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First nitroxide-mediated free radical dispersion polymerizations of styrene in supercritical carbon dioxide

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Abstract

Controlled/living character has been demonstrated for the first time in nitroxide-mediated free radical dispersion polymerizations in supercritical carbon dioxide. Styrene was polymerized in the presence of *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) at 110 °C. Stabilization was achieved using the inistab concept (initiator + stabilizer), employing a poly(dimethylsiloxane) (PDMS) based azo initiator as well as a polymeric alkoxyamine macroinitiator with the expected structure SG1-polystyrene-PDMS-polystyrene-SG1. In the presence of sufficient amounts of the inistab, the polymerizations proceeded to high conversion to yield the polymeric product as a powder. Control was indicated by the number-average molecular weights increasing linearly with conversion in reasonable agreement with the theoretical values. Although the molecular weight distributions were broad in many cases, chain extensions in bulk and solution using styrene indicated high degrees of 'living' character.

Keywords: Controlled/living radical polymerization; Supercritical carbon dioxide; Dispersion polymerization

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1. Introduction

There has been increased interest in environmentally friendly reaction media over the last decade with the aim of replacing environmentally hazardous organic solvents. Supercritical carbon dioxide ($scCO_2$) has attracted significant attention as a benign, inexpensive, non-flammable and widely available medium. In addition, it offers a range of advantages as a polymerization medium such as easy removal of solvent after polymerization, negligible chain transfer to solvent and tuneable solvent strength by changing temperature or pressure [1–3]. Amorphous fluoropolymers and silicones are soluble in CO_2, as well as most non-polar and some polar molecules of low molar mass [3]. However, most high molecular weight polymers exhibit very low solubility, and consequently CO_2 is a useful solvent for precipitation and dispersion polymerizations.

Dispersion polymerizations require a suitable stabilizer in order to prevent coagulation. In case of $scCO_2$, the stabilizer usually consists of a CO_2-philic segment which is almost always a siloxane or fluorocarbon and a CO_2-phobic segment to interact with the polymer [3,4]. Fluorinated surfactants are expensive, which has given rise to demand for cheaper siloxane based alternatives. Polydimethylsiloxane (PDMS) is however not able to stabilize styrene (S) dispersion polymerizations in $scCO_2$ as yields remain low and similar to S polymerizations without stabilizer [4]. PDMS-based stabilizers that are anchored to the PS particles either as PS-*b*-PDMS [4] or by use of the macromonomer technique [5] are much more effective. Another approach, employed in the current study, is to generate the stabilizer as a block copolymer in situ using a PDMS macro azoinitiator (VPS-0501). VPS-0501 (Scheme 1) has been applied to dispersion polymerization in $scCO_2$ for preparation of

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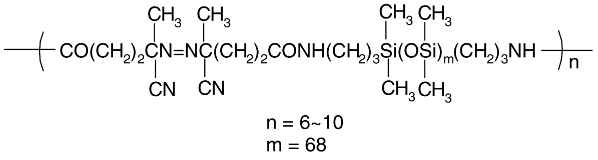


$$\left[CO(CH_2)_2\underset{CN}{\overset{CH_3}{C}}N{=}N\underset{CN}{\overset{CH_3}{C}}(CH_2)_2CONH(CH_2)_3\underset{CH_3}{\overset{CH_3}{Si}}(O\underset{CH_3}{\overset{CH_3}{Si}})_m(CH_2)_3NH \right]_n$$

$n = 6\sim10$
$m = 68$

Scheme 1. VPS-0501.

submicron-sized poly(methyl methacrylate) particles, demonstrating its ability to act as both initiator and stabilizer (inistab) [6].

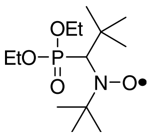
The field of controlled/living free radical polymerization has experienced an explosive growth in recent years [7,8]. Examples of the several different techniques developed include nitroxide-mediated radical polymerization (NMP) [9], atom transfer radical polymerization (ATRP) [10,11] and reversible addition fragmentation chain transfer (RAFT) [12]. In recent years, significant progress has also been made toward making these techniques compatible with heterogeneous polymerization processes [13,14]. There are to date only two reports dealing with controlled/living dispersion polymerization in $scCO_2$, both using ATRP; methyl methacrylate (MMA) using a fluorinated polymeric stabilizer [15] and employing a bromine-terminated PDMS inistab [16]. Precipitation NMP of S has been carried out in $scCO_2$ with varying degrees of success using 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) [17], and dispersion NMP using TEMPO in various media has been reported [18–20].

Herein, we report the first dispersion NMP in $scCO_2$. The nitroxide used was *N*-*tert*-butyl-*N*-(1-diethylphosphono-2, 2-dimethylpropyl) nitroxide (SG1) (Scheme 2), which can be used to control polymerizations of a variety of monomers at relatively low temperatures [21]. Several different approaches, all based on the use of the PDMS macro azoinitiator VPS-0501, were investigated, including the preparation of an alkoxyamine inistab species. The results are discussed in terms of the extent of control of the molecular weight distribution (MWD), the 'livingness' of the obtained polymer as assessed by chain extension experiments, the polymer yield and the particle morphology.

2. Experimental section

2.1. Materials

Styrene (S) was purified by distillation under reduced pressure. Reagent grade 2,2′-azo(isobutyronitrile) (AIBN; Wako) was purified by recrystallization. VPS-0501 (VPS; Wako) was used as received. The molecular weight of VPS was measured by GPC relative to PS standards: $M_n = 30,800$; $M_w = 48,900$. According to the manufacturer, the average number of azo moieties per molecule is eight ($n = 8$ (6–10) in Scheme 1). 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO; Aldrich) was used as received. SG1 was synthesized according to the literature [22]. The purity of the SG1 was measured by ^1H NMR by reacting the radical with pentafluorophenylhydrazine yielding 97% purity. Industrial grade CO_2 with a purity of 99.5% or higher was used as received (Kobe Sanso Co.). The 'heat treated' VPS (VPS_{ht}) was prepared by heating approximately 6 g VPS in a degassed and sealed glass ampoule at 70 °C for 12 h.



Scheme 2. SG1.

2.2. Alkoxyamine inistab synthesis

The bifunctional polymeric alkoxyamine inistab SG1-PS-PDMS-PS-SG1 was prepared by heating a solution of toluene containing 1.5 M S, 0.04 M VPS and 0.048 M SG1 for 14 h at 80 °C. Based on the rate of decomposition of the VPS azo moieties in *i*-propanol at 75 °C [23], this would result in complete decomposition. By analogy with SG1 and MMA-terminated radicals [24], it was presumed that the equilibrium constant for the reversible cleavage of the alkoxyamine formed by combination of SG1 and the radical generated on thermal decomposition of VPS would be very large and consequently render a macroinitiator based on SG1 and VPS unsuitable for use at 110 °C (the polymerization temperature in the current study). S was therefore added in order to convert the VPS-radicals to S-terminated radicals (which have a much lower equilibrium constant [25]). The high MW fraction of the alkoxyamine inistab was isolated by precipitation in methanol at room temperature, yielding $M_n = 16,600$ and $M_w/M_n = 1.39$.

2.3. Dispersion polymerization procedure

Dispersion polymerizations of S in $scCO_2$ were conducted in a 25 ml stainless steel reactor [26]. A typical polymerization was carried out as follows: S (5 g, 4.80×10^{-2} mol), VPS (1.3 g, 4.22×10^{-5} mol), AIBN (0.0031 g, 1.89×10^{-5} mol) and SG1 (0.052 g, 1.76×10^{-4} mol) (**Exp. 3d**) 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 subsequently raised to 110 °C by immersion in a temperature controlled oil bath with magnetic stirring at 600 rpm, during which the pressure increased to approximately 42 MPa. The polymerization was stopped by cooling the reactor in an ice–water bath, and the CO_2 was vented slowly. The polymer was obtained as a powder when the conversion was beyond approximately 70%. The polymer particles were observed with a Hitachi S-2500 scanning electron microscope (SEM). In case of lower conversions, the reaction mixture was dissolved in toluene and the polymer was precipitated out in methanol. The conversion was measured gravimetrically. The various polymerizations carried out are detailed in Table 1.

2.4. Chain extensions

S chain extensions were carried out at 110 °C for various times in degassed and sealed glass ampoules. Polymer 2c (Tables 1 and 2; 20% conversion sample; 0.098 g) in S (1.5 g, 1.44×10^{-2} mol), 1.5 h; Polymer 4a (15% conversion sample; 0.174 g) in S (1.5 g, 1.44×10^{-2} mol) with SG1 (1.0×10^{-4} g, 3.38×10^{-7} mol), 6 h; Polymer 5a (58% conversion sample; 0.606 g) in S (1.5 g, 1.44×10^{-2} mol) and toluene (4 g, 4.34×10^{-2} mol) with SG1 (2.0×10^{-4} g, 6.76×10^{-7} mol), 6 h.

2.5. Solution polymerizations (SG1)

A solution polymerization with 15 wt% VPS_{ht} relative to S was carried out as follows (**Exp 4c**): A degassed toluene (4 g) solution of S (1 g, 9.61×10^{-3} mol), VPS_{ht} (1.77×10^{-1} g, 8.12×10^{-6} mol), AIBN (1.72×10^{-3} g, 1.05×10^{-5} mol) and SG1 (6.88×10^{-3} g, 2.32×10^{-5} mol) was heated in a sealed glass ampoule at 110 °C for 52.5 h. A solution polymerization using the alkoxyamine inistab (**Exp. 5b**) was carried out by heating a degassed toluene (4 g) solution of S (1 g, 9.61×10^{-3} mol), SG1-PS-PDMS-PS-SG1 (3.76×10^{-1} g, 2.26×10^{-6} mol), and SG1 (6.0×10^{-4} g, 2.03×10^{-6} mol) at 110 °C for 24 h.

2.6. Bulk polymerizations (TEMPO)

S (5 g, 4.81×10^{-2} mol), VPS (1.3 g, 4.22×10^{-5} mol) and TEMPO (2.31×10^{-2}, 1.48×10^{-4} mol) were heated in a degassed and sealed glass ampoule at 125 °C for 5 h (**Exp. 1b** in Table 1). S (5 g, 4.81×10^{-2} mol), VPS_{ht} (1.3 g, 5.96×10^{-5} mol) and TEMPO (5.67×10^{-3} g, 3.63×10^{-5} mol) were heated in a degassed and sealed glass ampoule at 125 °C for 5 h (**Exp. 1c** in Table 1). The polymers resulting from the chain extensions, bulk and solution polymerizations were dissolved in toluene and precipitated out in methanol.

2.7. Theoretical molecular weight

The theoretical M_n ($M_{n,th}$) was calculated based on the number of chains being dictated by the number of radicals generated from decomposition of AIBN and VPS (as opposed to the amount of SG1) because of the significant excess of SG1. VPS contains on the average eight azo moieties per molecule, and it was thus approximated that the decomposition of one azo moiety of VPS resulted in the generation of one polymer chain (because the majority of species generated during VPS decomposition originate from VPS segments with one azo group at each end). $M_{n,th}$ was thus calculated from Eq. (1):

$$M_{n,th} = X_{R,AIBN}MW_{R,AIBN} + X_{R,VPS}MW_{R,VPS} + \frac{m_S\alpha_S MW_S}{(8f_{N=N(VPS)}m_{VPS}/MW_{VPS}) + (2f_{AIBN}m_{AIBN}/MW_{AIBN})} \qquad (1)$$

Table 1
Polymerization conditions (110 °C)

Exp.	System	Description	VPS[a] (wt%)	[AIBN] (mM)	[MI][b] (mM)	No. fraction VPS chains[c]	[T]/[N=N][d]
1a	D[e]	VPS/SG1	5	–	–	100	3.5
1b	B[f]	VPS/TEMPO	20	–	–	100	1.8
1c	B	VPS_{ht}/TEMPO	20	–	–	100	1.3
2a	D	VPS/AIBN/SG1	1.5	3.73	–	5	1.3
2b	D	VPS/AIBN/SG1	1.5	3.73	–	5	1.8
2c	D	VPS/AIBN/SG1	1.5	2.29	–	5	3.5
3a	D	VPS/AIBN/SG1	8	2.27	–	22	1.8
3b	D	VPS/AIBN/SG1	11	1.61	–	37	1.8
3c	D	VPS/AIBN/SG1	14	1.34	–	48	1.8
3d	D	VPS/AIBN/SG1	20	0.76	–	72	1.8
4a	D	VPS_{ht}/AIBN/SG1	20	1.97	–	26	1.87
4b	D	VPS_{ht}/AIBN/SG1	10	2.22	–	12	1.87
4c	S[g]	VPS_{ht}/AIBN/SG1	15	2.09	–	18	1.87
5a	D	MI		–	4.53		[SG1]/[MI] = 0.1
5b	S[g]	MI		–	0.91		[SG1]/[MI] = 0.1

D, dispersion; B, bulk; S, solution.

[a] Relative to styrene.

[b] Based on $M_n = 16{,}600$ ($M_w = 23{,}200$).

[c] Number fraction of chains from VPS (or VPS_{ht}) based on relative numbers of chains generated by decomposition of AIBN and VPS (VPS_{ht}) using $f_{AIBN} = 0.83$ and $f_{N=N(VPS)}$ (and VPS_{ht}) = 0.24, and VPS and VPS_{ht} containing 8 and 2, respectively, azo moieties per molecule; $M_n(VPS) = 30{,}800$; $M_n(VPS_{ht}) = 21{,}800$.

[d] Ratio of concentration of nitroxide and azo moieties (i.e. total concentration in AIBN, VPS, VPS_{ht}).

[e] $[S]_0 = 1.92$ M in all $scCO_2$ dispersion polymerizations.

[f] 125 °C.

[g] $[S]_0 = 1.68$ M in toluene.

Table 2
Polymerization results

Exp.	Time (h)	Conv. (%)	Initial $R_p \times 10^6$ (M s^{-1})	M_n	$M_{n,th}$[a]	M_w/M_n
1a	18	19	6.2	57,200	20,600	2.19
1b	5	54		29,800	36,600	1.54
1c	5	28		43,900	56,200	1.51
2a	37	45		36,200	14,400	1.85
2b	24	35		16,200	11,200	1.41
2c	12	12		7600	6400	1.24
	24	20		16,700	10,400	1.44
	48	40		25,100	20,400	1.52
	168	36		23,200	18,400	1.58
3a	61	62		38,920	26,800	2.08
	109	64		35,640	27,600	2.68
3b	24	39	7.2	30,500	20,800	1.76
	52.5	47		50,900	24,600	1.98
3c	24	32	8.6	31,600	17,800	1.7
3d	12	22	11.3	26,900	14,100	1.76
	24	36		29,800	20,400	2.04
	52.5	68		49,900	34,600	2.25
4a	12	15	11.6	24,600	9000	1.39
	24	44		36,400	23,600	1.87
	36	54		41,000	28,000	2.14
	52.5	89		51,500	43,900	1.56
4b	24	30	8.0	27,800	16,400	1.60
4c	52.5	50		36,000	24,800	1.54
5a	24	26	7.4	46,400	43,900	1.64
	52.5	58		80,400	77,500	2.29
	113	78		95,000	98,500	2.41
5b	24	41		48,300	59,700	1.72

Polymerization conditions described in Table 1. Only the R_p values relevant to the discussion in the text are listed.
[a] See text for details on calculation of $M_{n,th}$.

where $X_{R,AIBN}$ and $X_{R,VPS}$ denote the molar fractions of radicals generated from AIBN and VPS, respectively (accounting for the values of f_{AIBN} and $f_{N=N(VPS)}$; $X_{R,AIBN}+X_{R,VPS}=1$), $MW_{R,AIBN}$ and $MW_{R,VPS}$ are the molar masses of radicals generated from AIBN and VPS, respectively ($MW_{R,VPS}=6020$), f_{AIBN} and $f_{N=N(VPS)}$ are the initiator efficiencies of AIBN and the azo moieties of VPS, respectively, m denotes initial mass of reagent, and is the S fractional conversion. It has been estimated that $f_{AIBN}=0.83$ in scCO$_2$ at 59.4 °C [27] and $f_{N=N(VPS)}=0.24$ in *i*-propanol at 75 °C [23]. $MW_{VPS}=30{,}800$ ($=M_n$); MW_{VPS} (heat treated) $=21{,}800$ ($=M_n$). However, even if the polymerization proceeds in an ideal controlled/living manner in accordance with Eq. (1), the experimental M_n will differ from $M_{n,th}$, because the fraction of radicals generated by VPS which do not initiate chains (as accounted for by the term $f_{N=N(VPS)}$) will still make a contribution towards to experimental MWD. The non-initiating VPS chains are oligomeric/polymeric unlike non-initiating low molecular weight radicals derived from AIBN. In addition, there will be an error associated with experimental MWs, as measurements are relative to linear PS standard equivalents. It is noted that the calculation of $M_{n,th}$ based on the number of consumed monomer units and the number of chains is the same as for a homogeneous (bulk, solution) system. The possibility of bimodal (broad) MWDs resulting from simultaneous polymerization in the solution phase and the particle phase does not in itself affect M_n (but does affect M_w), because the number of chains remains the same.

2.8. Molecular weight measurements

Molecular weights were measured by gel permeation chromatography (GPC) using two S/divinylbenzene gel columns (TOSOH Corporation, TSKgel GMHHR-H, 7.8 mm i.d × 30 cm) with THF as eluent at 40 °C at a flow rate of a 1.0 mL/min employing a refractive index detector (TOSOH RI-8020/21). The columns were calibrated with six linear PS samples (1.05×10^3–5.48×10^6, $M_w/M_n=1.01$–1.15).

3. Results and discussion

3.1. Polymerization using VPS/SG1

Dispersion polymerization in scCO$_2$ was carried out at 110 °C using the inistab VPS (5 wt% relative to S, **Exp. 1a**) and the nitroxide SG1 with a molar ratio $[\text{SG1}]/[(\text{N}=\text{N})_{\text{VPS}}]=3.5$. In the case of NMP systems with a high equilibrium constant, addition of extra nitroxide when using alkoxyamines for initiation (corresponding to use of a high $[\text{SG1}]/[(\text{N}=\text{N})_{\text{VPS}}]$) is a useful approach to achieve improved control [8,28]. The MWD obtained at 19% conversion was very broad and bimodal (Fig. 1(a)).

In an attempt to investigate if the heterogeneous nature of the polymerization contributed to the bimodal characteristics, bulk polymerization using TEMPO and VPS (20 wt% rel. to S) at 125 °C was carried out (**Exp. 1b**). This also resulted in a bimodal MWD, suggesting that it was not due specifically to the heterogeneity of the system, but is a feature of the inistab (Fig. 1(b)). The inistab used, VPS, contains on average eight azo moieties per molecule, and thermal decomposition results in species that can grow from one end (the 'end groups' of the macroinitiator), but the majority of species may grow from both ends. The MWs of the peaks of the bimodal MWD differ by close to a factor of two, suggesting that the bimodality was a result of chains growing from one or both ends. Similar MWDs have been observed previously when using VPS in NMP [29]. An additional contributing factor to MWD broadening may be bimolecular termination by combination, which in the case of difunctional chains leads to the formation of 'living' chains of twice the molecular weight [30].

3.2. Polymerization using VPS/AIBN/SG1

In order to reduce the relative number of chains able to grow from both ends and thus reduce the bimodal character of the MWDs, polymerizations were carried out using AIBN and only 1.5 wt% VPS relative to S. Based on $f_{\mathrm{AIBN}}=0.83$ and $f_{\mathrm{N=N(VPS)}}=0.24$, approximately 95% of the chains would be initiated by AIBN (Table 1—**Exp. 2a–c**). In the case of conventional free radical dispersion polymerization of MMA initiated by AIBN in scCO$_2$, this level of VPS was sufficient to achieve satisfactory stabilization [26]. The effect of the molar ratio [SG1]/[I], where $[\mathrm{I}]=[(\mathrm{N=N})_{\mathrm{VPS}}]+[\mathrm{AIBN}]$, was investigated using ratios of 1.3, 1.8 and 3.5 (at 1.5 wt% VPS, **Exp. 2a–c**). The pronounced bimodal character of the MWDs disappeared for the ratios 1.8 and 3.5, with only the sample with the lowest ratio of 1.3 exhibiting a bimodal MWD (Fig. 2(a)). The values of M_w/M_n improved by increasing [SG1]/[I] from 1.3 to 1.8, but a further increase to 3.5 did not result in any significant improvement (Table 2). The value of M_n deviated significantly from $M_{n,\mathrm{th}}$ for [SG1]/[I] = 1.3, but relatively good agreement was observed for [SG1]/[I] = 1.8 and 3.5. The MWDs as a function of conversion for [SG1]/[I] = 3.5 are displayed in Fig. 2(b). Although the MWDs are relatively narrow, tailing on the low MW side is clearly visible except at the lowest conversion. Proper normalization of the MWDs (adjusting the area of the RI detector response vs. elution time to be proportional to the total mass of polymer before transformation to $w(\log M)$ vs. $\log M$ [31]) enables quantitative comparison of the MWDs. The low MW tail did not change significantly (in amount or MW) with conversion, thus suggesting that it consists of mainly dead polymer. However, chain extension using the polymer at 20% conversion (**Exp. 2c**) resulted in a clear shift to higher MW, indicating the vast majority of chains were capped by SG1 and thus 'living' (Fig. 3(a)). The polymerization ceased at approximately 40% conversion (**Exp. 2c**, [SG1]/[I] = 3.5), indicative of insufficient stabilization leading to coagulation and lower final conversion [4,15]. The long polymerization time may have also led to some decomposition of the nitroxide, hence the increase in MWD [32]. Thus, although decreasing the amount of VPS relative to AIBN leads to greater control as indicated by lower M_w/M_n

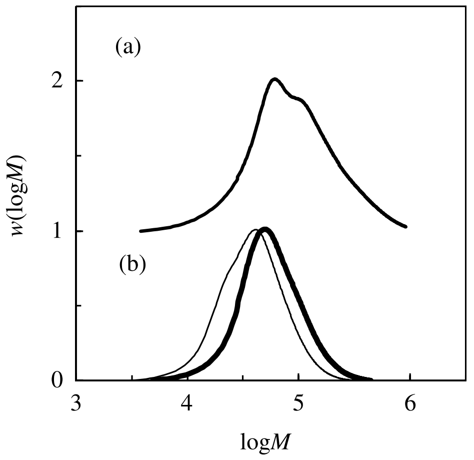


Fig. 1. (a) MWD of dispersion polymerization of S in scCO$_2$ using VPS (no AIBN) and SG1 at 110 °C (**Exp. 1a**; 19% conv.) (b) MWDs (normalized to peak height) of bulk polymerizations of S using VPS (no AIBN) and TEMPO (thin line; **Exp. 1b**; 54% conv.) and VPS$_{\mathrm{ht}}$ and TEMPO (thick line; **Exp. 1c**; 28% conv.).

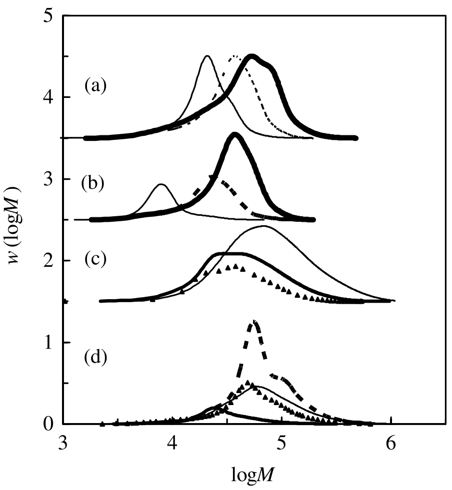


Fig. 2. MWDs of dispersion polymerizations of S in scCO$_2$ at 110 °C at different wt% VPS and [SG1]/[I] ratios. (a) 1.5 wt% VPS, [SG1]/[I] = 1.3 (thick line; **Exp. 2a**; 45% conv.), 1.8 (thin line; **Exp. 2b**; 35% conv.), 3.5 (dashed line; **Exp. 2c**; 40% conv.). MWDs normalized to peak height. (b) 1.5 wt% VPS, [SG1]/[I] = 3.5, **Exp. 2c**; 12% conv. (thin line), 20% conv. (dotted line), 40% conv. (thick line). (c) 20 wt% VPS, [SG1]/[I] = 1.8, **Exp. 3d**; 22% conv. (dashed line), 36% conv. (thin line), 68% conv. (thick line). (d) 20 wt% VPS$_{\mathrm{ht}}$, **Exp. 4a**; 15% conv (thick line), 44% conv. (triangles), 54% conv. (thin line), 89% conv. (broken line). Areas of GPC elution traces normalized to weight of polymer in polymerization mixture prior to transformation to $w(\log M)$ vs. $\log M$.

(as low as 1.24 with 1.5% VPS and [SG1]/[I] = 3.5), the limiting conversion is reduced due to insufficient stabilization.

In order to achieve high conversion and recover the polymeric product as a powder, dispersion polymerizations were carried out at higher inistab contents (8–20 wt% VPS, **Exp. 3a–d**). The amount of AIBN was adjusted in order for $M_{n,th}$ to remain the same ([SG1]/[I] = 1.8). High conversions were obtained, but the high amounts of VPS required for efficient stabilization resulted in broad bimodal MWDs (Table 2 and Fig. 2(c)). A significant decrease in R_p (see discussion below) was observed using 11 wt% VPS (**Exp. 3b**) in comparison with higher VPS contents, and the MWD was clearly bimodal at 14 wt% VPS (MWD not shown). The results are consistent with the expected relative number of chains from AIBN and VPS; in all **Exp. 3a–d**, both AIBN and VPS make significant contributions towards the number of chains, thus leading to bimodal MWDs (Table 1). The polymerization with 20% VPS reached the relatively high conversion of 68% after 52.5 h, and the polymer was obtained as a white powder. This was not the limiting conversion; the corresponding first-order plot is linear, indicating that longer polymerization times would lead to higher conversions. In the case of 20 wt% VPS, M_n increased linearly with conversion but was significantly higher than $M_{n,th}$ (Table 2). However, this may well originate in errors in $M_{n,th}$ due to the uncertainties involved in the calculation rather than being indicative of the controlled/living polymerization mechanism deviating from ideality.

The rates of polymerization (R_p) were estimated by multiplying the slopes of the first order plots with the initial S concentration (Table 2). The applicability of first-order kinetics is questionable due to the loci of polymerization being in both the continuous phase and the particles [33–35]. However, it does serve the purpose of somewhat crudely comparing R_p for different conditions. The values of R_p increased with increasing VPS content, consistent with earlier work which has established that R_p and the limiting conversion decrease as coagulation increases, i.e. as the amount of stabilizer is decreased [3,4,15,26].

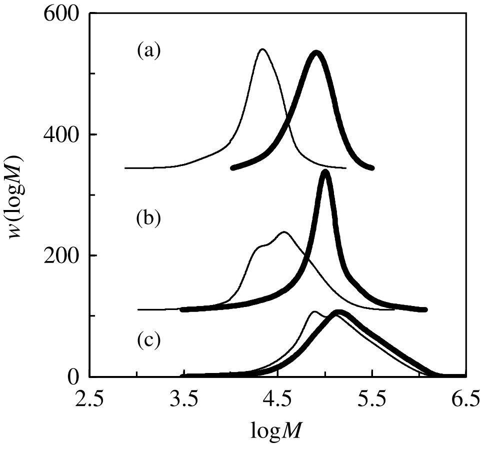


Fig. 3. Chain extensions with S at 110 °C. (a) MWD of original polymer (thin line; **Exp. 2c**; 20% conv.) and polymer after chain extension for 1.5 h (thick line; 15% conv., $M_n = 61,400$; $M_w/M_n = 1.32$). (b) MWD of original polymer (thin line; **Exp. 4a**; 15% conv.) and polymer after chain extension for 6 h (thick line; 24% conv., $M_n = 63,800$; $M_w/M_n = 1.79$). (c) MWD of original polymer (thin line; **Exp. 5a**; 58% conv.) and polymer after chain extension for 6 h (thick line; 17% conv., $M_n = 99,000$; $M_w/M_n = 2.43$).

3.3. Polymerization using VPS_{ht}/AIBN/SG1

In order to achieve low M_w/M_n coupled with optimum stabilization, the number of azo moieties in the VPS was reduced. This would result in a reduction in the relative number of chains able to grow from both ends, which is thought to be the main cause of the broad MWDs, while maintaining high levels of stabilizer. The number of azo moieties was reduced by heat treatment of VPS at 70 °C for 12 h. Based on $k_d = 6.5 \times 10^{-5}\ s^{-1}$ in *i*-propanol at 75 °C [23] for the VPS azo moieties and assuming an activation energy of 130 kJ mol^{-1}, approximately 75% of the azo moieties decomposed. The MWDs of the original VPS ($M_n = 30,800$) and the VPS obtained after heating (VPS_{ht}; $M_n = 21,800$) were relatively similar, although that of VPS_{ht} was somewhat broader (Fig. 4). The majority of radical species generated during the heat treatment would be expected to undergo combination or disproportionation. The broadening may originate from disproportionation involving shorter chains and combination involving longer chains. The possible occurrence of disproportionation is an inherent disadvantage, because the thus generated terminal double bonds may copolymerize with S. Moreover, disproportionation of monoradicals during the heat treatment would result in species incapable of initiation. However, model compound studies have indicated combination is the main pathway for methacrylonitrile-terminated species [36].

Bulk polymerization using VPS_{ht} and TEMPO (no AIBN) resulted in MWD with significantly less bimodal

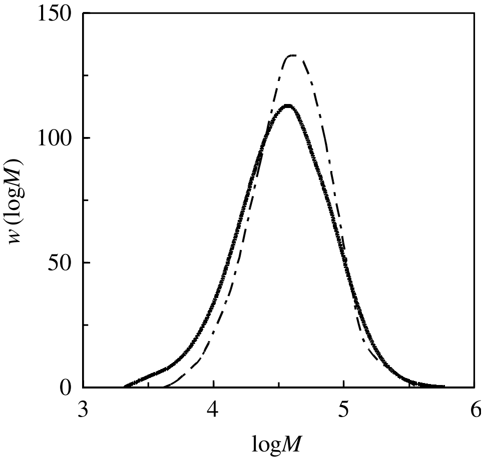


Fig. 4. MWDs of VPS (dashed line; $M_n = 30,800$, $M_w/M_n = 1.59$) and VPS_{ht} 'heat treated' (thick line; $M_n = 21,800$; $M_w/M_n = 2.76$). GPC elution traces normalized to same area before transformation to $w(\log M)$ vs. $\log M$.

features compared with a similar bulk polymerization with VPS (**Exp. 1c**, Fig. 1(b)). Dispersion polymerizations in $scCO_2$ were therefore carried out with 10 and 20 wt% VPS_{ht} and AIBN with [SG1]/[I] = 1.87 (**Exp. 4a** and **b**). The calculations of $M_{n,th}$ were based on VPS_{ht} containing two azo moieties per chain, i.e. a 75% reduction from eight. Compared to the VPS/AIBN polymerizations, the relative number of chains able to grow from both ends was further reduced due to the increased molar fraction of AIBN required (relative to VPS) in order for $M_{n,th}$ to be the same as for VPS (Table 2). However, some broadening may be caused by the large difference in MW of the initiating radical from AIBN and that of VPS_{ht}. Polymerization with 20 wt% VPS_{ht} (**Exp. 4a**) proceeded to high conversion (89% in 52.5 h) yielding polymer as a white powder with markedly lower M_w/M_n ($M_w/M_n = 1.39$ at 15% conversion) than the experiment containing non-heat treated VPS (**Exp. 3d**, Table 2 and Fig. 2). However, at higher conversions, the MWDs were still relatively broad and in particular the sample at 89% was clearly bimodal as might be expected considering that approximately 58% of the chains would originate from VPS_{ht}. The M_n values increased close to linearly with conversion, although the values were consistently higher than $M_{n,th}$. However, as mentioned earlier, there is considerable uncertainty involved in the calculation of $M_{n,th}$, especially at high VPS (VPS_{ht}) contents. Chain extension in bulk using the polymer sample at 15% conversion (**Exp. 4a**) revealed that the vast majority of chains appeared to be 'living' (Fig. 3(b)). The M_w/M_n for 10 wt% VPS_{ht} (**Exp. 4b**) was also somewhat lower than for the polymerization with 11% VPS (**Exp. 3b**).

The R_p values were similar to those for non-heat treated VPS (Table 2), with 20 wt% VPS_{ht} being significantly faster than the polymerizations at lower VPS_{ht} contents. A solution polymerization (80% toluene) with 15 wt% VPS_{ht} (**Exp. 4c**) also resulted in a broad MWD, again indicating that the bimodality is not a problem that is inherent to the dispersion polymerization.

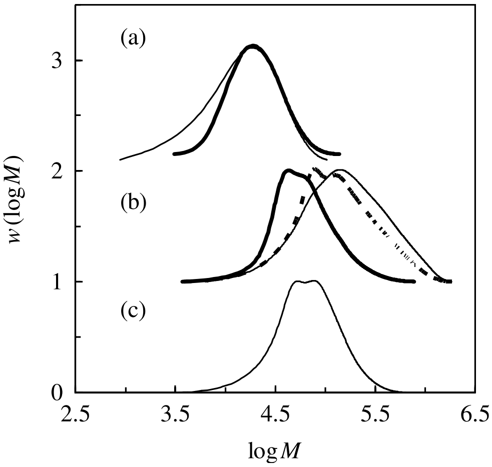


Fig. 5. (a) MWD of fractionated SG1-PS-PDMS-PS-SG1 (MI) (thick line), $M_n = 16{,}600$; $M_w/M_n = 1.40$, and non-fractionated (thin line) MI, $M_n = 9670$, $M_w/M_n = 1.96$. (b) MWD of $scCO_2$ dispersion polymerization of S using fractionated MI at 110 °C (**Exp. 5a**); 26% conv. (thick line), 58% conv. (dashed line), 78% conv. (thin line). (c) MWD of toluene solution polymerization of S using fractionated MI at 110 °C (**Exp. 5b**).

3.4. Polymerization using alkoxyamine-inistab

The MWD of the high MW fraction of the inistab, isolated by selective extraction, is displayed in Fig. 5(a) ($M_n = 16{,}600$; $M_w/M_n = 1.39$). It was anticipated that the contribution of chains with only one alkoxyamine functionality (corresponding to the mono-radicals generated on decomposition of VPS) would be minimized by removal of the low MW fraction. The majority of chains are thus expected to have the structure SG1-PS-PDMS-PS-SG1. Polymerization were carried out with $M_{n,th}$ (100% conv.) = 121,600 in the presence of 0.1 molar equivalents of SG1 (relative to macroinitiator; **Exp. 5a**). The results were similar to those obtained with VPS (and VPS_{ht}) and AIBN in terms of the broad MWDs (Fig. 5(b)), however, there was much improved agreement between M_n and $M_{n,th}$. Polymerization in toluene (**Exp. 5b**) using the same recipe as for the dispersion polymerization resulted in a very similar MWD (Fig. 5(c)). It can again be concluded that the bimodal feature of the MWD is not specifically associated with the heterogeneous polymerization. The likely reason for the bimodality is that the macroinitiator contains a significant number of chains that have only one alkoxyamine functionality and not the idealized two living ends. The value of R_p was similar to that of the polymerizations with 0–15 wt% VPS and VPS_{ht}.

Chain extension with S in toluene using the polymer sample at 58% conversion (**Exp. 5a**) again revealed that the vast majority of chains appeared to be 'living' (Fig. 3(c)). The very high degree of 'livingness' in the chain extensions may be related to the difunctional nature of the alkoxyamine MI [30]. Bimolecular termination or side reactions such as the decomposition of an alkoxyamine moiety into a hydroxylamine and unsaturated polymer [37] only leads to dead polymer for the chains with a single alkoxyamine moiety.

3.5. Particle size and morphology

Scanning electron micrographs of the polymer particles obtained at 68% conversion in the polymerization with VPS (20 wt% rel. S)/AIBN/SG1 (**Exp. 3d**) are displayed in Fig. 6. The particles are highly non-spherical and irregularly shaped. Non-spherical (but significantly smaller) particles resulted from the dispersion ATRP of MMA in $scCO_2$ at 65 °C using a bromine-terminated PDMS inistab species [16]. The appearance of the polymer particles in Fig. 6 is somewhat similar to that of the PS obtained by TEMPO-mediated precipitation polymerization in ethylene glycol/water [18], possibly indicating that the stabilization in the current study has been imperfect and significant coagulation has occurred. Attempts to redisperse the polymer particles in *n*-hexane were unsuccessful. The fact that a significant number of chains would grow from both ends leads to polymer where both ends (the PS parts) would be anchored in the particle, whilst the middle part of the chain extends into the $scCO_2$ medium. This may lead to a reduced thickness of the colloidal protective layer, and thus less effective stabilization [6]. The morphology may also be affected by the process of CO_2 removal because PS particles swell to a highly plasticized state in $scCO_2$. It has previously been speculated that the very broad particle size distributions (50 nm–10 μm) obtained in the attempted dispersion polymerization of the TEMPO/S system in *n*-decane at 135 °C was related to partial solubility of PS chains at the high temperature and relatively low molecular weights (compared to a conventional free radical polymerization), resulting in some particle formation on cooling [20], and it is possible that similar mechanisms are at play in the current study.

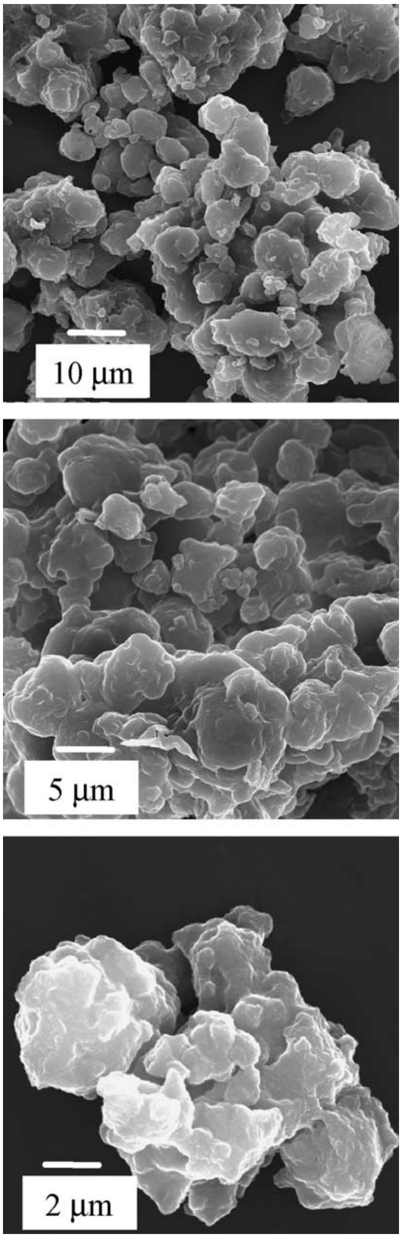


Fig. 6. SEM photographs of polymer particles obtained by nitroxide-mediated (SG1) free radical dispersion polymerization of St in scCO2 at 110 °C at 68% conv. (**Exp. 3d** in Tables 1 and 2).

4. Conclusions

It has been demonstrated for the first time that control/living character can be obtained in nitroxide-mediated free radical dispersion polymerizations of styrene in supercritical carbon dioxide. Polymerizations were carried out at 110 °C using the nitroxide *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1). A poly(dimethylsiloxane) (PDMS) based azo initiator (VPS) as well as a polymeric alkoxyamine macroinitiator were employed, both having the dual functions of initiator and stabilizer (inistab). A series of polymerizations using VPS, AIBN and SG1 in different stoichiometric ratios indicated that, provided that there is a sufficient amount of VPS present, polymerizations reach high conversion. A high degree of 'livingness' was demonstrated by the number-average molecular weights increasing linearly with conversion in reasonable agreement with the theoretical values, and successful chain extensions in solution or bulk. However, in many cases, the molecular weight distributions were relatively broad, although $M_w/M_n > 1.4$ was obtained at low conversions when a small amount of inistab ($VPS = 1.5\%$) and preliminary heat treatment of inistab ($VPS_{ht} = 20\%$) was carried out, respectively. Dispersion polymerization using a polymeric alkoxyamine macroinitiator with the expected structure SG1-polystyrene-PDMS-polystyrene-SG1 also proceeded to high conversion with high degree of 'livingness', but with broad molecular weight distributions. The broad molecular weight distributions are thought to be mainly caused by the simultaneous presence of species that are able to grow from one or both ends, and possibly also with some contribution from bimolecular termination (combination) of difunctional chains (which does not lead to dead polymer).

Acknowledgements

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