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Synthesis of triblock and random copolymers of 4-acetoxystyrene and styrene by living atom transfer radical polymerization

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Summary

Triblock copolymers containing polystyrene (PSt) and poly(4-acetoxystyrene) (PAcOSt) segments have been prepared by atom transfer radical polymerization (ATRP). In the first step one of the two monomers was polymerized in bulk using the initiating system α,α′-dibromo-p-xylene/CuBr/2,2′-bipyridine (1/1/3). Subsequently the resulting telechelic polymers with active bromo end group structures were used as macroinitiators for the polymerization of the second monomer under ATRP conditions. This process gave PAcOSt-PSt-PAcOSt and PSt-PAcOSt-PSt triblock copolymers with predetermined molecular weights and narrow molecular weight distributions. Polymerization of a mixture of equal molar amounts of the two monomers yielded a random copolymer with narrow molecular weight distribution.

Introduction

Block copolymers with well-defined structures are important for both scientific purposes and for applications in many different areas. Such polymers can be prepared by sequential chain polymerization if the propagation can be controlled to avoid chain breaking termination and transfer reactions. Following living anionic polymerization (1), advances in polymerization techniques over the last two decades have resulted in control of most the other types of addition polymerizations including group transfer (2), carbocationic (3-5), ring-opening metathesis (6) and most recently free radical (7-10) polymerizations. In the majority of the known living polymerizations reversible reactions occur between active (propagating) and dormant (inactive, nonpropagating) species. The active-dormant equilibria involve reversible deactivation and since the equilibria are shifted towards the terminative side, and the concentration of the terminated chains are usually higher by orders of magnitudes than that of the active propagating species, terminated chains with given endgroups can be easily prepared. The resulting reactive chain ends can be utilized in subsequent processes. The common features of such living polymerizations have previously been analyzed as quasiliving polymerizations (11,12).

Living radical polymerization processes developed during the last few years are currently in the focus of interest and major activity of numerous research and development groups worldwide. Following the initial work using reversible termination of growing chains in free radical polymerization (13,14) two major approaches have received broad attention for obtaining control of the radical chain growth. The first, developed mainly by Georges et al. (7) is a spontaneous dissociation of a dormant chain end structure in an equilibrium process to yield the propagating radical in low concentrations and a non-propagating radical species, often with alkoxyamine

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structure. The second approach developed by Wang and Matyjaszewski (9) and Sawamoto et al. (10) involves transition metal halide complexes. These systems are based on an equilibrium redox process catalysed by the transition metal compound whereby a dormant chain end structure with an active halogen group forms a propagating radical in low concentrations along with the oxidized form of the transition metal which accommodates the active halogen. This method is referred to as atom transfer radical polymerization (ATRP).

We became interested in the preparation of block copolymers of 4-acetoxystyrene and styrene and also of random copolymers of these two monomers with well-defined structures, due to the fact that the acetoxy groups represent protected phenolic groups in these polymers. Therefore, the resulting polymers can be transformed by hydrolysis into amphiphilic and at the same time reactive copolymers. Living polymerization 4-acetoxystyrene is limited to radical polymerization due to the chemical nature of the functional group (15). The homopolymerization of 4-acetoxystyrene by ATRP was recently investigated by us (16), and it was found that it conformed to living polymerization. Poly(4-acetoxystyrene) with predetermined molecular weights and narrow molecular weight distributions was obtained, and the kinetics and the development of the molecular weight with conversion indicated the absence of permanent termination and transfer reactions. This study deals with the preparation of triblock and random copolymers of 4-acetoxystyrene and styrene by living ATRP.

Experimental

Materials

4-Acetoxystyrene (AcOSt) (Hoechst Celanese Corporation, 97.2%) was purified by passing through a column of neutral alumina. Styrene (St) (Riedel deHaën, 99%) was first passed through neutral alumina and then vacuum distilled from CaH_2. α,α′-Dibromo-p-xylene (DBX) (Aldrich, 97%) was recrystallized from $CHCl_3$ and dried at room temperature under vacuum. Copper(I) bromide (Aldrich, 98%) and 2,2-bipyridine (bpy) (Aldrich, 99%) were used as received.

Synthesis of homopolymers and random copolymers of 4-acetoxystyrene and styrene

4-Acetoxystyrene or styrene or 50-50 mol % mixture of these monomers in case of the random copolymer, α,α′-dibromo-p-xylene, CuBr and bpy were placed in a dry, long glass tube with a magnetic stirring bar. The reaction mixture was degassed three times by the freeze-pump-thaw method. Each cycle took 20 minutes. Then polymerizations were started under conditions listed in Table 1. After stopping the reaction the solid reaction mixture was dissolved in THF and filtered on paper filter. The solution was concentrated and the polymer was precipitated into methanol, and was dried until constant weight in vacuo at room temperature.

Synthesis of block copolymers

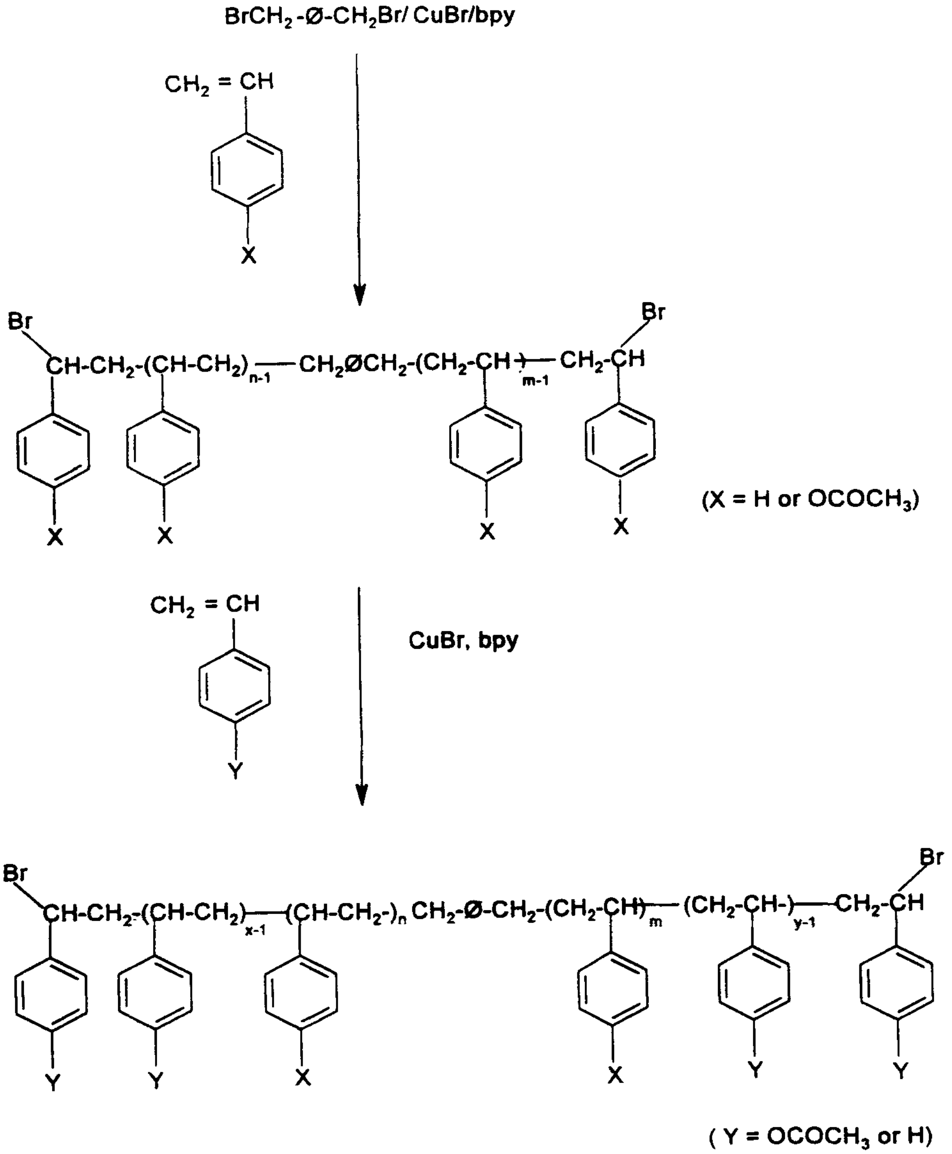
The difunctional homopolymer obtained in the first step was dissolved in the second monomer for triblock copolymer formation together with CuBr and bpy. After degassing three times the polymerization was carried out by heating under nitrogen. The polymerization conditions are listed in Table 1. The workup procedure was the same as for the homo- and random copolymers.

Gel permeation chromatography

GPC measurements were made with a Nucleosil® column set with three columns: 500Å, 7μ C4, 100Å, 5μ C8, and 50Å, 5μ C3. THF was used as eluent with 1 mL/min elution rate, and detection was carried out by a dual RI and viscosity detector (Viscotec Co.). Molecular weight averages and molecular weight distribution (MWD) were calculated by the use of universal calibration made with narrow MWD polystyrene standards.

Results and discussion

The strategy of the synthesis of PAcOSt-PSt-PAcOST and PSt-PAcOSt-PSt triblock copolymers is outliend in Scheme 1. The first step is the preparation of a telechelic macroinitiator with the DBX difunctional initiator (17) in conjunction with the CuBr/bpy complex. After purification and removal of the unreacted monomer, the resulting 1-bromo-1-phenylethyl-telechelic polymer is used as a difunctional macroinitiator for ATRP of the second monomer. This process leads to the desired ABA block copolymer.



Scheme 1. Synthesis of PAcOSt-PSt-PAcOSt and PSt-PAcOSt-PSt triblock copolymers by living ATRP.

Table 1. Polymerization conditions for and yield, M_n and M_w/M_n of the homopolymer macroinitiators, triblock and random block copolymers.

Sample No.	Initiator (g)	CuBr (g)	bpy (g)	Monomer (ml)	Temp. (°C)	Time (hrs)	Yield (%)	$M_n \cdot 10^{-3}$	M_w/M_n
1	0.179 DBX	0.195	0.637	6 St	110	18	94	10.0	1.24
2	2.112 Sample 1	0.061	0.198	6 AcOSt	90	15.5	73	21.0	1.15
3	0.1742 DBX	0.189	0.618	5 AcOSt	90	1.7	58	4.8	1.11
4	1.830 Sample 3	0.063	0.206	6 St	110	19	80	25.2	1.16
5[a]	0.229 DBX	0.249	0.813	6 St+AcOSt	110	19	100	9.0	1.14

[a] Mixture of St with AcOSt in 1:1 molar ratio.

Table 1 and Figures 1 and 2 summarize the results of this synthetic approach. PAcOSt-PSt-PAcOSt was obtained by initiating ATRP of AcOSt with a PSt sample (M_n = 10,000, M_w/M_n = 1.24). Polymerization of AcOSt with this macroinitiator led to significant increase of MW (M_n = 21,000) and even to narrowing the MWD (M_w/M_n = 1.15). This is better illustrated in Figure 1 which shows the GPC trace of the PSt macroinitiator and the PAcOSt-PSt-PAcOSt block copolymer. Polymerization of AcOSt resulted in significant shift to higher MWs indicating quantitative initiation by the 1-bromo-1-phenylethyl-telechelic PSt macroinitiator.

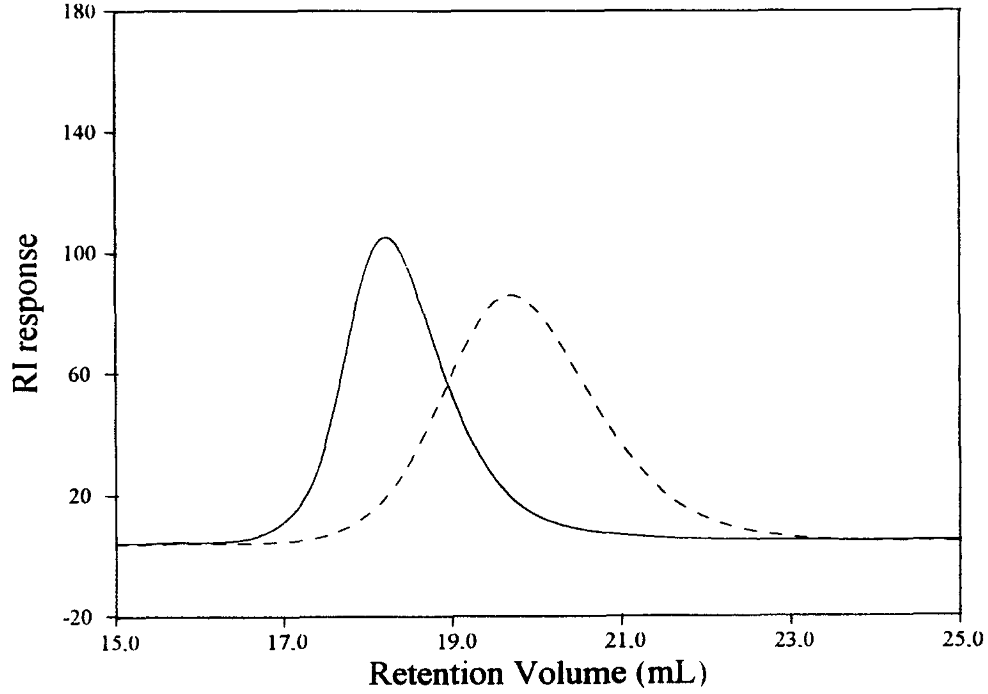


Figure 1. GPC traces of the PSt macroinitiator (sample 1) (---) and the PAcOSt-PSt-PAcOSt (sample 2) (—) block copolymer.

For the synthesis of PSt-PAcOSt-PSt a PAcOSt telechelic macroinitiator (sample 3) with M_n = 4,800 (M_w/M_n = 1.11) was prepared. After purification and drying, ATRP of St gave a block copolymer with M_n = 25,200. Figure 2 clearly exhibits the formation of the desired block copolymer with high blocking efficiency. As shown in this Figure, signal for the PAcOSt macroinitiator in the GPC trace of the block copolymer apparently cannot be detected. This indicates quantitative initiation by this macroinitiator, i.e. quantitative formation of PSt-PAcOSt-PSt by the living ATRP process.

An experiment was also carried out for the preparation of AcOSt/St random copolymer (sample 5). This process led to 100% consumption of both monomers and to a copolymer with narrow MWD (M_w/M_n = 1.14).

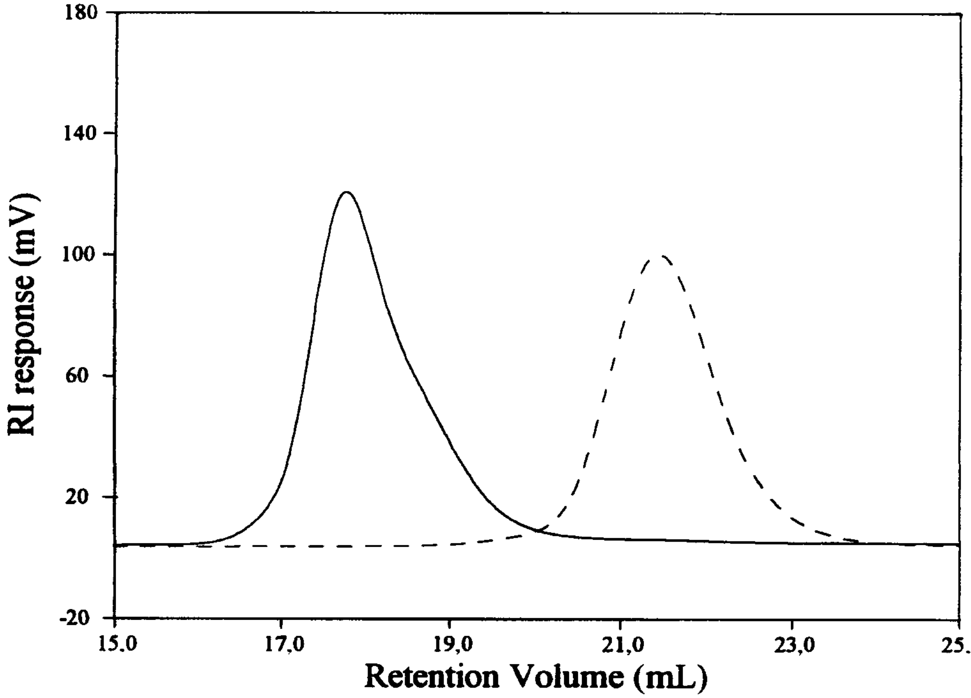


Figure 2. GPC traces of the PAcOSt macroinitiator (sample 3) (---) and the PSt-PAcOSt-PSt (sample 4) (—) block copolymer.

In conclusion, applying living ATRP of styrene and 4-acetoxystyrene by the difunctional α,α'-dibromo-p-xylene initiator gave 1-bromo-1-phenylethyl-telechelic macroinitiators for subsequent ATRP. Utilization of the resulting difunctional macroinitiators led to the synthesis of PAcOSt-PSt-PAcOSt and PSt-PAcOSt-PSt triblock copolymers. The PAcOSt segments can be transformed to poly(4-vinylphenol) chains. Amphiphilic block copolymers with controlled structures containing poly(4-vinylphenol) blocks are of interest in several potential applications.

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