measurements were made with a Nucleosil® column set consisting of three columns (250 × 8 mm): 500 Å, 7 μ C4, 100 Å, 5 μ C8, and 50 Å, 5 μ C3. THF was used as eluent with 1 ml/min elution rate. Detection was made by a dual RI and viscosity detector (Viscotek Co.). Molecular weight averages and molecular weight distribution (MWD) were calculated by calibration with polystyrene standards (Polymers Laboratories).

Results and discussion

The 1-chloro-1-phenylethyl-telechelic PIBs (Cl-PSt-PIB-PSt-Cl) containing short outer polystyrene segments were used to initiate ATRP of styrene and *p*-acetoxy-styrene in bulk and in solution. In the first step, Cl-PSt-PIB-PSt-Cl macroinitiators were synthesized by QLCP. Since the crossover reaction from the living PIB chain to styrene is a relatively rapid process, it is possible to add only few styrene units to the PIB chain²³. It is important to note that the very short PSt segments do not alter significantly the properties of the PIB midsegment. The resulting 1-chloro-1-phenylethyl endgroups are potential initiating sites for ATRP of many vinyl monomers. This combination of cationic and free radical processes can lead to a variety of new block copolymers which cannot be obtained by any direct polymerization techniques. This process is summarized for styrenic monomers, such as styrene and *p*-acetoxy-styrene, in Scheme 1.

In order to test this concept, first ATRP of styrene was studied by a low and a higher molecular weight Cl-PSt-PIB-PSt-Cl macroinitiator. The results of these experiments are summarized in Tab. 1 and Fig. 1–3. The low

Scheme 1: Formation of block copolymers by ATRP induced with the 1-chloro-1-phenylethyl-telechelic polyisobutylene



molecular weight Cl-PSt-PIB-PSt-Cl with narrow molecular weight distribution and relatively high styrene concentration was selected in order to provide sufficient separation in the SEC traces for obtaining detailed insight into the behavior of the bifunctional PIB macroinitiator under ATRP conditions. Since the PIB macroinitiator is soluble in styrene, bulk polymerization was attempted which resulted in 71% styrene conversion (see Tab. 1). As shown in Fig. 1, this bulk polymerization process led to a significant uniform shift in the SEC trace to lower elution volumes, i.e., to higher molecular weights, by ATRP of styrene with sample 1. The absence of any signal at the peak area of the PIB macroinitiator indicates quantitative consumption of Cl-PSt-PIB-PSt-Cl in the initiation process, on the one hand. The lack of a shoulder at higher elution volumes in the SEC trace of the block copolymer also provides proof for highly efficient initiation at both sides of Cl-PSt-PIB-PSt-Cl, on the other hand.

Another very important information also lies in the results of this experiment indicating the absence of detectable thermal initiation in ATRP of styrene in the bulk by the CuCl/bpy catalyst system. It was estimated that more than 4% of all the chains can be formed by thermal self-initiation in bulk ATRP of this monomer by 1-phenylethyl chloride under similar conditions³¹. Since our macroinitiator is bifunctional, the concentration of polystyrene chains formed by self-initiation should be ≈8% of the concentration of Cl-PSt-PIB-PSt-Cl, i.e., the concentration of the block copolymer. This is based on the plausible assumption that the thermally initiated

Tab. 1. Yield, \bar{M}_n , \bar{M}_w/\bar{M}_n and composition of block copolymers obtained by ATRP of styrene with 1-chloro-1-phenylethyl-telechelic polyisobutylene

Macroinitiator	Styrene (ml)	Xylene (ml)	Yield in %	\bar{M}_n	\bar{M}_w/\bar{M}_n	Styrene content by $^1\text{H NMR}$ in %	Theoretical styrene content in %
1 ^{a)}	5	–	71	38800	1.39	85	85
1 ^{a)}	1	5	33	12000	1.39	37	43
2 ^{b)}	5	–	45	52400	1.43	69	59

a) 0.7 g PIB, 0.022 g CuCl, 0.11 g bpy, 130 °C, 20 h.

b) 1.4 g PIB, 0.011 g CuCl, 0.053 g bpy, 130 °C, 20 h.

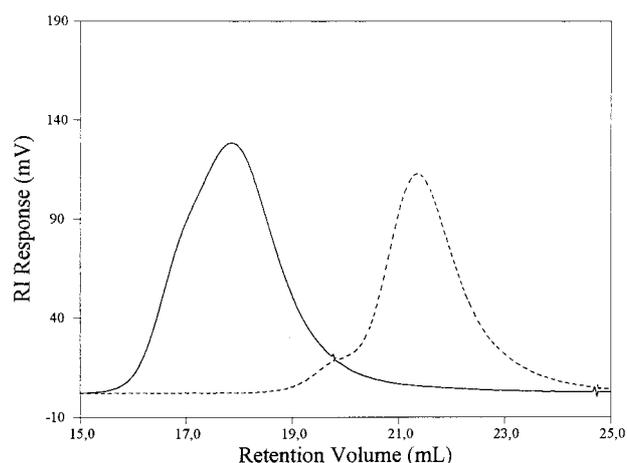


Fig. 1. SEC traces of sample 1 (---) and the PSt-PIB-PSt block copolymer (—) obtained by bulk polymerization of styrene with the PIB macroinitiator (see Experimental and Tab. 1 for details)

chains propagate with the same rate as PSt segments initiated by the PIB macroinitiator. As a consequence, a detectable amount of polystyrene homopolymer should be formed with molecular weight less than that of the outer PSt segments of the block copolymer. In this conclusion, it was considered that initiation by the 1-chloro-1-phenylethyl groups is quantitative and much faster than thermal initiation of styrene. Therefore, the latter process would lead to polystyrene homopolymer with a SEC trace appearing minimum at 21 ml or higher elution volumes. However, the applied detectors (RI, UV and viscosity) do not show any observable peak or distinct shoulder in the SEC curve as presented in Fig. 1. It was found that less than 1% PSt could be definitely detected by the SEC equipment. It is clearly seen in Fig. 1 that the peak area at higher than 21 ml elution volume is negligibly small, i. e., it is reasonable to conclude on the absence of homopolystyrene formation in this polymerization system. Therefore these results indicate that thermal self-initiation is either absent or undetectably negligible in CuCl/bpy catalyzed ATRP of styrene in the presence of an efficient initiator. Similar results were recently obtained by us

using 1-bromo-1-phenylethyl-telechelic poly(*p*-acetoxystyrene) as macroinitiator³²⁾. In this case, there is no sign of the presence of homopolymer, i. e., concluding on the absence of detectable thermal self-initiation is even more straightforward with this polymerization system. These experimental results cannot be interpreted in details yet. It can be considered that the expected amount of homopolystyrene formed by thermal self-initiation is overestimated by the kinetic data used by Wang and Matyjaszewski³¹⁾, or the reasons lies in the uncertainties about the precise mechanism of these processes, as it has been recently raised by Haddleton et al.³³⁾ However, in spite of these mechanistic uncertainties, these findings have significant synthetic consequences indicating that ATRP of styrene induced by well-defined macroinitiators can be successfully applied to prepare complex multicomponent macromolecular architectures with high precision and free from homopolymers formed by uncontrolled initiation.

Polymerization of styrene with sample 1 as macroinitiator was also carried out in xylene which is a good solvent for the monomer, PIB and polystyrene as well. This process resulted in 33% yield and a PSt-PIB-PSt block copolymer with 37% styrene content. The lower polymerization yield in solution than in bulk is undoubtedly due to the dilution by the solvent. As shown in Fig. 2, shift toward higher molecular weights can be detected in the SEC traces upon styrene polymerization by the Cl-PSt-PIB-PSt-Cl macroinitiator in this case. This indicates the formation of PSt-PIB-PSt triblock copolymer in xylene as cosolvent for the components.

Fig. 3 shows the GPC traces of Cl-PSt-PIB-PSt-Cl (sample 2) and the PSt-PIB-PSt block copolymer formed by bulk polymerization of styrene in the presence of CuCl/bpy catalyst. As exhibited in this figure, the SEC trace is shifted toward higher molecular weights upon styrene polymerization, indicating formation of the desired block copolymer. It has to be noted that homopolymer formation by thermal initiation should result in polystyrene homopolymer exhibiting a SEC peak at higher than 21.5 ml elution volume. This part of the elu-

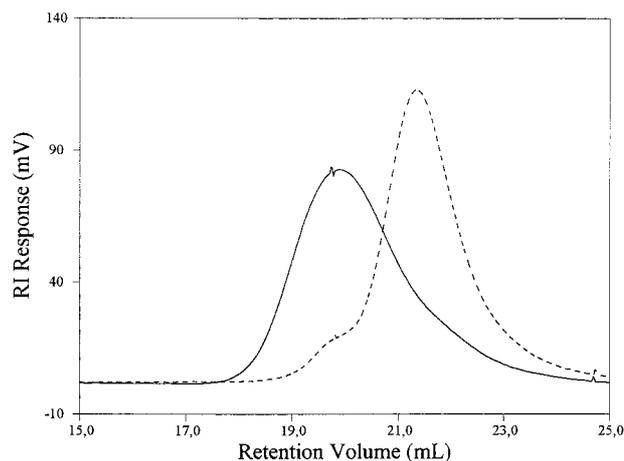


Fig. 2. SEC traces of sample 1 (---) and the PSt-PIB-PSt block copolymer (—) obtained by polymerization of styrene with the PIB macroinitiator in xylene (see Experimental and Tab. 1 for details)

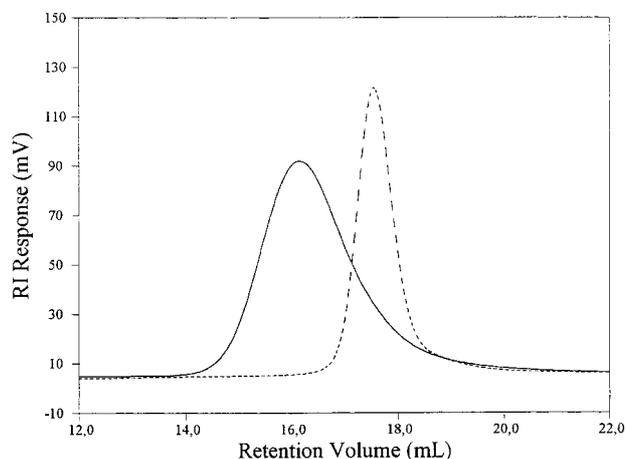


Fig. 3. SEC traces of sample 2 (---) and the PSt-PIB-PSt block copolymer (—) obtained by bulk polymerization of styrene with the PIB macroinitiator (see Experimental and Tab. 1 for details)

tion volumes is completely absent from the signal of the macroinitiator. Therefore, any detectable amount of homopolymer could be easily observed. However, there is no sign of the presence of PSt homopolymer in this range of the SEC elution volumes as presented in Fig. 3. This also strongly indicates that detectable thermal self-initiation during ATRP of styrene by the CuCl/bpy catalyst in the presence of the Cl-PSt-PIB-PSt-Cl macroinitiator is absent.

Preparation of ABA block copolymer containing poly(*p*-acetoxystyrene) (PpAcOSt) outer and PIB inner block was also attempted. Living polymerization of *p*-acetoxystyrene by the ATRP method with *p*-dibromoxylene initiator has recently been demonstrated by us³². In

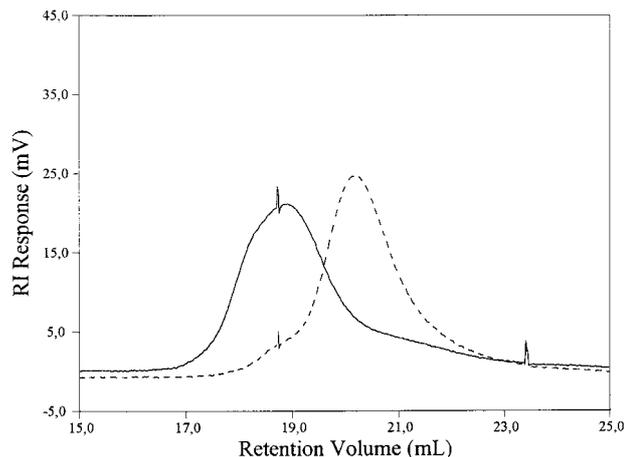


Fig. 4. SEC traces of sample 1 (---) and the PpAcOSt-PIB-PpAcOSt block copolymer (—) obtained by polymerization of *p*-acetoxystyrene with the PIB macroinitiator in xylene (0.135 mmol sample 1, 1 ml pAcOSt, 5 ml xylene, 0.333 mmol CuCl, 1.01 mmol bpy, 130 °C, 17 h)

order to test the initiating capability of the PIB macroinitiators, first homopolymerization of *p*-acetoxystyrene (pAcOSt) with 1-phenylethyl chloride (PhEtCl) model initiator was examined. In a typical homopolymerization PhEtCl/CuCl/bpy in 1:1:3 molar ratio were mixed with the monomer for bulk polymerization and also with xylene in other experiments. Quantitative initiation, and poly(*p*-acetoxystyrene)s with nearly theoretical molecular weight and narrow molecular weight distribution were obtained both in bulk and in xylene. For instance, bulk polymerization of 5 ml pAcOSt with 0.44 mmol PhEtCl for 20 h polymerization time at 130 °C led to 76% yield and PpAcOSt with $\bar{M}_n = 7900$ and $\bar{M}_w/\bar{M}_n = 1.32$. In solution (0.18 mmol PhEtCl, 1 ml pAcOSt and 5 ml xylene) 24 and 40 h polymerization time led to 62% ($\bar{M}_n = 4100$, $\bar{M}_w/\bar{M}_n = 1.24$) and 72% yields ($\bar{M}_n = 4300$, $\bar{M}_w/\bar{M}_n = 1.22$), respectively.

However, bulk polymerization of *p*-acetoxystyrene with sample 1 resulted in insufficient initiation, most likely because of the limited solubility of PIB in this monomer. Polymerization with the same macroinitiator in xylene led to 58% yield. Fig. 4 exhibits the SEC traces of the Cl-PSt-PIB-PSt-Cl macroinitiator and the product formed by polymerization of *p*-acetoxystyrene with this macroinitiator in xylene. Shifting towards higher molecular weights shows the formation of PpAcOSt-PIB-PpAcOSt block copolymers. However, the small shoulder in the SEC trace of this block indicates that unreacted macroinitiator is most likely still present in this system. This can be a sign of slow initiation. The reason for this observation might be due to the relatively low miscibility of the monomer with the macroinitiator. Other solvents or solvent mixtures can overcome this problem.

Conclusions

It has been found that well-defined block copolymers can be obtained by the combination of quasiliving carbocationic and atom transfer radical polymerizations. 1-Chloro-1-phenylethyl-telechelic polyisobutylenes obtained by the first process are efficient initiators of ATRP of styrene in bulk and in xylene solution. Our experiments were also designed for providing information on thermal self initiation of styrene under ATRP conditions. These attempts resulted in the striking observation which indicates that thermal initiation is absent, or at least under the detectable limit by SEC in ATRP, for this monomer by the CuCl/bpy catalyst. The synthetic advantage of these findings are straightforward: living ATRP or combination of this method with other polymerization techniques can provide a large variety of homopolymer-free, well-defined macromolecular systems.

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