**Communication:** The living radical polymerization of 4-acetoxystyrene via the RAFT process has been achieved employing bulk, solution and emulsion techniques. The rate of polymerization was studied between 60 °C and 90 °C. Increasing the temperature increases the rate of polymerization without affecting the polydispersity. Poly(4-acetoxystyrene) with narrow polydispersity (1.08) was obtained. Various novel dithiocarboxylic esters and dithiocarbamates were screened as chain-transfer agents for the RAFT polymerization of 4-acetoxystyrene. The block copolymerization of poly(4-acetoxystyrene) with styrene leading to poly(4-acetoxystyrene)-*block*-polystyrene confirmed the presence of active chain ends in the first block. The acetoxy polymers were hydrolyzed to the corresponding hydroxy polymers under mild basic conditions.

Effect of temperature on the radical polymerization of 4-acetoxystyrene in the RAFT process. Reaction conditions were the same as in Figure 1.
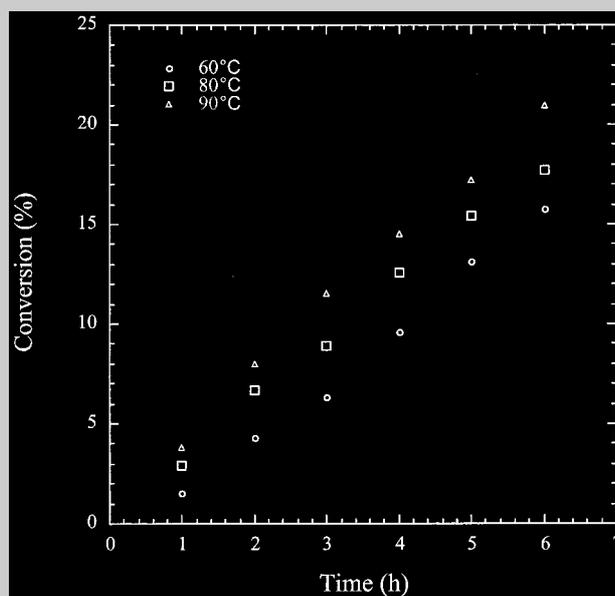
Reversible Addition-Fragmentation Chain-Transfer Polymerization for the Synthesis of Poly(4-acetoxystyrene) and Poly(4-acetoxystyrene)-*block*-polystyrene by Bulk, Solution and Emulsion Techniques

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Introduction

The synthesis of well-defined polymer architectures via living radical polymerization has become a major aspect of polymer chemistry in recent years.[1] Living radical polymerization has several advantages over other living polymerization methods (e.g., anionic) including the tolerance to a wide range of monomers with various functional groups, facile copolymerization, undemanding reaction conditions and feasibility in the presence of water. Although living radical polymerization was investigated in 1982 by Otsu et al.,[2] extensive research in this area was conducted only after the discovery of the use of

stable nitroxides as reversible termination reagents.[3, 4] During the last few years, several techniques, such as stable free-radical polymerization (SFRP),[4–7] atom-transfer radical polymerization (ATRP)[8–11] and reversible addition-fragmentation chain-transfer (RAFT),[12–22] have been explored for living radical polymerization.

The preparation of linear polymers possessing phenolic functional groups on the monomer unit has attracted much attention due to their potential industrial applications in the areas of photoresists, adhesives, metal treatment, plastic additives and as stabilizers in emulsion polymerization and polymer blends.[24–26] Poly(4-hydroxystyrene) is an important linear phenolic polymer, which can be prepared by the hydrolysis of poly(4-acetoxystyrene). Recently, the polymerization of 4-acetoxystyrene

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by means of ATRP and SFRP has been reported to obtain well-defined poly(4-acetoxystyrene).[23, 26–29] However, the application of the RAFT process towards the preparation of such a novel polymer has not been reported yet. In this communication, we present our preliminary results on the living radical polymerization of 4-acetoxystyrene to prepare poly(4-acetoxystyrene) and poly(4-acetoxystyrene)-*block*-polystyrene using the RAFT process in bulk, solution and emulsion.

Experimental Part

Materials

4-Acetoxystyrene and styrene were purchased from Acros, USA, and distilled under reduced pressure prior to use. 2,2′-Azoisobutyronitrile (AIBN) was obtained from Aldrich and used as received. *S*-Thiobenzoylthioglycolic acid (**1**, Acros) was recrystallized from ethanol and used as a chain-transfer agent (CTA). All other CTAs were prepared using a procedure developed in our laboratory.[30, 31] The purity of all CTAs was confirmed by means of ^{1}H NMR, ^{13}C NMR and IR spectroscopy, as well as GC-MS and found to be >99%. All other reagents used for solution and emulsion polymerizations were of high purity.

Characterization

The homo and block copolymers prepared in bulk, solution and emulsion were precipitated as per the procedure given in our earlier work.[27] Molecular weight and molecular weight distributions (MWD) were determined by means of gel permeation chromatography (GPC) using a Waters 515 pump, equipped with 4120 refractive index detector and four Waters Styragel HR columns (4.6 mm ID × 300 mm). Tetrahydrofuran was used as the eluant at a flow rate of 0.3 mL/min at 30 °C. All molecular weights are reported relative to the calibration with polystyrene standards. The characterization of homo and block copolymers before and after hydrolysis were determined by means of ^{1}H NMR (Varian Unity 500 at 500 MHz) and IR spectroscopy (Perkin-Elmer FT-IR spectrometer PARAGON 1000).

Bulk Polymerization

In a typical experiment, 5.0 g (3.1×10^{-2} mol) of 4-acetoxystyrene were placed in a Schlenk tube and degassed with nitrogen. Then 0.065 g (3.1×10^{-4} mol) of CTA **1** and 0.010 g (6.1×10^{-5} mol) of AIBN were added to 4-acetoxystyrene and heated to 90 °C for several hours. Intermediate samples were withdrawn at regular time intervals and analyzed by means of GPC.

Solution Polymerization

The solution polymerization of 4-acetoxystyrene was performed employing a method similar to the polymerization in bulk except the use of an appropriate solvent. For this purpose, solvents such as benzene, chlorobenzene and 1,2-dichlorobenzene were used. The intermediate and final polymers were analyzed by means of GPC.

Emulsion Polymerization

The emulsion polymerization was performed (70 °C, N$_2$) by adding a pre-emulsified (via sonication) mixture of distilled water (10 mL), monomer (10 g), sodium dodecylsulfate (SDS, 0.5 g) and **1** (50 mg) to a 250-mL flask containing 15 mL water, SDS (0.5 g), and potassium persulfate (KPS, 25 mg).

Results and Discussion

Bulk Polymerization

The results of the bulk polymerization of 4-acetoxystyrene at 90 °C using the RAFT process are shown in Figure 1. A linear increase in molecular weight with conversion and narrow decreasing polydispersities indicate that the concentration of growing radicals is constant. Moreover, the experimental molecular weight closely agrees with the theoretical molecular weight estimated by the equation $\overline{M}_{n,th} = M_{Monomer} \times$ fractional conversion $\times$ [4-acetoxystyrene]/[CTA], which is in accordance with the proposed RAFT mechanism. The nonlinearity of the curve at higher conversion has been noticed previously in controlled radical polymerizations and was ascribed to autoacceleration due to the increasing viscosity of the medium.[29] Furthermore, a series of polymerizations was carried out at temperatures of 60 °C, 80 °C and 90 °C (Figure 2). At low conversions, an approximately linear plot for time vs conversion was obtained at all temperatures and the rate of the reaction increased with increasing temperature. Although the reaction is first order with respect to monomer, the initial rates at low conversions were used to make relative comparisons of the reaction rates. Additionally, the polydispersity remained constant at
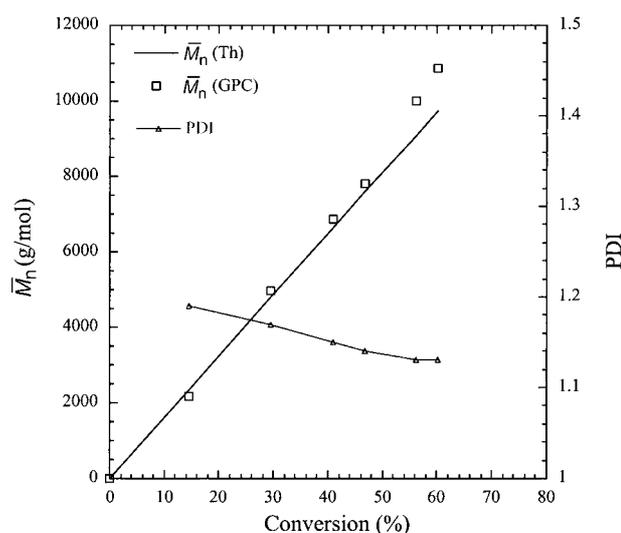

Figure 1. Number-average molecular weight and polydispersity for the bulk polymerization of 4-acetoxystyrene using [4-acetoxystyrene]/[**1**]/[AIBN] = 100:1:0.2. Reaction conditions: 90 °C; final reaction time, 24 h.
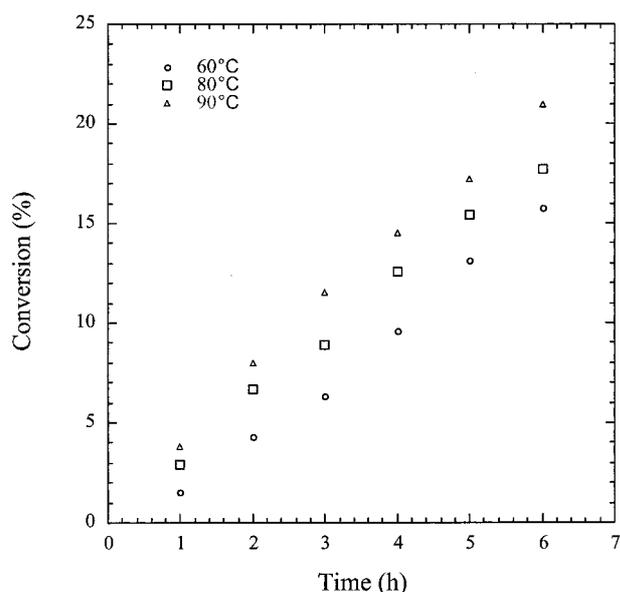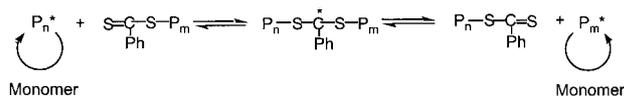
Figure 2. Effect of temperature on the radical polymerization of 4-acetoxystyrene in the RAFT process. Reaction conditions were the same as in Figure 1.

Scheme 1.

approximately 1.15. This can be explained by the following factors. In radical polymerization at higher temperatures, it has been well established that the activation energy for radical propagation is appreciably higher than that of termination.[1] Thus, k_p/k_t increases with temperature and a control of the polymerization is maintained at higher temperatures. Additionally, the transfer constant for the CTA may increase with temperature, which ensures a rapid rate of exchange between the dormant and the active chains (Scheme 1). Hence, the rate of reversible addition and fragmentation increases leading to a higher rate of polymerization while maintaining the living character of the polymerization.

Figure 2 also shows a relatively low dependence of the initial rate of polymerization on temperature. The temperature dependence of the rate of polymerization was compared to known results for the thermal self-initiated polymerization of styrene.[32] This comparison confirmed the substantially lower temperature dependence and a slightly higher rate of polymerization.

Solution Polymerization

The solution polymerization of 4-acetoxystyrene in the presence of CTA **1** was carried out at 90 °C in three different solvents (benzene, chlorobenzene and 1,2-dichlorobenzene) with a monomer concentration of 50%. The molecular weight increased in a linear fashion with

conversion and time. However, the rate of the polymerization in solution was comparatively lower than that in bulk polymerization and longer reaction times were required to achieve higher conversions. Polymers prepared in solution showed slightly broader polydispersities (PDI = 1.36–1.45) than was observed in bulk polymerization. This could be due to the generation of new initiating species at longer reaction times, which can initiate polymerization at the later stages of the polymerization. Similar MWD broadening was also observed for other living radical polymerizations in solution, particularly at higher conversion.[33, 34]

Emulsion Polymerization

The polymerization of 4-acetoxystyrene in emulsion using **1** as a CTA and potassium persulfate as the initiator in the RAFT process at 70 °C led to a stable latex of poly(4-acetoxystyrene) ($\overline{M}_n$ = 5550 g/mol and PDI = 1.61) with 70% conversion in 12 h. The molecular weight of the intermediate latexes was found to increase linearly with conversion. However, it is interesting to note that the polydispersity of the polymer increases with time and conversion. This could be due to the prolonged conversion of **1** into polymer chains and a slow rate of exchange reaction between dormant chain and growing radicals in comparison with propagation.[19, 20] Particle-size measurements were made using light scattering and capillary hydrodynamic fractionation techniques. Results indicate that the diameter of the majority (>90%) of the latex particles was approximately 55 nm.

Screening of Chain-Transfer Agents

Dithiocarboxylic esters are key species, which control the overall polymerization in the RAFT process.[15] Moreover, the introduction of functionalities on the CTA could lead to the synthesis of polymers with active functional groups at the chain end. Therefore, it is worthwhile to screen various functional dithiocarboxylic esters and diothiocarbamates for the polymerization of 4-acetoxystyrene under RAFT conditions. In this study, the synthesis of various dithiocarboxylic esters and diothiocarbamates (Figure 3) was undertaken and the resulting CTAs were subjected to the RAFT polymerization of 4-acetoxystyrene in order to prepare well-defined functional polymers. All polymerizations were carried out under similar reaction conditions for 8 h. It can be seen from Table 1 that the activity of all CTAs was found to be quite similar except the *N*-containing dithio compounds. Broader polydispersity was observed for the CTAs of type **10** and **11**, although these two have excellent homolytic leaving groups attached to the sulfur atom. For these CTAs the delocalization of the non-bonded electron pair on the nitrogen atom attached to the thiocarbonyl group may lower the reactivity of the carbon-sulfur double bond, thus inhibiting the addition of propagating radicals to the
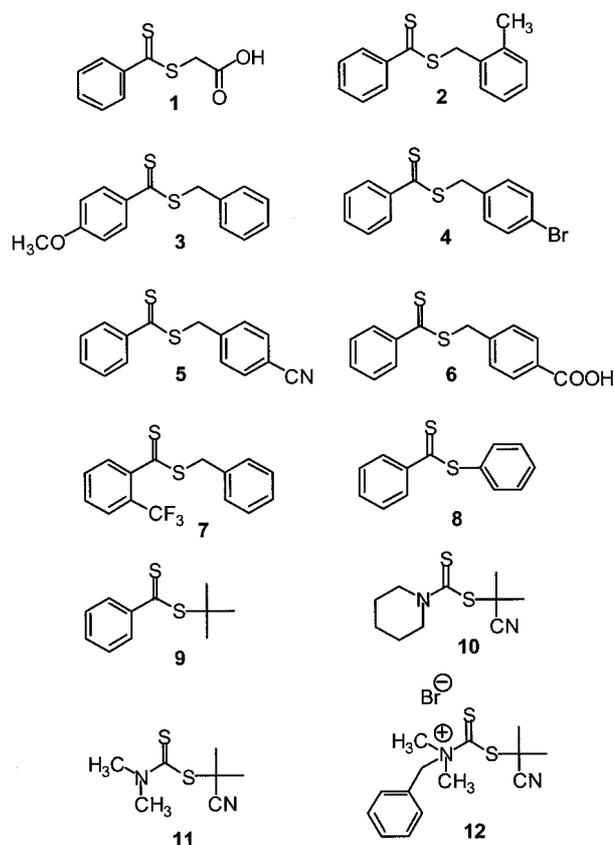
Figure 3. Chain-transfer agents (CTAs) used for the RAFT polymerization of 4-acetoxystyrene.

Table 1. Screening of various dithio chain-transfer agents for the living radical polymerization of 4-acetoxystyrene; [4-acetoxystyrene]/[CTA]/[AIBN] $\approx$ 100:1:0.2; reaction temperature: 90 °C; reaction time: 8 h.

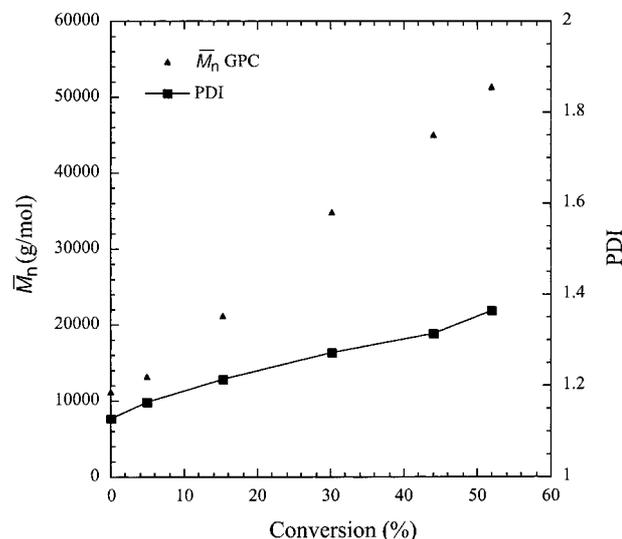| CTA	Conversion	$\overline{M}_n$ (GPC)	$\overline{M}_n$ (calculated)	PDI
	%	g/mol	g/mol	
1	40.2	6626	6525	1.12
2	36.5	6510	5924	1.18
3	38.9	4052	5147	1.12
4	29.1	4956	4183	1.08
5	31.4	6310	5696	1.23
6	29.7	4501	4320	1.18
7	45.5	9828	9690	1.14
8	39.5	2155	2550	1.23
9	19.1	2705	3080	1.20
10	31.4	6310	5096	1.69
11	29.7	4501	4820	1.84
12	41.3	10240	8560	1.35

Figure 4. Block copolymerization of poly(4-acetoxystyrene) and styrene in the presence of AIBN at 90 °C; final reaction time, 6 h.

sulfur atom.[15, 34–36] In order to modify the electronic nature of the nitrogen atom, CTA **11** was quarternized to produce CTA **12**, which was found to be more effective in controlling the polymer chain ($\overline{M}_n$ = 10 240 and PDI = 1.35). Further work on related compounds is in progress.

Block Copolymerization

The poly(4-acetoxystyrene) prepared in bulk using the RAFT process was used as a macromonomer for copolymerization studies after purification by re-precipitation and the removal of residual monomer. Styrene was used as a second monomer in this study. The block copolymerization was carried out in bulk at 90 °C in the presence and absence of AIBN. The clear solution becomes more viscous with time and eventually solidifies. The polymerization of the purified poly(4-acetoxystyrene) ($\overline{M}_n$ = 10 000, PDI = 1.12) with styrene in the presence of AIBN (Figure 4) proceeded fast (6 h) affording the corresponding block copolymer ($\overline{M}_n$ = 51 300, PDI = 1.39) with 53% conversion of the second monomer. The number-average molecular weight increased linearly with conversion as compared to the value of 10 000 for the macroinitiator. However, the rate of polymerization of such a system in the absence of AIBN was found to be slow ($\overline{M}_n$ = 11 100, PDI = 1.12 in 24 h). It had been reported previously that

initiator (AIBN) was added in block polymerizations under RAFT conditions to afford block copolymers with narrow PDI.[14]

Deacylation of Homo and Block Copolymers

The transformation of the acetoxy groups in poly(4-acetoxystyrene) and poly(4-acetoxystyrene)-*block*-polystyrene to give hydroxy polymers was carried out in a basic methanol/water mixture according to the procedure given by Barclay et al.[23] The polymer before and after hydrolysis was characterized by means of GPC, IR and 1H NMR spectroscopy. The polydispersity of the hydroxy polymer was found to be slightly broader (1.45) than that of the acetoxy polymer (1.12) as was observed by Barclay et al. This could be due to chain-end recombination or other side reactions under the deblocking conditions. The dis-

appearance of the strong band for the acetoxy carbonyl absorption at 1764 cm^{-1} in the IR and the disappearance of the intense signal at 2.3 ppm for the acetyl protons of homo and block copolymers in the ^{1}H NMR spectra confirmed the removal of the acetyl groups.

Conclusions

In this paper we have systematically studied the synthesis of well-defined poly(4-acetoxystyrene) in bulk, solution and emulsion using the RAFT polymerization process. Various functional CTAs were prepared and found to be effective for the synthesis of well-defined polymers. Bulk polymerization afforded polymers with narrower polydispersity than under solution or emulsion conditions. Block copolymerization could be easily achieved applying the RAFT procedure indicating the active nature of the chain end. Poly(4-acetoxystyrene) and poly(4-acetoxystyrene)-*block*-polystyrene were hydrolyzed under mild basic conditions to give poly(4-hydroxystyrene) and poly(4-hydroxystyrene)-*block*-polystyrene, respectively, with narrow polydispersities.

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