

Monodisperse, Micron-Sized Reactive Low Molar Mass Polymer Microspheres by Two-Stage Living Radical Dispersion Polymerization of Styrene

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ABSTRACT: Living/controlled radical dispersion polymerization of styrene was carried out in ethanol and in ethanol–water mixtures in the presence of perfluorohexyl iodide ($C_6F_{13}I$, 2–5 wt % based on styrene) as a degenerative chain transfer (DCT) agent or 1-cyano-1-methylpropyl dithiobenzoate (CMPDB, 0.5 and 1.0 mol % based on styrene) as a reversible addition–fragmentation chain transfer (RAFT) agent. These reagents disrupt the nucleation stage of particle formation when present at the start of the reaction. If their addition is delayed until the nucleation stage is complete, the reaction acquires the characteristics of a living/controlled radical polymerization: M_n increases linearly with the monomer conversion, and the molar mass distribution is much narrower (minimal M_w/M_n : 1.2) than polystyrene prepared without $C_6F_{13}I$ or CMPDB. For reactions in ethanol, at low molar mass, the particles formed have a broad size distribution as a consequence of the solubility of the polymer at the reaction temperature, followed by precipitation upon cooling. When the reactions were run in a more polar medium (95 wt % aqueous ethanol), the polymer molecules precipitated as they were formed and were absorbed by the existing particles in the solution. The particles formed had an average diameter in the range 1–3 μm with a very narrow size distribution ($CV < 1\%$). The polymer chains in these particles are reactive and chain-extendible.

Introduction

Over the past 25 years there has been a strong interest in the synthesis of polymer particles with micrometer dimensions and a narrow size distribution. These types of particles are used as spacers in liquid crystal displays and as carriers in biodiagnostic applications. Several research groups have described the preparation of micron-sized polymer particles by a stepwise seeded swelling polymerization procedure in which a swelling step by monomer is an essential feature of forming large particles.^{1–3} The monodisperse seed particles they used are typically sub-micron in diameter and are prepared by emulsion polymerization. In addition, the many subtle features of this approach to particle synthesis limit the scope and scale of these reactions. Dispersion polymerization represents an alternative approach to the synthesis of micrometer-sized particles.^{4,5} The reaction can be carried out in one pot, and is easily scalable, but has other disadvantages. While the particles obtained are often characterized by a very narrow size distribution, there are problems with batch-to-batch control over particle diameter. Until recently, it has been also difficult to prepare functional or cross-linked particles by this route.

In principle, it should be possible to combine these techniques, to use dispersion polymerization to prepare monodisperse seed particles with diameters larger than 1 μm that could be grown to a much larger size via a suspension polymerization in water. This would work best if the particles prepared as the seed contained only low molar mass polymer, so that it could be effectively swollen by the monomer added to the seed particles in water. This approach might be even more attractive if the polymer in the seed particles were synthesized by a living/controlled polymerization reaction so that the chains in the seed could be extended and incorporated into the final polymer as the particle size increased.

This goal remains elusive and has to be approached in several steps. One can imagine using chain transfer agents to reduce the molar mass of the seed particles. The chain transfer agent (CTA) serves the dual role of terminating growing chains and subsequently initiating new chains. The choice of a chain transfer agent in a given reaction depends on a balance between the transfer rate of the CTA and the propagation rate of the monomer. For optimum chain transfer agents, these two rates should be similar, and the chain transfer constant has a value near unity.

While many groups have investigated the use of chain transfer agents in solution polymerization and emulsion polymerization,^{6–8} there have been fewer studies of chain transfer in dispersion polymerization. We know of only two publications that examined these reagents in any detail.^{9,10} Both report problems related to the presence of a chain transfer agent in the reaction. For example, in the dispersion polymerization of styrene in ethanol,⁴ micron-sized monodisperse particles are obtained when no CTA is present. However when even small amounts of a chain transfer agent such as carbon tetrabromide (CBr_4)¹⁰ were added to the reaction, many attractive features of the reaction disappeared. The polymerization rate decreased, and the particle size distribution broadened considerably. In the presence of 0.36 wt % butanethiol chain transfer agent, polydisperse particles were obtained. The GPC chromatograms of these particles contained several broad peaks, and the ratio M_w/M_n was around 100.⁹

We recently discovered that many of the problems associated with dispersion polymerization could be overcome if one delayed the addition of problematic reagents until the nucleation stage was complete, and the particle number in the reaction became constant. We called this methodology “two-stage” dispersion polymerization.¹¹ The fundamental hypothesis was that the nucleation stage in dispersion polymerization reactions is short-lived but very sensitive to perturbation, whereas the particle growth stage is more robust. In this way, for dispersion

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copolymerization of styrene in ethanol, we were able to prepare monodisperse PS particles containing a covalently bound fluorescent dye,¹² PS particles cross-linked with ethylene glycol dimethacrylate (EGDMA) or divinylbenzene (DVB),¹³ and carboxylic acid-functionalized PS particles.¹⁴ The same approach works for CBr₄ as a chain transfer agent to lower the molar mass of polystyrene, and one obtains particles of the same size and narrow particle size distribution with or without chain transfer agent if one delays adding the CBr₄ until the reaction turns turbid.¹⁵

These kinds of low molar mass PS particles have several disadvantages as seed particles for further seeded polymerization. One disadvantage is that PS chains in seed particles may be incompatible (or immiscible) with the polymer produced by polymerization of the second monomer used to swell the seeds. Phase separation may occur in the resulting particles; non-spherical particles may form, and coagulation may occur. Another disadvantage is that these PS oligomers are not chain-extendible or cross-linked when cross-linked particles are needed. It is a difficult, time-consuming, and high-cost process to remove these oligomers from the final particles.

It is well-known that living/controlled radical polymerization is a useful technique for a preparation of chain-extendible polymers. The different methods that lead to controlled radical polymerization are based on either a reversible termination (mainly nitroxide-mediated radical polymerization¹⁶ and atom transfer radical polymerization¹⁷) or a reversible chain transfer reaction.^{18,19} In the case of reversible transfer, the activation process is based on a bimolecular reaction between an active macromolecule and a dormant one, leading to the exchange of the ω -end group. It can be a direct exchange as in the so-called degenerative chain transfer (DCT) technique where an iodine atom is exchanged.¹⁸ Another more recent approach is reversible addition–fragmentation chain transfer (RAFT),¹⁹ in which case chains are end-functionalized by a dithioester or trithiocarbonate that is exchanged via an addition–fragmentation process. In such systems, a conventional radical initiator is needed together with the specific transfer agent, and a great advantage of the reversible transfer technique is that the experimental conditions can be very close to conventional ones, in terms of temperature, monomer concentration, and reaction process.

In recent years, several research groups have explored the possibility of using living/controlled polymerization techniques in dispersion polymerization. Mülhaupt and co-workers²⁰ reported using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-mediated radical chemistry for the attempted dispersion polymerization of styrene in *n*-decane at 135 °C using a “Kraton” stabilizer. SEM images revealed a very broad particle size distribution (50 nm–10 μ m). Armes and co-workers²¹ reported living radical chemistry with TEMPO in both alcoholic and aqueous alcoholic media using poly(*N*-vinylpyrrolidone) (PVP) as a steric stabilizer at 112–130 °C. The addition of TEMPO had a profound effect on the polymerization chemistry: only moderate monomer conversions and only relatively low molar mass polystyrene chains were obtained. All TEMPO-synthesized latexes had spherical particle morphologies and very broad size distributions. Choe’s group in Korea described experiments involving dispersion photopolymerization of styrene plus poly-(*N*-vinylpyrrolidone) stabilizer in ethanol in the presence of a RAFT agent.²² They varied the amount of the RAFT agent, in both the absence and presence of a conventional initiator, azobis(isobutyronitrile) (AIBN), at various temperatures. Both the molar mass distribution and the particle size distribution were very broad. Conducting living or controlled radical polymeri-

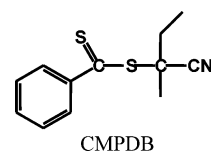
zation via dispersion polymerization has remained a challenge.

In this work, we present our results of a study of the controlled radical dispersion polymerization of styrene in the presence of chain transfer agents. One set of experiments employed perfluorohexyl iodide (C₆F₁₃I) as a degenerative chain transfer (DCT) agent. The second set of experiments use 1-cyano-1-methylpropyl dithiobenzoate (CMPDB) as a RAFT agent. Other groups have obtained interesting results with the C₆F₁₃I system, both for bulk polymerizations¹⁸ and for miniemulsion polymerization.²³ CMPDB was used as the RAFT agent to mimic the structure of the initiator 2, 2′-azobis(2-methylbutyronitrile) (AMBN). Using the two-stage dispersion polymerization strategy, we obtained monodisperse, micron-sized PS particles consisting of chain-extendible low molar mass polymer.

Experimental Section

Reagents. All organic reagents were used without further purification, including styrene (Aldrich), methanol, ethanol, poly(vinylpyrrolidone) (PVP, M_w = 55 000 g/mol, Aldrich), Triton X-305 (70% solution in water, Aldrich), 2,2′-azobis(2-methylbutyronitrile) (AMBN, Wako Pure Chemical Industries Ltd.), perfluorohexyl iodide (C₆F₁₃I, 99%, Aldrich), and phenylmagnesium bromide (1 N in THF, Aldrich).

Synthesis of RAFT Agent CMPDB. CMPDB was prepared according to the method described in Patent WO9905099. A



solution of 0.03 mol of phenylmagnesium bromide in 30 mL of anhydrous THF was added to a 150 mL flask. Carbon disulfide (2.28 g, 0.03 mol) was added to the solution at room temperature slowly, and the reaction was allowed to stir magnetically at room temperature overnight. Then the mixture was poured into water and acidified with dilute hydrochloric acid. The solution was extracted with chloroform (20 mL \times 3). After the solvent was removed on a rotary evaporator, crude dithiobenzoic acid was obtained, and it was used directly in the following step. The purity of the crude dithiobenzoic acid is high (¹H NMR, CDCl₃, 300 MHz, δ : 8.0–8.1 ppm (d, 2H, C₆H₄), δ 7.54–7.62 ppm (m, 1H, C₆H₄), δ 7.35–7.43 ppm (m, 2H, C₆H₄), δ 6.3–6.5 ppm (s, 1H, SH)).

Crude dithiobenzoic acid (4.9 g, 0.032 mol) was added to ethyl acetate (20 g) and treated with dimethyl sulfoxide (DMSO, 1.4 g, 0.018 mol) under nitrogen protection for 7 h at room temperature. To this solution AMBN (4.6 g, 0.024 mol) was added, and the mixture was heated at 80 °C for 16 h. After evaporating the solvent, crude CMPDB was obtained. The pure CMPDB was obtained as a dark red oil by chromatography on a silica gel column with hexane: ether = 9:1 as the eluent. (¹H NMR, CDCl₃, 300 MHz, δ : 7.85–7.93 ppm (d, 2H, C₆H₄), δ 7.50–7.60 ppm (m, 1H, C₆H₄), δ 7.30–7.40 ppm (m, 2H, C₆H₄), δ 2.0–2.4 ppm (m, 2H, –CH₂–) δ 1.90–1.93 ppm (s, 3H, –CH₃) δ 1.18–1.24 ppm (m, 3H, –CH₃ in –CH₂CH₃). The yield is about 50% and the purity is about 96%.

One-Stage Dispersion Polymerization. The standard recipe for the dispersion copolymerization of styrene with C₆F₁₃I in ethanol is listed in Table 1. The following procedure was used: All the ingredients were added to a 250 mL three-neck reaction flask equipped with a condenser and a gas inlet. After a homogeneous solution was formed at room temperature, the solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. Then the flask was placed in a 70 °C oil bath and stirred mechanically at 100 rpm. The monomer conversion was determined gravimetrically by removing aliquots during the polymerization.

Two-Stage Batch Dispersion Polymerization. The standard recipe for the two-stage dispersion copolymerization of styrene with C₆F₁₃I in ethanol is listed in Table 1. The following procedure was

Table 1. Standard Recipe for the Dispersion Polymerization of Styrene with Degenerative Transfer Agent in Ethanol (Amounts in grams)

materials		one-stage	two-stage	
			1st stage	2nd stage
monomer	styrene	6.25	6.25	6.25
DCT agent	C ₆ F ₁₃ I	0.125		0.25
medium	ethanol	18.75	18.75	18.75
stabilizer	PVP	1.0	1.0	
costabilizer	Triton X-305	0.35	0.35	
initiator	AMBN	0.25	0.25	

used: All of the stabilizer (PVP), the co-stabilizer (Triton X-305) and initiator (AMBN), and half of the monomer and ethanol were added to a 250 mL three-neck reaction flask equipped with a condenser and a gas inlet. After a homogeneous solution formed at room temperature, the solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min. Then the flask was placed in a 70 °C oil bath and stirred mechanically at 100 rpm. The C₆F₁₃I or CMPDB was dissolved in the remaining styrene plus ethanol at 70 °C under nitrogen. After the C₆F₁₃I or CMPDB had dissolved and the polymerization reaction had run for 1 h, the hot C₆F₁₃I or CMPDB solution was added into the reaction flask. Aliquots were taken at different reaction times for GPC, SEM, and conversion measurements.

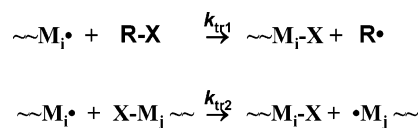
Characterization of Particles. The particle size was examined by both optical microscopy (Olympus, X41) and scanning electron microscopy (SEM, Hitachi S-5200). To prepare samples for optical microscopy, the final polymer particle suspension was diluted with water, and a drop was placed on a clean glass microscope slide. SEM samples were prepared with a drop of diluted suspension on a mica film. The particle size and size distributions were examined by SEM. A particle size histogram was constructed from measurements of 200–300 individual particles in the electron micrographs.

The molar mass and molar mass distributions of the constituent polymers were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) using polystyrene calibration standards with molar mass ranging from 600 to 411 000. GPC measurements were performed on a Waters liquid chromatograph equipped with a Waters 480 R410 differential refractometer (RI) detector. The polymer samples for GPC analysis were prepared as follows: The particles were centrifuged at 2000 rpm for 10 min. The precipitated particles were redispersed into fresh ethanol/water (95/5, w/w) and centrifuged again. This process was repeated four times. After the particles were dried, they were dissolved in THF, and the solution was passed through a 0.45 μm filter before injecting it into the GPC column. The ¹H NMR spectra were recorded in CDCl₃ solutions by using a Mercury 300 MHz. Chemical shifts are reported in ppm, downfield of internal TMS, and are referred to as s (singlet), d (doublet), and m (multiplet).

Results and Discussion

Both RAFT and DCT are living radical polymerization systems based on a reversible transfer mechanism. The reversible reaction is between a dormant chain and an active radical, in which an end group originating from the transfer agent is exchanged between the two chains. With DCT, there is a direct exchange involving, for example, an iodine atom. With RAFT, an addition–fragmentation process is used to exchange a moiety such as a dithioester between the two chains. With the reversible transfer mechanism, a conventional initiator is used to initiate the chains. The transfer agent is then consumed by the radicals originating from the initiator decomposition. The total number of chains in the system is the sum of the transfer agent and primary radical molecules.

Before comparing DCT and RAFT reactions of styrene in dispersion polymerization, we will review briefly important concepts about chain transfer processes. The chain transfer step of both DCT and RAFT reactions can be described by the

Chart 1

reaction in Chart 1, where k_{tr} is the second-order rate constant for transfer. Here R–X represents the DCT or RAFT agent, $\sim\text{M}_i\cdot$ refers to a propagating chain consisting of M_i monomers, and $\sim\text{M}_j\text{-X}$ is a dormant chain bound to the entity subject to transfer. For normal chain transfer agents in uncontrolled free radical polymerization and for DCT and RAFT agents at low monomer conversion, the decrease in number-averaged chain length is described by the Mayo equation

$$\frac{1}{x_n} = \frac{1}{(x_n)_0} + C_{tr} \frac{[\text{CTA}]}{[\text{M}]} \quad (1)$$

where x_n is the number-averaged degree of polymerization, and the subscript 0 refers to the reaction in the absence of CTA. [CTA] is the concentration of chain transfer agent, [M] is the monomer concentration, and C_{tr} , the chain transfer constant, is the ratio of k_{tr} to the propagation rate constant k_p .

During a reversible chain transfer reaction mechanism, two chain transfer constants should be considered. The first one (C_{tr1}) describes the consumption of the chain transfer agent and controls the increase in molar mass vs monomer conversion. The second one (C_{tr2}) describes the degenerative exchange reaction between an active chain and a dormant one and affects the polydispersity index ($M_w/M_n = 1 + 1/C_{tr2}$ at 100% conversion).²⁴ For C₆F₁₃I and styrene, a value of $C_{tr1} = 1.4$ and a value $C_{tr2} = 3.8$ were reported by Goto et al.²⁵ For the RAFT agent CMPDB and styrene, both C_{tr1} and C_{tr2} were larger than 20.¹⁹

One of the main objectives in a living reversible transfer reaction is a linear increase in M_n or x_n with increasing conversion. The living nature of chain propagation is enhanced by early consumption of the transfer agent; thus, C_{tr1} should have a value much larger than unity. In addition, there should be a large excess of transfer agent to initiator.

In a dispersion polymerization, the monomer, polymeric stabilizer, initiator, and solvent constitute the initial reaction mixture. The reaction begins as a homogeneous solution polymerization, and grafting to the stabilizer chain competes with homopolymerization. The homopolymer chains grow in size until they become insoluble in the reaction medium. The solubility of these polymers is a function of their molar mass, composition, the reaction temperature, and the composition of the reaction medium. A polymer with a molar mass larger than a certain critical value ($M > M_{crit}$) precipitates and aggregates to form colloiddally unstable precursor particles (nuclei). These nuclei coalesce and adsorb stabilizers from the medium onto their surface until they become colloiddally stable. At this point, particle nucleation ceases. Once the total number of particles in the system is fixed, the nucleation stage of the reaction is over. Once the nucleation stage is complete, polymerization initiated in the continuous phase leads to growing radicals that are eventually captured by existing particles. As these particles grow in size, polymerization occurs predominantly within these particles.

The addition of chain transfer agents decreases the molar mass of the polymer formed in the reaction. As we will see below, the lower molar mass has two consequences. First, it delays the nucleation stage, leading to a loss of control over particle

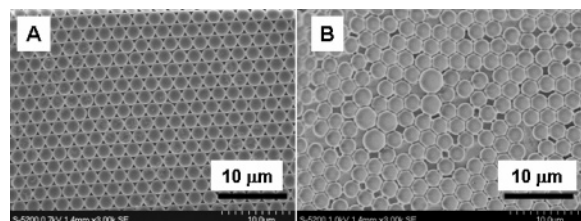


Figure 1. SEM images of PS particles prepared by conventional dispersion polymerization in ethanol: (A) without any $C_6F_{13}I$, (B) with 2 wt % of $C_6F_{13}I$.

size distribution. This problem can be overcome by delaying the addition of the chain transfer agent until after the nucleation stage is complete. The second effect is that chains produced in the reaction with $M < M_{crit}$ remain soluble in the medium and only precipitate when the reaction is cooled. This also results in a broad particle size distribution as new particles are formed in this precipitation step. This problem can largely be overcome for polystyrene by employing ethanol–water mixtures as the reaction medium to reduce the value of M_{crit} . As in our previous report on CBr_4 as a chain transfer agent,¹⁵ we find much better control over particle size distribution for reactions run in 95/5 w/w ethanol/water than in ethanol itself.

$C_6F_{13}I$ as a Degenerative Chain Transfer Agent. $C_6F_{13}I$ is a degenerative chain transfer agent for radical polymerization of styrene, with a value of $C_{tr} = 1.4$.²³ The transfer process takes place in two successive steps. The first is the conventional transfer to the chain transfer agent $C_6F_{13}I$, producing new chains with a perfluorohexyl group at one end and an iodine atom at the other end ($X = I$ in Chart 1). The second step is the transfer of the iodine atom from an end-functionalized chain to a propagating macroradical, which is a thermodynamically neutral exchange process. As shown in Chart 1, this second step does not create new chains but contributes to the extension of the existing chains. In this work, $C_6F_{13}I$ was used in radical dispersion polymerization of styrene in ethanol and in ethanol–water mixtures.

Reactions in Ethanol. We compared two different dispersion polymerization strategies. First we carried out traditional (one-stage) dispersion polymerization reactions of styrene in which all of the ingredients were present at the beginning of the reaction.²⁶ Figure 1A,B shows the SEM images of PS particles prepared by this method. The recipe is given in Table 1. In the absence of $C_6F_{13}I$, the resulting particles were monodisperse and spherical (Figure 1A, O-1 in Table 2). In the presence of 2 wt % of $C_6F_{13}I$, the average diameter of PS particles increased and the particle size distribution was broader (Figure 1B, O-2 in Table 2). These results are similar to those of Ahmad and

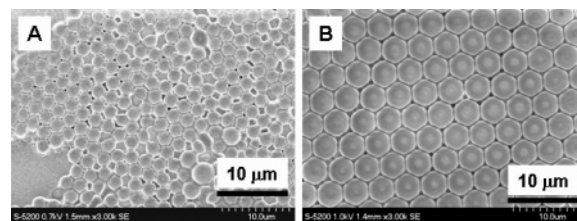


Figure 2. SEM images of PS particles prepared in ethanol by the two-stage method with 2 wt % $C_6F_{13}I$ (based on total styrene) at different reaction times: (A) 3 and (B) 24 h.

Tauer,¹⁰ who obtained polydisperse PS particles using only 0.5 wt % CBr_4 as a chain transfer agent.

We found that when 2 wt % $C_6F_{13}I$ was present at the beginning of the reaction, the nucleation stage, as inferred from the onset of turbidity, became much longer, increasing from less than 10 min to more than 15 min. It should be noted that under our preferred reaction conditions the initiator was added at room temperature, and the solution needed more than 5 min to reach 70 °C. As we mentioned above, a CT agent, such as $C_6F_{13}I$, present at the beginning of a dispersion polymerization reaction, leads to a significant fraction of chains with $M < M_{crit}$. This delays the onset of nucleation and broadens the particle size distribution.

In our two-stage dispersion polymerization strategy, we defer the addition of the problematic reagents like CT agents until the nucleation stage is complete. Yasuda et al.²⁷ showed that the nucleation stage for dispersion polymerization of styrene in ethanol is complete at less than 1% of conversion. We often take the onset of turbidity in a reaction as the signature of the end of the nucleation stage but sometimes wait, as we do here, for 1 h after the beginning of the reaction to add the CT agent. This corresponds to ~5% monomer conversion.

Figure 2 shows the results of a reaction in which 2 wt % of $C_6F_{13}I$ (based upon total styrene) mixed with styrene and ethanol was added 1 h after the start of polymerization. Aliquots were taken from the reaction flask at different polymerization times. Surprisingly, at low monomer conversion, polydisperse particles were formed (Figure 2A, 3 h, 13% conversion). As the reaction continued, the particle size distribution narrowed considerably (Figure 2B, T-1 in Table 2, 24 h, 90% conversion). Some particles at 13% conversion appeared nonspherical in SEM images, probably as a result of evaporation of unreacted monomer during drying. The unreacted monomer is also likely to soften the particles, leading to particle deformation when these particles come in contact with each other. A similar result for 5 wt % $C_6F_{13}I$ in ethanol (T-2 in Table 2) is presented in the Supporting Information. The resulting PS particles at 13%

Table 2. Effect of $C_6F_{13}I$ or CMPDB on the Molar Mass, Molar Mass Distribution, the Particle Size, and Size Distribution

no.	$C_6F_{13}I$ wt %	$D_{av},^a \mu m$	$CV,^b \%$	\overline{M}^{exp}	PDI	$\overline{M}_{n,cal}$ At 100% conv ^f	method	medium
O-1	0	2.0	<1	21 200	3.65		one-stage	ethanol
O-2	2	2.5	8			23 300	one-stage	ethanol
T-1	2	3.3	<3	16 000	2.19	23 300	two-stage	ethanol
				90% ^e				
T-2	5	3.3	5.0	10 670	1.84	9300	two-stage	ethanol
				95% ^e				
T-4 ^c	5	2.7	<2	11 240	2.04	9290	two-stage	ethanol/water
				95% ^e				
T-5 ^c	1.0 ^d	2.0	<3	4000	1.49	10 400	two-stage	ethanol/water
				40% ^e				
T-6 ^c	0.5 ^d	2.0	<2	12 900	2.30	20 900	two-stage	ethanol/water
				50% ^e				

^a D_{av} : the average diameter of the particles. ^b $CV = 1/n \sum_{i=1}^n (|D_i - D_{av}|/D_{av})$. ^c Ethanol/water (95/5, wt/wt) was used as the reaction medium in the first stage, and $C_6F_{13}I$ mixed with styrene and ethanol/water (95/5, wt/wt) was added batch-wise 1 h after the start of polymerization. ^d CMPDB, mol % based on styrene. ^e Monomer conversion of this sample. ^f Theoretical value of M_n , calculated as $10^4([M]_0/[C_6F_{13}I]_0)$.

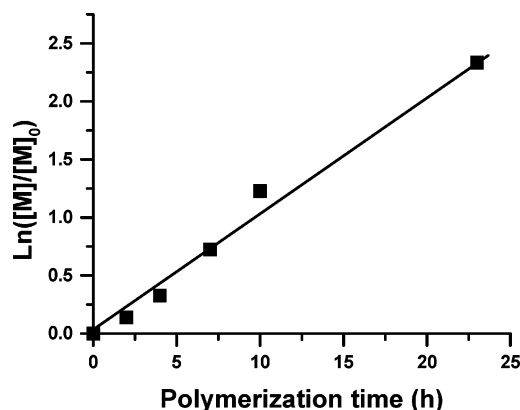


Figure 3. Plot of $\ln([M]/[M]_0)$ vs time for the two-stage dispersion polymerization of styrene in ethanol in the presence of 2 wt % $C_6F_{13}I$ (based on total styrene).

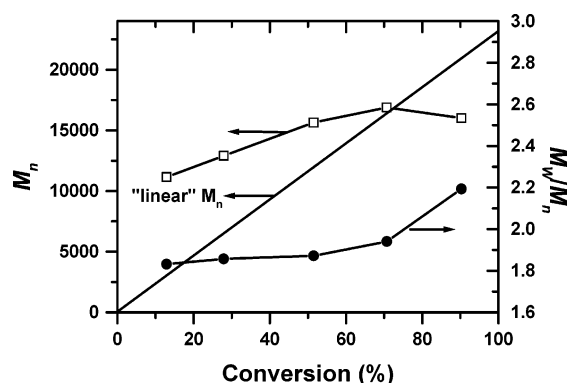


Figure 4. Number-average molar mass and molar mass distribution vs monomer conversion for the two-stage dispersion polymerization of styrene in ethanol in the presence of 2 wt % of $C_6F_{13}I$. Linear $M_n = \text{conversion} \times 10^4([M]_0/[C_6F_{13}I]_0)$.

conversion exhibited a very broad size distribution (Figure S1A). The resulting PS particles at 90% of conversion were relatively uniform in size (Figure S1B), but a small fraction of smaller and larger particles could be seen in some SEM images.

Information about the reaction kinetics is presented in Figure 3, where we show that the plot of $\ln([M]/[M]_0)$ vs time is linear. At the very beginning of the reaction, the polymerization rate is slower due to the solution polymerization mechanism. GPC traces show that the sample at 13% conversion had $M_n = 11\,000$, slightly lower than the critical molar mass in ethanol at 70 °C (12 000),²⁷ and the sample at 90% conversion had $M_n = 16\,000$. A similar result was also obtained for 5 wt % $C_6F_{13}I$ in ethanol.

The indication of the controlled nature of the polymerization in the presence of $C_6F_{13}I$ is the linear increase of M_n with monomer conversion up to about 50% conversion, as shown in Figure 4. For this reaction, M_w/M_n values (ca. 1.8) were much narrower than those obtained without $C_6F_{13}I$ ($M_w/M_n > 3.0$) but much broader than those obtained by ideal living polymerization systems due to the relatively low value of the chain transfer constant.

Tests of the reaction without any $C_6F_{13}I$ present indicated that monodisperse seed particles were formed in-situ in less than 15 min. We infer that low molar mass polymer was formed in the reaction in the presence of $C_6F_{13}I$ and that much of this polymer remained in solution at 70 °C. This polymer precipitated when the reaction was cooled, forming new particles in an uncontrolled fashion. Because these PS chains each have an iodine atom at one end, these chains can be extended gradually to higher molar mass at higher conversions. Once the molar

mass of these PS chains exceeds M_{crit} , they should be captured by the existing seed particles. At high conversion, there was nearly no free oligomer dissolved in ethanol at 70 °C. Therefore, no new particles formed upon cooling, and monodisperse particles were obtained. When larger amounts of $C_6F_{13}I$ were employed, more polymer chains with $M < M_{crit}$ were produced. The size distribution of the resulting particles was also very broad.

Reactions in Ethanol–Water Mixtures. To reduce the solubility of PS to promote precipitation of PS oligomers onto existing PS particles, we ran reactions in a more polar reaction medium. A number of authors have shown that dispersion polymerization of styrene can be run in water–ethanol mixtures.^{9,15,28} The overall influence of adding a small amount of water to the traditional one-stage dispersion polymerization reaction is to decrease particle size while maintaining the narrow size distribution.⁹ This approach provides one strategy to decrease the critical molar mass of the growing polymer.

We investigated whether this change of reaction medium, incorporated into the two-stage method, would maintain the narrow particle size distribution and at the same time permit the use of large quantities of the DCT agent. We carried out a series of reactions in an ethanol/water (95/5 w/w) medium with different amounts of $C_6F_{13}I$. When $C_6F_{13}I$ (5 wt % based on total styrene) mixed with styrene and ethanol/water (95/5) was added 1 h after the start of the reaction, monodisperse PS particles were obtained (Figure S2D in the Supporting Information). It appears that as long as the system is kept above the critical molar mass for the polymer, the two stage method is effective at producing particles with a narrow size distribution.

In the Supporting Information, we present a plot (Figure S3) of $\ln([M]/[M]_0)$ vs time for the second stage of a reaction in ethanol–water (95/5) in the presence of 5 wt % $C_6F_{13}I$. This result is very similar to that for the two-stage reaction in pure ethanol in the presence of 2 wt % $C_6F_{13}I$ and indicates that this amount of $C_6F_{13}I$ has no evident effect on the styrene polymerization rate for the two-stage method. GPC chromatograms (Figure S4 in the Supporting Information) and the M_n vs conversion curve (Figure S5) show that M_n increases linearly with conversion. The M_w/M_n values are also much narrower than that for PS prepared without $C_6F_{13}I$. The observed shift of the GPC peak between 13% monomer conversion ($M_n = 7690$, $M_w/M_n = 2.10$) and 77% ($M_n = 12\,030$, $M_w/M_n = 1.78$) together with the decrease of M_w/M_n is a good indication that a chain extension process has occurred as expected when a degenerative transfer reaction takes place. Moreover, the theoretical molar mass was reached at the final conversion, indicating complete consumption of $C_6F_{13}I$. This result also implies that most chains have an iodine atom at the end and can be extended by the degenerative transfer reaction when a second load of monomer is added. We also note that the extrapolated value of M_n at low conversion is much smaller than in the case of 2 wt % $C_6F_{13}I$. In both reactions, the polymer chains produced by DCT agent remain “living” and chain-extendible.

At very high conversions (above 70%), M_n leveled off and M_w/M_n was broadened. For dispersion polymerization at high conversion, most of the $C_6F_{13}I$ was consumed, and most of the remaining monomer and initiator were dissolved in the continuous medium. Under these circumstances, there is not enough monomer within the particles for the polymer chains in the particles to grow. Uncontrolled radical polymerization in the medium dominated the reaction. To avoid this problem, it is necessary to stop the reaction below 70% conversion in order to keep most polymer chains in the particles living.

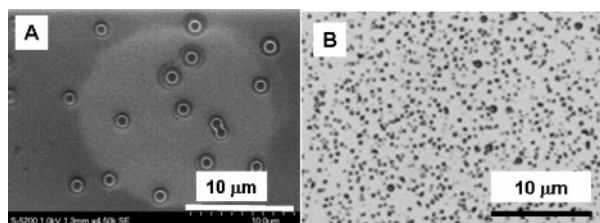


Figure 5. SEM (A) and optical microscopy (B) images of PS particles prepared by the two-stage controlled dispersion polymerization in ethanol–water mixture (95/5, wt/wt) at a conversion of 6% (St: CMPDB:AMBN = 200:2:1, mole ratio): (A) precipitated particles, (B) serum diluted with water.

Two-Stage RAFT Dispersion Polymerization. As in the case of DCT, the challenge is to achieve reaction conditions that yield living, extendible polymers while maintaining control over the size and size distribution of the polymer particles obtained. The chain transfer constant for RAFT is expected to be much larger than that for $C_6F_{13}I$. The magnitude of C_{tr} is estimated to be more than 20 for CMPDB as a RAFT agent for radical polymerization of styrene.^{19a} As a consequence, we anticipated that we would be able to achieve narrower molar mass polydispersities with RAFT dispersion polymerization than with DCT, with a theoretical polydispersity index of PS using CMPDB as a RAFT agent on the order of 1.05.

Dispersion polymerization reactions involving CMPDB as a RAFT agent were run in ethanol–water (95/5). This medium was used both for the nucleation stage in the absence of the RAFT agent and for the second stage. CMPDB was added along additional solvent and monomer 1 h after the start of the reaction. Samples were taken at different conversions, diluted with water, and examined by SEM and optical microscopy. We found that at low conversions the recovered PS particles were very polydisperse. To investigate what happened in this system, a sample was taken at a low conversion (6%), centrifuged to sediment the particles, and separated into a particle component and a transparent serum. The precipitated particles were redispersed into water to prevent any absorbed oligomer from diffusing into the medium. The homogeneous serum was diluted with water, and it immediately became milky due to the precipitation of dissolved oligomer.

Figure 5A shows the SEM image of the precipitated particles, indicating these particles are highly monodisperse. In this image, one can see an example of two particles that fused into a dimer particle as the sample dried on the grid. Particle fusion is likely promoted by the low molar mass of the polymer. Figure 5B shows an optical microscopy image of the diluted serum, indicating the formation of polydisperse particles due to the precipitation of the soluble low-molar-mass PS chains when water was added.

Figure 6 shows the GPC curves of the polymer in the precipitated particles and isolated from the serum at 6% conversion. There are two well-resolved peaks for the polymer obtained from the particles, a large and broad peak ($M_n = 16\,000$, $M_w/M_n = 2.4$) corresponding to the polymer formed in the absence of the RAFT agent (in the first stage), and another smaller, narrower peak ($M_n = 800$, $M_w/M_n = 1.15$) corresponding to the oligomers formed in the presence of the RAFT agent. There is only one main narrow peak ($M_n = 600$, $M_w/M_n = 1.20$) for the serum corresponding to the oligomers formed in the presence of the RAFT agent. Because the molar mass of these PS chains is far below the critical molar mass in the medium at the polymerization temperature, only a very small fraction of the oligomers were absorbed by the seed particles present in the reaction.

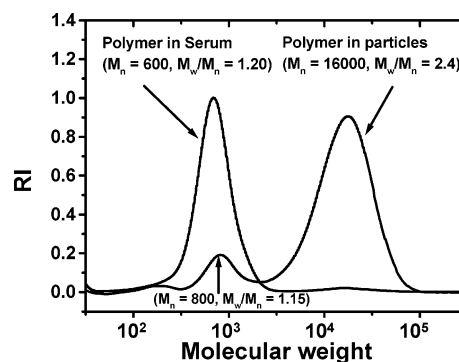


Figure 6. GPC chromatograms of PS in precipitated particles and serum at a low conversion (6%) for the two-stage method in ethanol–water mixture (95/5, w/w) (St: CMPDB:AMBN = 200:2:1, mole ratio).

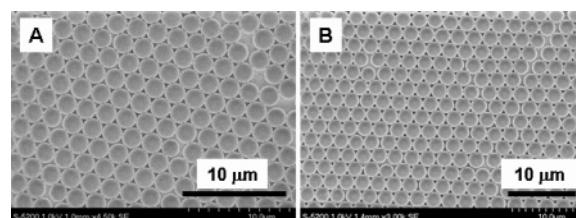


Figure 7. SEM images of PS particles prepared by the two-stage method in the presence of RAFT agent in ethanol–water mixture (95/5, w/w): (A) sample taken at the conversion of 40% (St: CMPDB:AMBN = 200:2:1, mole ratio); (B) sample taken at the conversion of 50% (St: CMPDB:AMBN = 200:1:0.75, mole ratio).

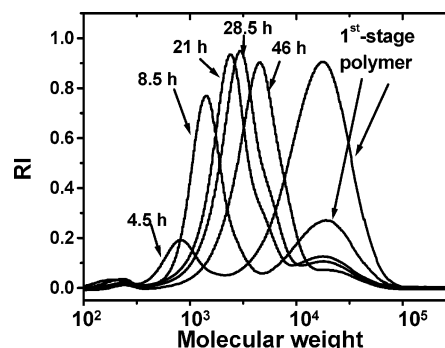


Figure 8. GPC chromatograms of PS particles prepared by the two-stage living dispersion polymerization in ethanol–water (95/5, w/w) at different reaction times (St: CMPDB:AMBN = 200:2:1, mole ratio) (4.5 h: $M_n = 800$, $M_w/M_n = 1.20$; 8.5 h: $M_n = 1300$, $M_w/M_n = 1.19$; 21 h: $M_n = 2200$, $M_w/M_n = 1.38$; 28.5 h: $M_n = 2700$, $M_w/M_n = 1.47$; 46 h: $M_n = 4000$, $M_w/M_n = 1.49$).

Figure 7A shows an SEM image of the particles at 40% conversion ($M_n = 4000$, $M_w/M_n = 1.5$), indicating these particles are nearly monodisperse. A small fraction of larger particles can be seen in other images of this sample. In a separate experiment, we examined the particles formed at 50% conversion (Figure 7B), when the molar mass of the PS chains ($M_n = 12\,900$, $M_w/M_n = 2.3$) was above the critical molar mass in the medium at the polymerization temperature. Here the particles are highly monodisperse. We infer that most or all of the polymer molecules in the system exceed their solubility and are captured by existing particles.

GPC curves for one reaction at different conversions are presented in Figure 8. As the polymerization proceeds, the PS chains grow longer. At low conversion, the peak due to polymer formed in the first stage in the absence of RAFT agent is prominent, but it becomes less significant as the reaction proceeds. The solubility of the PS chains decreases with increasing conversion for the PS formed in the second stage,

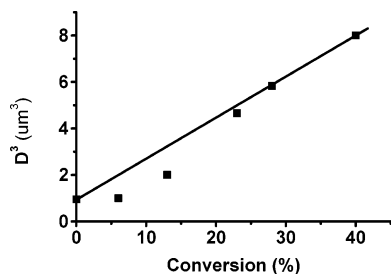


Figure 9. Volume of particles (D^3) vs monomer conversion for the two-stage method in ethanol–water mixture (95/5, w/w) (St:CMPPDB:AMBN = 200:2:1, mole ratio). The solid line is the theoretical plot of D^3 vs monomer conversion, and 0% conversion refers to the point at which the RAFT agent was added to the reaction.

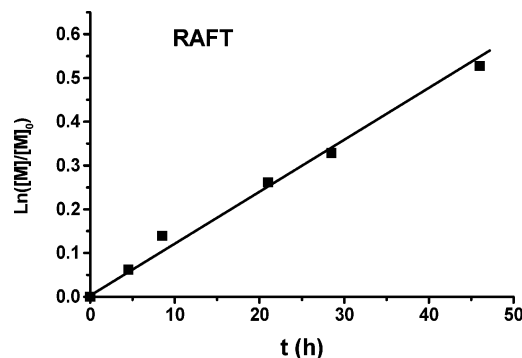


Figure 10. Plot of $\ln([M]/[M]_0)$ vs polymerization time for the two-stage living dispersion polymerization in ethanol–water mixture (95/5, w/w) (St:CMPPDB:AMBN = 200:2:1, mole ratio).

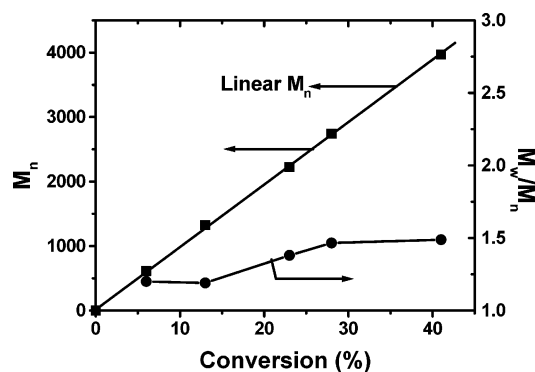


Figure 11. Number-average molar mass and molar mass distribution vs monomer conversion for the two-stage method in ethanol–water mixture (95/5, w/w) (St:CMPPDB:AMBN = 200:2:1, mole ratio). Linear M_n = conversion $\times 10^4([M]_0/[CMPPDB]_0)$.

and the fraction of the oligomer or polymer absorbed by the existing particles becomes larger. In Figure 9 we present a plot of D^3 (D is the mean particle diameter) as a function of monomer conversion. At late stages of the reaction, D^3 increases linearly with conversion. The fact that the particle volume at a low conversion is lower than predicted also indicates some oligomers are not absorbed by the existing seed particles.

As in the case of the DCT polymerization, the plot of $\ln([M]/[M]_0)$ vs polymerization time curve is linear (Figure 10) for the RAFT reaction. The data in Figure 11 show that M_n increases linearly with conversion and extrapolate to $M_n \approx 0$ at zero time. The M_w/M_n values are also much narrower than for the PS prepared without CMPPDB. All these features are characteristics of living radical polymerization and are consistent with a large value of C_{tr} .

Conclusion

Dispersion polymerization of styrene in ethanol in the presence of chain transfer agents leads to a substantial broadening of the particle size distribution and a delay in the onset of particle nucleation. If the addition of a DCT agent such as $C_6F_{13}I$ or a RAFT agent such as CMPPDB is delayed until the nucleation stage is complete and the CT agent is added with a mixture of additional monomer and solvent, one can obtain particles containing lower molar mass polymer, but with the same particle size and a similar narrow size distribution as in the case where no chain transfer agent is present. Other complications arise if the polymer molar mass is reduced below the critical value M_{crit} for precipitation from the medium at the reaction temperature. These problems may be overcome by adding small to modest amounts of water to the reaction medium to reduce the solubility of the polymer in the reaction medium.

The polymer chains formed in the presence of $C_6F_{13}I$ or CMPPDB are chain-extendible. M_n increased linearly with the increase of conversion. When the M_n of the polymer chains is above M_{crit} , they will be captured by the seed particles formed during the nucleation stage in the absence of the DCT or RAFT agent. Colloidally stable, monodisperse particles containing extendible polymer chains were prepared for both living radical polymerization systems.

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Supporting Information Available: Additional information about reactions in the presence of 5 wt % $C_6F_{13}I$: SEM images of particles prepared in ethanol and in ethanol–water, GPC plots as a function of reaction time, kinetic data and plots of M_n and M_w/M_n vs conversion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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