Nitroxide-Mediated Radical Dispersion Polymerization of Styrene in Supercritical Carbon Dioxide Using a Poly(dimethylsiloxane-*b*-methyl methacrylate) Stabilizer[†]

Ronan McHale,[‡] Fawaz Aldabbagh,*,[‡] Per B. Zetterlund,[§] Hideto Minami,[§,⊥] and Masayoshi Okubo*,[§,⊥]

Department of Chemistry, National University of Ireland, Galway, Ireland; Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Kobe 657-8501, Japan; and Graduate School of Science and Technology, Kobe University, Kobe 657-8501, Japan

Received May 22, 2006; Revised Manuscript Received July 24, 2006

ABSTRACT: Nitroxide-mediated controlled/living dispersion polymerization of styrene in supercritical carbon dioxide ($scCO_2$) has been performed successfully to high conversion using *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) and a poly(dimethylsiloxane-*b*-methyl methacrylate) stabilizer at 110 °C. The molecular weight distributions were narrow ($M_w/M_n = 1.12-1.43$), and the number-average molecular weight (M_n) values agreed well with theory. A large excess of free SG1 was required to obtain satisfactory control in the dispersion polymerization, possibly due to SG1 partitioning. The critical degree of polymerization at which the polymer precipitates (J_{crit}) was determined as 28 by visual observation using a novel approach. Polymerizations conducted in solution (toluene) proceeded at a similar rate (∼20% faster) to those in $scCO_2$. The number of chains increased with conversion in both dispersion and solution, with the greater increase being observed in the dispersion system.

Introduction

Dispersion polymerization is a versatile technique for preparation of polymer particles in the submicron and micron range.[1,2] Through utilization of a suitable solvent (solvent for the monomer but nonsolvent for the polymer) and an appropriate stabilizer, stable polymer dispersions can be readily obtained. The vast majority of research in this area has traditionally exploited organic solvents, from hydrocarbons such as the alkanes[3] to more polar alcoholic media.[4,5] Recently, however, supercritical carbon dioxide ($scCO_2$), a more environmentally benign alternative, has received attention.[6] The use of CO_2 in this manner leads to a process that recycles a greenhouse gas and circumvents the use of conventional organic solvents. CO_2 has added attributes of being inexpensive, nonflammable, and widely available. The pioneering work of DeSimone and coworkers[7,8] has shown that $scCO_2$ can be readily applied as a solvent for dispersion polymerizations. At supercritical conditions CO_2 has a solubility parameter, dielectric constant, and density comparable to those of liquids, while its surface tension and viscosity are comparable to those of gases.

The use of amphiphilic diblock copolymers as stabilizers in $scCO_2$ dispersions has become widespread. These operate on the basis that one segment anchors to the growing polymer particle by way of a chemical or physical interaction[6] while the other segment, which is CO_2-philic and normally either a fluorocarbon[7−9] or siloxane[10−12] based polymer, extends into the continuous phase to sterically stabilize the particle.

Controlled/living radical polymerization (CLRP) provides a method of synthesizing polymers with designed microstructure and low polydispersity. A number of these systems have been developed and are based on either reversible deactivation (nitroxide-mediated radical polymerization (NMP)[13] and atom transfer radical polymerization[14,15]) or reversible transfer mechanisms (reversible addition−fragmentation chain transfer[16] and iodine transfer polymerization[17]). Recent efforts have attempted to harmonize controlled/living technologies with industrially important heterogeneous systems.[18−21] A notable point of investigation is the possibility of using CLRP as a means to elucidate more information about the mechanism of a dispersion polymerization, as discussed within the context of this paper. Precipitation NMP of styrene (S) has been performed in $scCO_2$ using 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO),[22] and TEMPO based dispersion NMP has been reported in media other than $scCO_2$.[23−25] The first attempts of applying CLRP to a $scCO_2$ dispersion polymerization involved ATRP. These comprised of the polymerization of methyl methacrylate using a fluorinated polymeric stabilizer[26] and the use of bromine terminated poly(dimethylsiloxane) (PDMS) as both initiator and stabilizer, the so-called *inistab* technique.[27] RAFT polymerization has also been conducted in $scCO_2$, both in solution[28,29] and in dispersion.[30] The first dispersion NMP in $scCO_2$ was recently reported by this collaboration.[31] Various approaches were investigated using *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) and a PDMS-based inistab. Controlled/living character was demonstrated by a linear increase in M_n with conversion and successful chain extensions. However, stabilization resulting in high conversions (and isolation of the polymer as a dry powder) was only achieved when sufficient amounts of inistab were added. The use of high levels of inistab resulted in broad molecular weight distributions (MWDs) due to initiating species growing from one or both ends.[31]

The primary aim of the present paper is to achieve controlled/living character for the dispersion polymerization of S in $scCO_2$ up to high conversion, thus enabling isolation of the polymer as a dry powder upon venting of the CO_2. It is demonstrated that this is possible for SG1 mediated polymerizations by

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[†] Part CCLXXVIII of the series “Studies on Suspension and Emulsion”.

[‡] National University of Ireland.

[§] Department of Chemical Science and Engineering, Kobe University.

[⊥] Graduate School of Science and Technology, Kobe University.

* Corresponding author. Tel and Fax: +81-(0)78-8036161; e-mail: okubo@kobe-u.ac.jp.

10.1021/ma061154n CCC: \$33.50

employing poly(dimethylsiloxane-*b*-methyl methacrylate) as stabilizer and 2,2′-azo(isobutyronitrile) (AIBN) as initiator. Comparisons with solution NMP experiments are presented in an attempt to further understand the effect of heterogeneity on the progression of dispersion NMP.

Experimental Section

Materials. Styrene (S) (Showa Kobunshi, >99%) and reagent grade toluene (Nacalai Tesque, 99%) were purified by distillation under reduced pressure. Reagent grade 2,2′-azo(isobutyronitrile) (AIBN; Wako, 98%) was purified by recrystallization. Poly(dimethylsiloxane-*b*-methyl methacrylate) (PDMS-*b*-PMMA; Polymer Source, Canada, >99%) was used as received. According to the manufacturer the PDMS segment had a number-average molecular weight (M_n) of 8000, while the PMMA segment had M_n = 4000, with an overall $M_w/M_n = 1.09$. SG1 was synthesized according to the literature.[32] The purity of the SG1 was measured by ^{1}H NMR spectroscopy by reacting the radical with pentafluorophenylhydrazine, yielding 97% purity. TEMPO (Tokyo Chemical Industry, >98%) and industrial grade CO_2 (Kobe Sanso Co., >99.5%) were used as received.

Dispersion Polymerization Procedure. Dispersion polymerizations were conducted in a 25 mL stainless steel reactor.[33] Each polymerization corresponds to one batch reaction; i.e., it was not possible to withdraw samples from the reactor. A typical polymerization was carried out as follows (e.g., the 6 h dispersion polymerization): S (10 g, 9.6×10^{-2} mol), PDMS-*b*-PMMA (0.75 g, 7.5 wt % relative to S), AIBN (0.0246 g, 1.5×10^{-4} mol), and SG1 (0.147 g, 4.97×10^{-4} mol) were added to the reactor, a vacuum was applied, and subsequently the reactor was pressurized with CO_2 to 7 MPa at room temperature using a high-pressure pump. The reactor temperature was then raised to 110 °C by immersion in a temperature-controlled oil bath with magnetic stirring at 600 rpm. The pressure rose to ~42 MPa and remained at this level (±2−3 MPa) for the duration of the reaction. Characterization (6 h dispersion polymerization): conversion = 9.4%; $M_n = 4270$; $M_w/M_n = 1.12$. Conversion was measured by gravimetry after dissolution of the product obtained from the reactor in toluene, precipitation of this solution in an excess of methanol, filtration, and finally drying in vacuo at room temperature overnight. At S conversions above 80%, the polymer was obtained as a powder. In the case of the 85% conversion polymerization, a small (weighed) sample of this was taken for analysis prior to dissolution and subsequent precipitation. As the stabilizer also precipitated out, its initial mass was subtracted from the final mass of polymer obtained for calculation of monomer conversion. The polymer particles were observed using a transmission electron microscope (TEM) (H-7500, Hitachi High Technologies Co., Tokyo, Japan). The hydrodynamic diameter of the particles (redispersed in *n*-hexane) was measured using dynamic light scattering (DLS) (DLS-700, Otsuka Electronics Co., Ltd., Kyoto, Japan) at the light scattering angle of 90° at room temperature. Number- (d_n) and weight-average (d_w) particle diameters were obtained using the Marquadt Analysis routine.

Solution Polymerizations. A typical solution polymerization was carried out as follows (e.g., the 6 h polymerization): a degassed toluene (2.43 g) solution of S (2.00 g, 1.92×10^{-2} mol), AIBN (0.00490 g, 2.99×10^{-5} mol), and SG1 (0.0294 g, 9.93×10^{-5} mol) was heated in a sealed glass ampule at 110 °C in a temperature-controlled oil bath for 6 h. After this time the polymerization was quenched by immersing the ampule into an ice−water bath. Subsequently, the mixture was poured into an excess of methanol to precipitate the formed polymer. Conversion was measured by gravimetry after filtration and drying. Characterization (6 h solution polymerization): conversion = 12.0%, M_n = 5060; $M_w/M_n = 1.08$.

Chain Extensions. A typical chain extension was carried out as follows: a degassed bulk solution of S (2 g, 1.92×10^{-2} mol), alkoxyamine (M_n = 16 000 $M_w/M_n = 1.27$; 0.200 g, 1.25×10^{-5} mol), and SG1 (0.00050 g, 1.7×10^{-6} mol) was heated in a sealed glass ampule at 110 °C for 24 h. The polymer was precipitated, filtered and dried as above. Conversion = 86%; M_n = 102 000; $M_w/M_n = 1.69$.

Critical Degree of Polymerization (J_{crit}) and Solubility Measurements. The degree of polymerization at which an individual polymer chain becomes insoluble in the continuous phase is denoted J_{crit}. A precipitation polymerization was conducted in a 90 mL reactor equipped with a sapphire viewing window as follows: S (36.0 g, 0.346 mol), AIBN (0.0246 g, 1.5×10^{-4} mol), and TEMPO (0.0427 g, 2.73×10^{-4} mol) were charged to the reactor. (The only rationale for the use of a larger reactor in this case was its possession of a viewing window. The smaller reactor used in all other polymerizations did not possess a viewing window, and as such these polymerizations were not monitored visually.) After applying a vacuum and heating to 110 °C in an oil bath, the pressure was raised to the same level used for all the dispersion polymerizations (~42 MPa). The nature of the polymerization medium was observed periodically (every 30 min) through the sapphire window until it turned turbid (43.5 h, ~1% conversion) at which stage the polymerization was immediately stopped. The value of J_{crit} was taken as the number-average degree of polymerization of the isolated polymer (obtained from GPC analysis). A solubility test of the stabilizer was conducted in the same reactor as follows: S (36.0 g, 0.346 mol) and PDMS-*b*-PMMA (0.200 g, 1.66×10^{-5} mol) were charged to the reactor. As above, the reactor was heated to 110 °C before the pressure was raised by the addition of CO_2. At ~15 MPa pressure, the originally soluble stabilizer precipitated from solution resulting in a turbid mixture. Addition of further CO_2, bringing the pressure to ~42 MPa, resulted in no further change.

Molecular Weight Measurements. Molecular weights were measured by gel permeation chromatography (GPC) using two S/divinylbenzene gel columns (TOSOH Corp., TSK gel GMHHR-H, 7.8 mm, i.d. × 30 cm, separation range per column: approximately $50-4 \times 10^8$ g/mol (exclusion limit)) with THF as eluent at a flow rate of 1.0 mL/min employing an ultraviolet (UV) or refractive index (RI) detector (both TOSOH) as necessity dictated. The columns were calibrated with six linear polystyrene (PS) samples ($1.05 \times 10^3-5.48 \times 10^6$, $M_w/M_n = 1.01-1.15$).

Simulations. Simulations were carried out using the software PREDICI[34] (version 5.51.4).

Results and Discussion

Stabilizer. For dispersion polymerizations in $scCO_2$ reported to date, the amphiphilic diblock stabilizer used contained a polymer-philic block composed of the same monomeric units as the monomer being polymerized.[10] However, in this work the stabilizer PDMS-*b*-PMMA was selected over PDMS-*b*-PS because the former is “UV invisible”. Thus, GPC UV detection enabled measurement of the MWD of the formed PS without interference from the stabilizer. The anchor solubility balance (ASB) of the PDMS-*b*-PMMA stabilizer, i.e., the ratio of the molecular weights of the polymer-philic PMMA segment to the CO_2-philic PDMS segment, was chosen as it falls approximately midway within the range 1:3 and 3:1 reported to be most suitable.[1]

A solubility test of the PDMS-*b*-PMMA stabilizer under the polymerization conditions indicated the stabilizer was not fully soluble despite the high initial S content (40 wt %) employed. Conventional understanding of dispersion polymerization stipulates that for a stabilizer to be effective it should be completely soluble under initial reaction conditions. However, it has been shown recently[35] that as long as some portion of the stabilizer is soluble, a stabilizer can act efficiently. The ability of the stabilizer to partition due to the existence of a balance between distinct CO_2-philic and polymer-philic portions was cited as being more important than overall solubility.

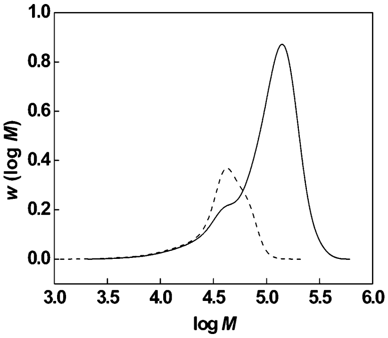

Figure 1. Molecular weight distributions (normalized to weight of polymer) of polystyrene produced in the *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated, poly(dimethylsiloxane; PDMS)-*b*-poly(methyl methacrylate; PMMA) stabilized dispersion polymerization of styrene (S) in supercritical carbon dioxide at 110 °C (dashed line, 85% conversion, $M_n = 30\,600$; [S] = 40 wt %, [PDMS-*b*-PMMA] = 7.5 wt % relative to S, [2,2′-azo(isobutyronitrile); AIBN] = 6×10^{-3} M, [SG1] = 1.39×10^{-2} M (40% excess SG1 used here only; 100% excess used in all subsequent dispersion polymerizations. Excess calculated relative to the original number of alkoxyamine species as based on an initiator efficiency (*f*) for AIBN of 0.83 in 100% scCO$_2$ at 59.4 °C[36])) and its bulk styrene chain extension at 110 °C (solid line, 24% conversion, $M_n = 68\,100$; [polymer] = 3.96×10^{-3} M (based on M_n of original alkoxyamine = 30 600), [SG1] = 1.024×10^{-3} M).

Initial investigations to optimize conditions for the SG1-mediated dispersion polymerization of S in scCO$_2$ showed high conversion was not reached unless the stabilizer content was sufficiently high; 2.5 and 5 wt % stabilizer (relative to S), with 10% excess SG1 relative to the original number of alkoxyamine species (based on initiator efficiency (*f*) for AIBN of 0.83 in 100% scCO$_2$ at 59.4 °C[36]) resulted in 45 and 65% conversion in 48 h, respectively. Polymerizations conducted in the presence of 7.5 wt % stabilizer and 100% excess of SG1 gave 74 and 85% conversion in 48 and 72 h, respectively. Despite the higher SG1 concentration used in the latter polymerizations (which in itself would lead to lower polymerization rate), the increase in stabilizer content led to higher conversions. Therefore, 7.5 wt % was used for the mainstay of polymerizations in this study. If the number of stabilizer molecules is insufficient to form an adequate protective layer on the particles, coagulation occurs, leading to low polymerization rates and low final conversions.[10]

Initial Nitroxide Concentration. At lower initial SG1 concentrations than that eventually used, significant broadening and nonlivingness of the MWDs occurred. For example, 10% excess of SG1 gave $M_w/M_n = 1.77$ at 65% conversion (5 wt % stabilizer), and 40% excess resulted in $M_w/M_n = 1.44$ at 85% conversion (7.5 wt % stabilizer; the stabilizer content may also affect M_w/M_n). The MWD in the latter experiment and the chain extension conducted to ascertain its livingness are presented in Figure 1.

The pronounced low molecular weight (MW) shoulder of the chain extension experiment constitutes dead chains of the original MWD. The addition of excess nitroxide can be useful in preventing excessive bimolecular termination at an early stage of NMP for systems with a high equilibrium constant K[37] ($K = k_d/k_c$, where k_d is the activation and k_c the deactivation rate coefficient, respectively) such as the S/SG1 system ($K = 2.1 \times 10^{-9}$ M at 110 °C[38,39]). However, an excess of no more than 10% is usually adequate to fulfill such a purpose for S/SG1.[37] Thus, the poor control in our dispersion system at the nitroxide concentrations discussed above is probably attributable to the heterogeneity of the system, perhaps nitroxide partitioning between the continuous and the particle phase.[40] However, it cannot be excluded that limited solubility of SG1 in the scCO$_2$/S medium may also be a factor. To overcome any such effects, the polymerizations were conducted in the presence of 100% excess of nitroxide.

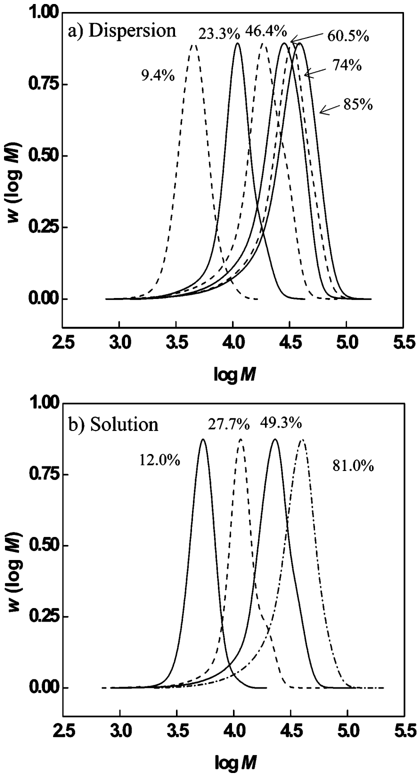

Figure 2. Molecular weight distributions (normalized to peak height) of the *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated and poly(dimethylsiloxane; PDMS)-*b*-poly(methyl methacrylate; PMMA) stabilized dispersion polymerization (a) of styrene (S) in supercritical carbon dioxide at 110 °C ([S] = 40 wt %, [PDMS-*b*-PMMA] = 7.5 wt % relative to S, [2,2′-azo(isobutyronitrile); AIBN] = 6×10^{-3} M, [SG1] = 1.99×10^{-2} M (100% excess)), and the SG1-mediated solution (b; toluene) polymerization of S at 110 °C ([S] = 3.84 M, [AIBN] = 6×10^{-3} M, [SG1] = 1.99×10^{-2} M (100% excess)). Conversions as indicated.

Determination of J_{crit}. The living nature of the polymerization, most notably the fact that M_n increased linearly with conversion, allowed experimental determination of J_{crit} as ~28 (see Experimental Section). The approach employed is not applicable to a conventional radical dispersion polymerization (i.e., nonliving) because, in such, high MW polymer is formed within seconds. This is a novel approach as, to the best of our knowledge, CLRP has not been used in this way to determine the J_{crit} of heterogeneous systems by simple observation. It is unlikely the nature of the nitroxide has any effect on J_{crit} of alkoxyamine chains, especially for the chain lengths discussed here (much greater than oligomeric). The simplicity in determining J_{crit} in this manner highlights a distinct advantage of employing CLRP over conventional radical polymerization in fundamental mechanistic/kinetic investigations of heterogeneous systems.

Dispersion Polymerization of Styrene in scCO$_2$. The MWDs at different conversions for the SG1-mediated dispersion polymerization of S in scCO$_2$ at 110 °C are displayed in Figure 2a. The MWDs were monomodal throughout the polymerization, which is indicative of the polymerization occurring predominantly in one phase. If significant polymerization had occurred in both the solution phase and the particle phase, unequal partitioning of monomer and nitroxide between the phases would most likely result in two distinct distributions of chains. From

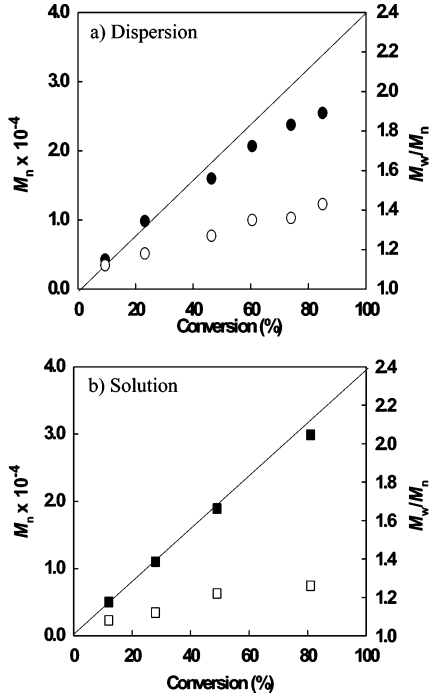

Figure 3. Plots of number-average molecular weight (M_n) (●, ■) and polydispersity (M_w/M_n) (○, □) vs conversion for *N*-*tert*-*N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated dispersion (a) and solution (b) polymerizations of styrene. See Figure 2 for conditions. Lines represent theoretical M_n values ((2,2′-azo(isobutyronitrile) (AIBN) initiator efficiencies: $f_{AIBN}{}^{36} = 0.83$ in dispersion, $f_{AIBN}{}^{41} = 0.82$ in solution).

a highly symmetrical and narrow MWD at 9.4% conversion, broadening in the form of a low MW tail and a slight high MW shoulder emerges as the polymerization proceeds.

The evolutions of M_n and M_w/M_n with conversion are displayed in Figure 3a. M_n remained close to the theoretical values ($M_{n,th}$ was calculated on the basis of the number of radicals generated as opposed to relative to the amount of nitroxide due to the vast excess of SG1 employed; $M_{n,th} = ([S]_0\alpha_S M_S)/2f\,[AIBN]_0$, where $f = 0.83$ (dispersion),[36] $f = 0.82$ (solution),[41] α_S is S conversion, and M_S is the molar mass of S) up to ~50% conversion, from where it deviated downward (consistent with an increase in the number of chains as discussed below). The M_w/M_n values increased with conversion, ranging from 1.12 at 9.4% conversion up to 1.43 at 85% conversion. These M_w/M_n values represent significant improvement compared to the higher values (almost all >1.4) previously reported for the SG1-mediated dispersion polymerization of S in $scCO_2$.[31] The linear first-order plot (Figure 4) indicates that the concentration of propagating species ([P•]) remained approximately constant throughout the polymerization. (The applicability of first-order kinetics in a dispersion polymerization is questionable due to the presence of two phases; however, a first-order plot does provide a crude measure of [P•] vs time.)

A bulk chain extension of the 46.4% conversion polymerization is presented in Figure 5a. A separate low MW peak, representing dead chains, is clearly visible in the chain extended distribution. After converting this trace to a number distribution (*P*(*M*) vs *M*, Figure 5b) and integration of the low MW peak (nonextended chains, MW < ~29 000) relative to the overall distribution, it was calculated that ~25% of chains are nonliving at this stage of the polymerization. It is apparent from the extended distribution that the low MW tail in the original distribution is not entirely dead; dead chains exist throughout the entire distribution.

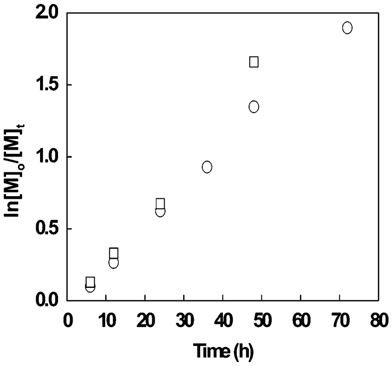

Figure 4. First-order plots of the *N*-*tert*-*N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated dispersion polymerization (○) and solution polymerization (□) of styrene in supercritical carbon dioxide and toluene, respectively, at 110 °C. See Figure 2 for conditions.

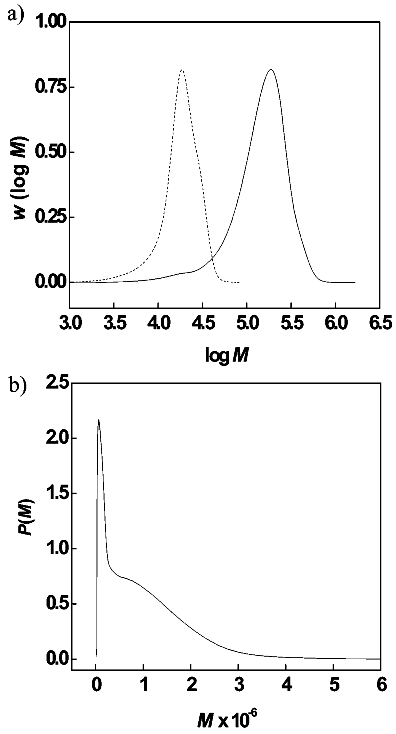

Figure 5. (a) Molecular weight distributions (normalized to peak height) of polystyrene produced in the *N*-*tert*-*N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated, poly(dimethylsiloxane)-*b*-poly(methyl methacrylate) stabilized dispersion polymerization of styrene in supercritical carbon dioxide ($scCO_2$) at 110 °C (dashed line, 46.4% conversion, $M_n = 15\,990$; see Figure 2 for conditions) and its bulk S chain extension at the same temperature (solid line; 90% conversion, $M_n = 96\,600$; [polymer] $= 5.72 \times 10^{-3}$ M (based on $M_n = 15\,990$), [SG1] $= 1.48 \times 10^{-3}$ M). (b) *P*(*M*) vs *M* (number distribution; area normalized to unity) of the chain extended polymer in (a).

Solution Polymerizations. S polymerizations were performed in toluene under similar conditions to those used in the dispersion polymerization, i.e., the same initial [S], [AIBN], and [SG1], the only difference being the exclusion of the now redundant stabilizer. The MWDs of the polymers formed in the solution polymerizations are monomodal and narrow up to high conversion (Figure 2b), not distinctly different from those of the dispersion polymerization (Figure 2a). The M_n values exhibit excellent linear agreement with conversion for the entire polymerization, with only a slight downward trend at high conversion (Figure 3b). The M_w/M_n values range from 1.08 at 12% conversion to 1.26 at 81% conversion. Overall, these M_w/M_n values indicate a somewhat greater degree of control in

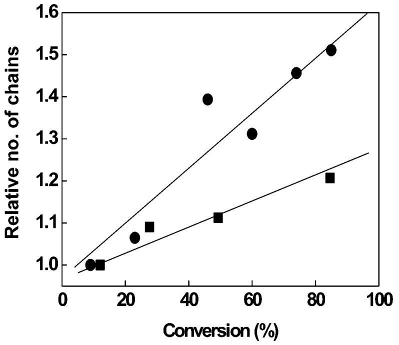

Figure 6. Relative number of chains as a function of conversion for the *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated, poly(dimethylsiloxane)-*b*-poly(methyl methacrylate) stabilized dispersion polymerization of styrene in supercritical carbon dioxide at 110 °C (●) and the corresponding toluene solution polymerization (■). Trend lines added as a guide only. See Figure 2 for conditions.

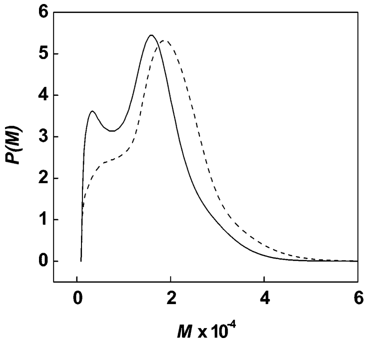

Figure 7. Plots of $P(M)$ vs M (number distributions; areas normalized to unity) for the *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated, poly(dimethylsiloxane)-*b*-poly(methyl methacrylate) stabilized dispersion polymerization of styrene in supercritical carbon dioxide at 110 °C (46.4% conversion, solid line) and the corresponding solution polymerization sample (49% conversion, dashed line). See Figure 2 for conditions.

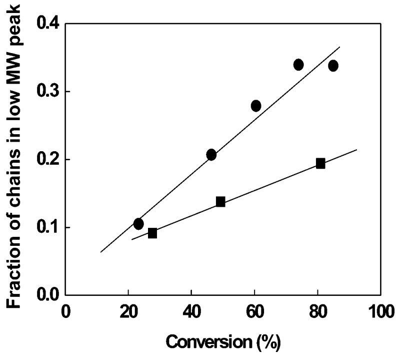

Figure 8. Plot of the number fraction of chains in the low molecular weight peaks of the relevant number distributions as a function of conversion for the *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated, poly(dimethylsiloxane)-*b*-poly(methyl methacrylate) stabilized dispersion polymerization of styrene in supercritical carbon dioxide (●) and the corresponding toluene solution polymerization (■) at 110 °C. Trend lines added as a visual guide only. See Figure 2 for conditions.

solution relative to dispersion. The first-order plot for this polymerization (Figure 4) reveals an increase in R_p (and $[P^\bullet]$) at higher conversion. Such behavior has been observed previously in homogeneous S polymerizations conducted in the presence of a large excess of SG1.[42]

Number of Chains. The relative number of chains (calculated by integration of $P(M)$ vs M obtained from the appropriately normalized weight distributions[43]) increases with conversion in both the solution (~20% increase between 12 and 81% conversion) and dispersion (~50% increase between 9.4 and 85% conversion) polymerizations (Figure 6).

A clearer illustration of subtle disparities between MWDs can be obtained by comparing number distributions.[43] Such plots are presented for the 46.4% conversion dispersion polymerization and the 49% conversion solution polymerization in Figure 7. While there is distinct broadening toward the low MW regions in both cases, it is clear that in the case of the dispersion polymerization a much higher proportion of lower MW chains exist.

Simulations conducted in the present study using PREDICI[34] (results not shown), employing literature rate coefficients[37] (including thermal initiation[44]), showed that a low MW peak somewhat similar to those observed here appears in NMP systems with a high equilibrium constant (K) such as S/SG1/AIBN if the initial nitroxide concentration is lower than the total concentration of radicals generated by initiator decomposition (due to extensive bimolecular termination at low conversion prior to accumulation of excess nitroxide). In the present study a large excess of nitroxide was employed. Moreover, a plot of the number fraction of chains in the low MW peak of the number distributions with conversion (Figure 8; the low MW region taken to be all chains below the MW at the "minimum point" in the bimodal $P(M)$ vs M plot) reveals the number fraction of low MW chains increased with conversion in both solution and dispersion, thus clearly ruling out the above as a possible cause of the low MW peak. The trend in Figure 8 is similar to that observed in Figure 6. Consider, as an example, the dispersion polymerization; ~50% new chains are formed throughout its course (Figure 6). As a fraction of overall chains this equates to 33%, which is in good agreement with the number fraction of chains in the low MW peak at the highest conversion. This agreement (also observed in the solution polymerization) suggests the vast majority of new chains reside in the low MW peak. Considering the above, two foremost questions arise: (i) why is there significant increase in chain numbers in both solution and dispersion polymerizations, and (ii) why is this increase greater in dispersion?

Polymerization Rates. The R_p values were similar in dispersion and solution (Figure 4); the initial R_p was ~20% higher in solution than dispersion. At conversions lower than that corresponding to J_{crit} (where the dispersion system would be homogeneous) one would expect R_p to be similar in the two systems. However, according to $J_{crit} \approx 28$, the system becomes heterogeneous as early as ~7.5% conversion (based on linear M_n vs conversion; Figure 3a). The value of R_p in homogeneous NMP with the rate of thermal initiation ($R_{i,th}$) = 0 follows[45]

$$\ln\left(\frac{[M]_0}{[M]}\right) = \left(\frac{k_p K[PT]_0}{[T^\bullet]_0}\right)t \qquad (1)$$

in the limit of a large initial excess of nitroxide ($[T^\bullet]_0 \gg (3k_t K^2 [PT]_0{}^2 t)^{1/3}$). The subscript 0 denotes initial concentrations, k_p and k_t are the propagation and termination rate coefficients, respectively, K is the equilibrium constant, and PT and $T^\bullet$ denote alkoxyamine and nitroxide, respectively.

Under conditions when eq 1 is applicable, R_p is independent of [PT] and $[T^\bullet]$ for a given $[PT]/[T^\bullet]$. In the dispersion and solution NMP discussed here, a vast excess of SG1 was employed. Therefore, if the particle phase is considered the only locus of polymerization (i.e., after the degree of polymerization $> J_{crit}$) and if all (or a sufficiently high fraction of) SG1 and S are located in the particles, then eq 1 predicts the same R_p in dispersion and solution, if $R_{\mathrm{i,th}}$ is sufficiently low (addressed below). If all S and SG1 are located in the particles the [S], [PT], and [SG1] are higher in the particles than in the solution polymerization, but the ratio [PT]/[T$^\bullet$] would be the same.

Simulations using PREDICI[34] based on eqs 2−4 were carried out to elucidate the influence of $R_{\mathrm{i,th}}$, which is not zero under the conditions of the present study (thus, strictly speaking, rendering eq 1 inapplicable).

$$\frac{\mathrm{d}[\mathrm{PT}]}{\mathrm{d}t} = k_{\mathrm{c}}[\mathrm{P}^\bullet][\mathrm{T}^\bullet] - k_{\mathrm{d}}[\mathrm{PT}] \tag{2}$$

$$\frac{\mathrm{d}[\mathrm{T}^\bullet]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{PT}] - k_{\mathrm{c}}[\mathrm{P}^\bullet][\mathrm{T}^\bullet] \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{P}^\bullet]}{\mathrm{d}t} = k_{\mathrm{d}}[\mathrm{PT}] - k_{\mathrm{d}}[\mathrm{P}^\bullet][\mathrm{T}^\bullet] - 2k_{\mathrm{t}}[\mathrm{P}^\bullet]^2 + R_{i,\mathrm{th}} \tag{4}$$

Parameter values employed: (S/SG1/110 °C); k_{d}[39] $= 3.73 \times 10^{-3}$ s^{-1}; k_{c}[38,39] $= 1.8 \times 10^{6}$ M^{-1} s^{-1}; k_{t}[46] $= 1.57 \times 10^{8}$ M^{-1} s^{-1}; k_{p}[47] $= 1.58 \times 10^{3}$ M^{-1} s^{-1}; $R_{\mathrm{i,th}}$ ($= k_{i,\mathrm{th}}[\mathrm{S}]_0^3$) $= 2.83 \times 10^{-8}$ (dispersion), 2.41×10^{-9} (solution) M s^{-1}, where $k_{i,\mathrm{th}}$[44] $= 4.26 \times 10^{-11}$ M^{-2} s^{-1}. Reactant concentrations: dispersion (considering particle phase only and assuming all reactants located in particles only): $[\mathrm{S}]_0 = 8.7$ M; $[\mathrm{AIBN}]_0 = 13.6$ mM; $[\mathrm{SG1}]_0 = 44.9$ mM. Assuming $f_{\mathrm{AIBN}} = 0.83$, the concentration of PT generated is [PT] = 22.6 mM, and the concentration of free SG1 is [SG1] = 22.3 mM. Solution: $[\mathrm{S}]_0 = 3.84$ M; $[\mathrm{AIBN}]_0 = 6.0$ mM; $[\mathrm{SG1}]_0 = 19.8$ mM. Assuming $f_{\mathrm{AIBN}} = 0.83$ the concentration of PT generated is [PT] = 9.89 mM, and the concentration of free SG1 is [SG1] = 9.91 mM. Simulations yield a steady-state value of $[\mathrm{P}^\bullet] = 2.1 \times 10^{-9}$ M for both dispersion and solution, consistent with the linear first-order plot and eq 1. The slope of the experimental (dispersion) first-order plot (Figure 4) gives $[\mathrm{P}^\bullet] = 4.8 \times 10^{-9}$ M, which is in good agreement with the simulations considering uncertainties in the value of f_{AIBN} and other rate coefficients used in the model. The values of [P$^\bullet$] of the two simulations are only negligibly influenced by $R_{i,\mathrm{th}}$ if this quantity is low enough; [P$^\bullet$] (dispersion and solution) is affected by less than 2% if $R_{i,\mathrm{th}} < 3 \times 10^{-8}$ M s^{-1}.

The straightforward application of eq 1 to explain the R_{p} data is complicated by the facts that (i) not all monomer is located in the particles and also (ii) SG1 partitioning to the solution phase (higher SG1 levels were required in dispersion than solution, suggesting SG1 partitioning may play a role). It is highly plausible that the monomer concentration in the particles is significantly higher than that in the solution polymerization. Kumar et al.[48] investigated the solubility of S oligomers in scCO$_2$ and could best explain their data by invoking a value of 0.125[48,49] for the partition coefficient of S between solid PS and scCO$_2$ (g of S in g of scCO$_2$/(g of S in g of PS)). Wu et al.[50] arrived at a very similar value of ∼0.1 for the same partition coefficient. On the basis of a scCO$_2$ density of 0.8 g cm^{-3} at 40 MPa and 110 °C,[51] a partition coefficient for S between scCO$_2$ and PS (particles) of 0.1 results in ∼61% of S being located in the particles at 25% conversion and ∼76% at 50% conversion.

There is no evidence to suggest that k_{p} of the S polymerization is altered significantly, if at all, in scCO$_2$.[52] The propagation step remains under chemical control to ∼75% conversion in S bulk polymerization at 70 °C,[53] and even higher conversion at 110 °C,[54] and thus diffusion-controlled propagation is not an issue. The conversion dependence of k_{t}, coupled with the observation by Beuermann at al.[55] that k_{t} of S is increased in scCO$_2$, is not important because of the use of a large excess of nitroxide; hence, the termination rate exerts no significant influence on R_{p} (eq 1). For the same reason the fact that k_{t} would certainly be lower in the particles of the dispersion polymerization relative to the solution (toluene) polymerization (due to the higher polymer content of the particles) is inconsequential.

Chain Transfer. Chain transfer to CO$_2$ (purity >99.5%) does not occur.[6] The contribution of chain transfer to toluene in the solution polymerizations is expected to be negligible.[56] Hydrogen abstraction from the stabilizer is deemed unlikely, as aside from intrinsically low reactivity toward such reactions,[57] 2-cyano-2-propyl (from AIBN) and PS radicals are much more likely to react with S or SG1 which are present in large excess. Hydrogen abstraction by the cyano-isopropyl radical or PS radicals from the PDMS segment of the stabilizer is negligible.[58] The MWDs in Figure 2a also support negligible chain transfer to stabilizer by way of an absence of a high MW peak in those MWDs of a lower MW than that of the stabilizer. The fact that the only significant difference in chain numbers occurs at very low MW (∼5000 and lower) also suggests that these extra chains could not arise from chain transfer to stabilizer ($M_{\mathrm{n}} = 12\,000$). Chain transfer to residual impurities is also deemed unlikely, primarily due to the rigorous purity of all reagents used and the level of impurities necessary to form new chains to the extent observed here.

It is proposed that chain transfer to monomer may play a significant role in determining the overall number of chains and the number fraction of dead chains. Detailed simulations using PREDICI, taking chain-length-dependent termination and propagation into account, result in low MW shoulders similar to those observed here. Further investigation of this, which has implications for NMP (and indeed CLRP in general) in homogeneous systems, goes beyond the scope of the present study and will be reported in a future publication.[59] It remains unclear, however, why the number of chains increased more significantly in dispersion than solution (Figure 6).

Thermal Initiation. A commonly forwarded explanation for an increase in chain numbers in NMP of S in dispersed systems is the thermal initiation of S.[60,61] As discussed above, it is highly likely that the concentration of S in the particles is much greater than that in the solution polymerizations.[48,50] On the basis of $k_{i,\mathrm{th}} = 4.26 \times 10^{-11}$ M^{-2} s^{-1} (110 °C)[44] and the dependence of [S] on time in Figure 4, thermal initiation results in 1.1 and 6.9% new chains in solution and dispersion (assuming all S in particles) over the reported conversion ranges, respectively. This rationale is in keeping with the higher rate of generation of new chains observed experimentally in dispersion compared to solution, but the magnitude of the values obtained only accounts for a small proportion of the extra chains.

SG1 Decomposition. Decomposition of SG1 and the resulting radical formation[41] may also contribute to the increase in number of chains with conversion. These newly generated radicals would add to S and thus initiate new chains. A half-life of 15 h has been reported for SG1 at 120 °C.[62] Although the temperature employed in this study is slightly lower, significant decomposition of SG1 is conceivable over the polymerization times employed. Assuming decomposition only occurs when the nitroxide is in the dissociated state, it is plausible the large excess of SG1 employed would lead to an increased rate of generation of new chains via this mechanism. A solution (toluene) polymerization of S in the presence of only 10% excess SG1 was conducted to ascertain the magnitude of the effect of large excess of SG1 on the rate of generation of new chains. The

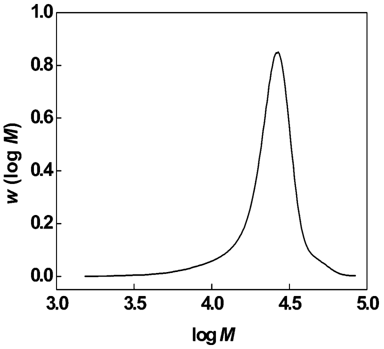

Figure 9. MWD of the polymer formed in the solution (toluene) polymerization of styrene (S) (59%, 17 h) in the presence of 10% excess *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) relative to the number of propagating radicals; $M_n = 20\,900$, $M_w/M_n = 1.21$, [S] = 3.84 M, [2,2′-azo(isobutyronitrile)] = 6×10^{-3} M, [SG1] = 1.09×10^{-2} M.

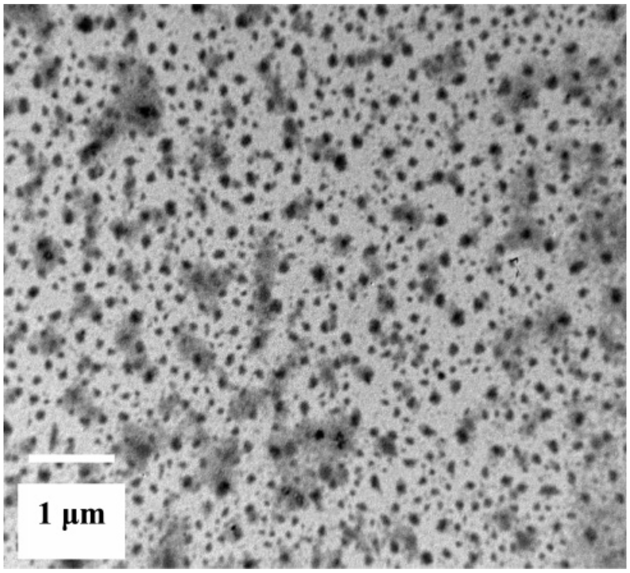

Figure 10. Transmission electron micrograph of polystyrene particles prepared by the *N-tert-N*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1) mediated, poly(dimethylsiloxane)-*b*-poly(methyl methacrylate) stabilized dispersion polymerization of styrene in supercritical carbon dioxide at 110 °C (85% conversion, $M_n = 25\,460$, $M_w/M_n = 1.43$; see Figure 2 for conditions).

MWD of the polymer obtained in this experiment (Figure 9) displays very similar broadening at low MW compared to the MWDs obtained in the presence of the higher SG1 loading. (The corresponding $P(M)$ vs M plot of Figure 9 was bimodal, similar to Figure 7.) Conversion to a number distribution and appropriate integration (as described previously) indicates ∼17% of chains to reside in the low MW region at 59% conversion. This value is close to the number of chains observed in this region at 100% excess nitroxide and similar conversions: ∼14% of chains at 49% conversion and ∼20% of chains at 81% conversion. It can be concluded that decomposition of free SG1 is of minor significance with regards to generation of new chains in these polymerizations. Importantly, this experiment also intimates that chain transfer to the large excess of SG1 employed in the dispersion and solution polymerizations is also not a factor in new chain generation.

Particle Size. DLS measurements at 85% conversion resulted in a number-average diameter (d_n) of 147 nm and a weight-average diameter (d_w) of 203 nm. The particles were also examined using transmission electron microscopy (TEM; Figure 10). A suitable solvent system was not found to remove residual stabilizer from the polymer particles, thus affecting the aesthetic nature of this analysis. The information in terms of particle size and distribution that was garnered from the TEM analysis does, however, appear to be consistent with the DLS data.

Conclusions

Nitroxide-mediated dispersion polymerization of S was carried out successfully to high conversion in supercritical $scCO_2$ using the nitroxide SG1 and a PDMS-*b*-PMMA stabilizer at 110 °C. The polymeric product was recovered as a powder at 85% conversion, with a number-average particle diameter of ∼150 nm. SG1 concentrations normally employed in SG1-mediated bulk polymerization of S resulted in high degrees of nonlivingness, possibly due to SG1 partitioning effects. This was overcome by using a large excess of free SG1. The M_n values agreed well with theory, and M_w/M_n values were between 1.12 and 1.43. The degree of polymerization at which an individual polymer chain becomes insoluble in the continuous phase was determined as $J_{crit} = 28$ by visual observation, illustrating the potential of using controlled/living radical polymerization to elucidate mechanistic details of radical dispersion polymerizations. Low MW shoulders were present in the number distributions in both dispersion and the corresponding solution (toluene) polymerization. Moreover, the number of chains increased with conversion in both solution and dispersion, but more so in dispersion. The number of new chains generated matched the number fraction of chains in the low MW shoulder; i.e., the low MW shoulder consisted of new chains.

Acknowledgment. This work was partially supported by the Support Program for Start-ups from Universities (No. 1509) from the Japan Science and Technology Agency (JST), the Grant-in-Aid for Scientific Research (Grant 17750109) from the Japan Society for the Promotion of Science (JSPS), and by the Irish Research Council for Science, Engineering and Technology (IRCSET) by way of an Embark Postgraduate Scholarship for Ronan McHale.

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MA061154N