Macromolecules **1998,** *31,* 2883−2888

Living Free-Radical Dispersion Polymerization of Styrene

Laurence I. Gabaston, Richard A. Jackson, and Steven P. Armes*

School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.

Received December 23, 1997; Revised Manuscript Received March 4, 1998

ABSTRACT: Polystyrene latexes were synthesized via living free-radical chemistry with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in both alcoholic and aqueous alcoholic media using poly(*N*-vinylpyrrolidone) (PVP) as a steric stabilizer at 112−130 °C. Genuine dispersion polymerization was only achieved in ethylene glycol or ethylene glycol−water mixtures. In the absence of TEMPO, near-quantitative monomer conversions, high molecular weights, broad molecular weight distributions, and submicrometer-sized latexes were obtained. The addition of TEMPO had a profound effect on the polymerization chemistry: only moderate monomer conversions (as low as 20%, with a maximum conversion of 60% obtained after 71 h) and larger, typically micrometer-sized, latexes were obtained with TEMPO-mediated syntheses. Polydispersities (M_w/M_n's) as low as 1.11 were achieved in the presence of TEMPO, but only relatively low molecular weight polystyrene chains were obtained. All TEMPO-synthesized latexes had spherical particle morphologies and very broad size distributions, as evidenced by scanning electron microscopy (SEM) and disk centrifuge photosedimentometry (DCP), respectively. Surprisingly, high Γ values were calculated for the adsorbed PVP stabilizer, which suggests that it is not located exclusively on the outside of the polystyrene latex particles.

Introduction

In dispersion polymerization the monomer and polymeric stabilizer are both soluble in the continuous phase. As polymerization proceeds, the monomer is converted into insoluble polymer and phase separation occurs. The stabilizer adsorbs onto the resulting microscopic polymer nuclei and prevents macroscopic precipitation via a steric stabilization mechanism. In some cases it is believed that polymerization occurs in the monomer-swollen particles. At the end of the polymerization a stable colloidal dispersion of polymer latex particles is obtained.

Usually, dispersion polymerization is achieved using conventional free-radical chemistry, but in recent years several research groups have explored the possibility of using "living" polymerization techniques. For example, Schwab and Murray[1] described the anionic dispersion polymerization of styrene in nonpolar media. Similarly, Jenkins and co-workers[2] polymerized methyl methacrylate in *n*-heptane via so-called group transfer polymerization (GTP). In both cases poly(styrene-*block*-propylene-*alt*-ethylene) "Kraton" block copolymers were used as steric stabilizers. In theory, the application of living polymerization techniques should allow the synthesis of near-monodisperse latex particles comprising chains of narrow molecular weight distribution. Furthermore, the problem of secondary particle nucleation, which often occurs when further monomer is added to a conventional dispersion polymerization, can be avoided. Recently, both these principles have been elegantly demonstrated by Awan and co-workers,[3] who polymerized styrene in *n*-hexane at 28 °C using classical "living" anionic chemistry in the presence of a polystyrene-*block*-polybutadiene "Stereon" stabilizer. Similar results have also been reported by Slomkowski's group,[4,5] who polymerized both ϵ-caprolactone and L,L-lactide via anionic ring-opening chemistry in a mixed solvent medium. These studies are undoubtedly of considerable academic interest, but given its sensitivity to protic impurities such as water, it is rather unlikely that anionic polymerization chemistry would be sufficiently robust to allow latex syntheses on an industrial scale. On the other hand, the pseudoliving free-radical polymerization chemistry recently pioneered by Georges and co-workers[6,7] for styrenic monomers can be carried out in water−alcohol mixtures. Here 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) acts as a reversible capping agent for the growing polystyrene radicals and hence greatly suppresses chain termination reactions.

Very recently, Mülhaupt and co-workers[8] reported using TEMPO-mediated free-radical chemistry for the attempted dispersion polymerization of styrene in *n*-decane at 135 °C using a "Kraton" stabilizer. Only three latex syntheses were reported, yielding polymers with polydispersities of 1.29, 1.41, and 1.52, respectively. In each case, narrower polydispersities were obtained in bulk polymerizations conducted in the absence of stabilizer and electron microscopy studies revealed very broad particle size distributions (50 nm to 10 μm). In one latex synthesis (D22) turbidity was not observed until the extent of styrene polymerization had exceeded 30%. This strongly suggests that, initially at least, only solution polymerization occurred. Indeed, this possibility was conceded by the German group. Clearly, at the relatively high reaction temperature of 135 °C (which is required for successful TEMPO-mediated styrene polymerizations[9]) the *n*-decane is a reasonable solvent for the growing low molecular weight polystyrene chains. Indeed, Mülhaupt and co-workers state explicitly that a possible explanation for the observed broad latex size distributions "may be partial solubility of polystyrene chains, enhanced by high reaction temperature and styrene content and low molar masses, thus leading to particle formation on cooling." In recent unpublished work we investigated the TEMPO-mediated polymerization of styrene in *n*-octane, *n*-nonane, and *n*-dodecane using the same Stereon stabilizer as

---

* To whom correspondence should be addressed.

S0024-9297(97)01856-1 CCC: $15.00

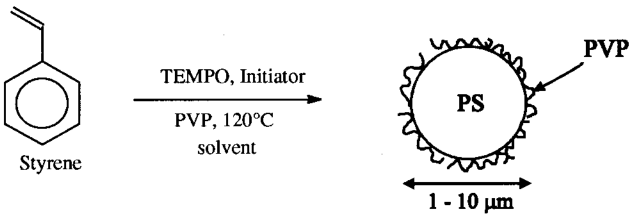

Figure 1. Schematic formation of PVP-stabilized polystyrene latex via dispersion polymerization using TEMPO-mediated free-radical chemistry.

described by Awan et al.[3] We concluded that the solubility of the polystyrene chains in the continuous phase was too high for such syntheses to be termed genuine “dispersion” polymerizations.

In this paper we report our latest attempts to exploit TEMPO-mediated living free-radical chemistry for the dispersion polymerization of styrene in *alcoholic* and *aqueous alcoholic* media (see Figure 1). This continuous phase was selected since it is a markedly poorer solvent for polystyrene than *n*-alkanes. Poly(*N*-vinylpyrrolidone) (PVP) was chosen as a steric stabilizer since it had been previously used by both ourselves and several other research groups[10−12] for the synthesis of near-monodisperse micrometer-sized polystyrene latexes *via* conventional nonliving free-radical chemistry.

Experimental Section

All reagents were purchased from Aldrich, except PVP (MW 40 000; Fluka). Styrene was purified by passing through an alumina column to remove inhibitor. The general procedure used to prepare the polystyrene latexes in aqueous ethylene glycol was based in part on the formulation described by the Xerox group for the *solution* polymerization of sodium 4-styrenesulfonate.[7] When using aqueous ethylene glycol media, the styrene (10.0 g), poly(*N*-vinylpyrrolidone) (1.00 g), sodium bisulfite (0.17 g), and TEMPO (0.375 g) were added to the aqueous ethylene glycol mixture (75−95% ethylene glycol; 80 cm^3) at room temperature under nitrogen. When using alcoholic solvents, styrene (10.0 g), PVP$_{360\,000}$ (2.00 g), and TEMPO (0.040 g) were dissolved in 50 cm^3 of the appropriate alcohol (*n*-butanol, *n*-pentanol, *n*-octanol, ethylene glycol) at room temperature under nitrogen. Potassium persulfate (0.33 g; for aqueous ethylene glycol media) and benzoyl peroxide (0.053 g, alcoholic media) were added at 60 and 90 °C, respectively, and aged under nitrogen for 1 h at these temperatures. In each case the temperature was then raised to 120 °C and the reaction was stirred for 24−96 h, after which the resulting latex particles were centrifuged and redispersed in methanol. This centrifugation/redispersion cleanup cycle was repeated twice to ensure removal of any excess stabilizer and unreacted styrene monomer. When the TEMPO adduct 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane, synthesized as described by Hawker et al.,[13] was used as initiator, the following procedure was used: styrene (10 g, 9.6×10^{-2} mol), TEMPO adduct (0.129 g, 4.9×10^{-4} mol), PVP (1.008 g, 12.6 g L^{-1}), and aqueous ethylene glycol (80 cm^3) were stirred together under nitrogen at 120 °C for 24 h. The particles obtained were then purified as described above. In all runs the conversion of styrene to polystyrene was calculated by gravimetry.

Disk centrifuge photosedimentometry (DCP) was used to assess the weight-average particle diameter and polydispersity of the polystyrene latexes. The centrifugation rate was adjusted depending on the size of the latex particles being measured. Typically, centrifugation rates of around 2000−4000 rpm were used for latexes greater than 1 μm in diameter and 6000−10 000 rpm for the smaller latexes. The densities of the dried latexes were measured by helium pycnometry.

Molecular weights were determined by gel permeation chromatography (GPC) using two PLgel 3 μm Mixed “D” and Mixed “E” columns (Polymer Labs) and a refractive index detector. Polystyrene calibration standards (MW 220 500−2850) were used with a THF mobile phase at a flow rate of 1 mL/min.

Scanning Electron Microscopy (SEM). Morphology studies were carried out using a Leica Stereoscan 420 instrument operating at 20 kV with a probe current of 10 pA. The samples were mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample-charging problems.

FTIR spectra (Specac diamond ATR “golden gate” accessory) of the dried latexes were recorded using a Nicolet Magna 550 series II instrument, and their specific surface areas were determined using a Quantachrome NOVA 1000 semiautomated BET instrument using a nitrogen adsorbate at 77 K. Elemental microanalysis studies were performed by Medac Ltd.

Results and Discussion

Latex Syntheses in Alcoholic Media. Styrene was polymerized in various alcohols using PVP as a steric stabilizer (see Table 1). A broad molecular weight distribution ($M_w/M_n = 1.69$) and a relatively high molecular weight (15 600) were obtained for conventional free-radical polymerization in the absence of TEMPO, as expected (see entry 1 in Table 1). The mean latex diameter (D_w) was ca. 0.5 μm, and a relatively broad DCP size distribution was obtained ($D_w/D_n = 1.3$). The polydisperse nature of this latex is most likely due to the relatively high polymerization temperature employed compared to the literature.[10−12] On the other hand, addition of the TEMPO capping agent produced polystyrene chains with reasonably narrow molecular weight distributions (entries 2−5) and, with the exception of the last entry, significantly lower molecular weights than obtained in the absence of TEMPO. Visual inspection of these latex syntheses confirmed that no turbidity was observed at the polymerization temperature of 120 °C; particle formation only occurred on cooling the reaction solutions. Thus, styrene polymerization generally occurred in *solution*; no doubt this is due to the increased solubility of the low molecular weight polystyrene chains in the various *n*-alcohols at elevated temperature. It is also consistent with the relatively broad latex size distributions obtained. The exception is the latex synthesized in ethylene glycol (last entry in Table 1). In this case turbidity was observed at the polymerization temperature, as expected for a genuine dispersion polymerization. The higher molecular weight of 23 100 obtained under these conditions is also consistent with this hypothesis. It is noteworthy that the characteristics of the solution-polymerized latexes are generally quite similar to those reported by Mulhaupt and co-workers for their latex syntheses in *n*-decane.

Latex Syntheses in Aqueous Ethylene Glycol. In view of the relatively high viscosity of ethylene glycol, and given that the Xerox group had reported[7] high conversions for the solution polymerization of sodium 4-styrenesulfonate in a 3:1 ethylene glycol−water solution, it was decided to explore the dispersion polymerization of styrene in ethylene glycol−water mixtures. Since water is a very poor solvent for polystyrene, its addition should allow genuine dispersion polymerization conditions to be maintained. PVP was again used as the steric stabilizer. The styrene monomer was initially immiscible in the aqueous ethylene glycol mixture up to 60 °C but it became miscible (a necessary condition

Table 1. Effect of Varying the Alcoholic Dispersion Medium on the Molecular Weight, Molecular Weight Distribution, Particle Size and Particle Size Distribution of the PVP-Stabilized Polystyrene Latexes ([PVP] = 40 g L^{-1}, Temperature 115–120 °C, TEMPO/Initiator Molar Ratio = 1.2)

styrene conc (mol/L)	TEMPO added?	alcohol	time (h)	M_n	M_w/M_n	D_w[a] (μm)	D_w/D_n
1.9	no	*n*-pentanol	24	15600	1.69	0.5	1.3
1.9	yes	*n*-pentanol	24	1600	1.11	0.8[b]	2.1
1.9	yes	*n*-butanol	96	3400	1.22	6.0	1.3
1.9	yes	*n*-octanol	24	1000	1.06	1.4[b]	2.5
1.9	yes	ethylene glycol	24	23100	1.28	1.8	2.3

[a] As determined by disk centrifuge photosedimentometry. [b] Bimodal size distribution indicated by DCP.

Table 2. Effect of Varying Synthesis Parameters on the Polystyrene Molecular Weight, Molecular Weight Distribution, and Latex Particle Diameter ([Styrene] = 1.2 mol L^{-1}, TEMPO/Initiator Molar Ratio = 2, Reaction Time 24 h, Temperature 112–130 °C (Depending on Ethylene Glycol–Water Composition))

exp no.	EG/H_2O w/w %	added nitroxide?	$PVP_{360\,000}$ conc (g/L)	% conversion	M_n	M_w/M_n	BET surface area (m^2g^{-1})	particle diameter[a] (μm)	% PVP in latex[b]	Γ[a] (mg/m^2)
1	75:25	none	12.6	35	23400	3.01	27.0	0.20	6.8	2.69
2	75:25	TEMPO	0	20	2800	1.15	0.4	precipitate		
3	75:25	TEMPO	12.6	17	4600	1.25	7.3	0.73	5.0	7.34
4	85:15	TEMPO	12.6	25	2200	1.12	3.6	1.50	3.2	9.11
5	95:5	TEMPO	12.6	45	7200	1.30	10.0	0.53	5.1	5.23
6	95:5	TEMPO adduct	12.6	54	13400	1.31	1.5	3.64	2.3	15.14

[a] Mean particle diameter (*d*) calculated from the BET surface area (A_s) using $A_s = 6/(\rho \cdot d)$, where ρ is the density of polystyrene as measured by helium pycnometry. Γ values were calculated using the BET surface areas in combination with the corresponding PVP contents. It was assumed that all of the PVP was on the outside of the PS latex. [b] Calculated from CHN microanalyses, allowing for the nitrogen content of the polystyrene chains due to TEMPO.

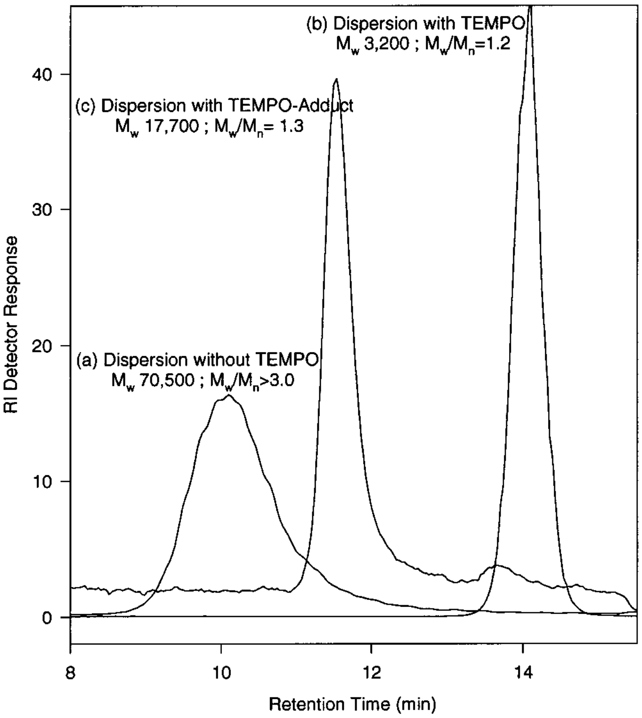

Figure 2. GPC analyses of selected polystyrene latexes obtained using (a) conventional free-radical polymerization in the absence of TEMPO and (b) TEMPO-mediated and (c) TEMPO-adduct living free-radical polymerization in ethylene glycol–water mixtures at 120 °C using a PVP steric stabilizer.

for dispersion polymerization) at and above 110 °C. Our results are summarized in Table 2.

A broad molecular weight distribution ($M_w/M_n = 3.01$; see entry 1 in Table 2 and the GPC trace in Figure 2) was obtained for the conventional free-radical polymerization of styrene in the absence of TEMPO, as expected.[14] Again, the polydisperse particle size distribution found for this latex (D_w/D_n = 1.71 by DCP) is probably due to the relatively high reaction temperature utilized compared to the literature.[10–12] In contrast, addition of TEMPO produced relatively narrow molecular weight distributions ($M_w/M_n \sim 1.12$ to 1.31; see Figure 2), which are characteristic of a “pseudo-living” polymerization.[6] Assuming 100% conversion, the theoretical polystyrene molecular weight calculated from the styrene/TEMPO molar ratio is 4100 (i.e., a DP of 40 styrene units). However, polystyrene molecular weights obtained from GPC were in the 2800–7200 range. Since conversions were low (17–45%), this suggests inefficient initiation. Similar results have been obtained by Keoshkerian et al. for the solution polymerization of sodium 4-styrenesulfonate.[7]

Entry 2 in Table 2 refers to a styrene polymerization carried out in the presence of TEMPO but in the absence of PVP stabilizer. As expected, macroscopic precipitate was recovered, rather than a stable latex. As far as we are aware, this is the first example of a precipitation polymerization using TEMPO chemistry. GPC analysis of this precipitated polystyrene in THF indicated a rather low molecular weight polystyrene with a relatively narrow molecular weight distribution (M_w/M_n = 1.15). SEM studies of this precipitate revealed a featureless, amorphous morphology with no discernible grain size (see Figure 3b). These observations are consistent with the relatively low BET surface area of 0.40 m^2 g^{-1} determined for this material.

As the proportion of ethylene glycol in the dispersion medium was increased from 75% to 95% (entries 3–5 in Table 2), the reflux temperature of the solvent mixture could be increased from 112 to 130 °C). This led in turn to an increase in conversion from 17 up to 45%. In fact, problems were encountered with the aqueous ethylene glycol mixtures due to the immiscibility of the styrene monomer in this mixed solvent at temperatures below 110 °C. This is consistent with the precipitation of polystyrene chains of relatively low molecular weight.

The average particle diameter of the polystyrene latex synthesized in the absence of TEMPO is 0.20 μm. This value was calculated from its BET surface area using $A_s = 6/(\rho d)$, where A_s is the specific surface area, ρ is

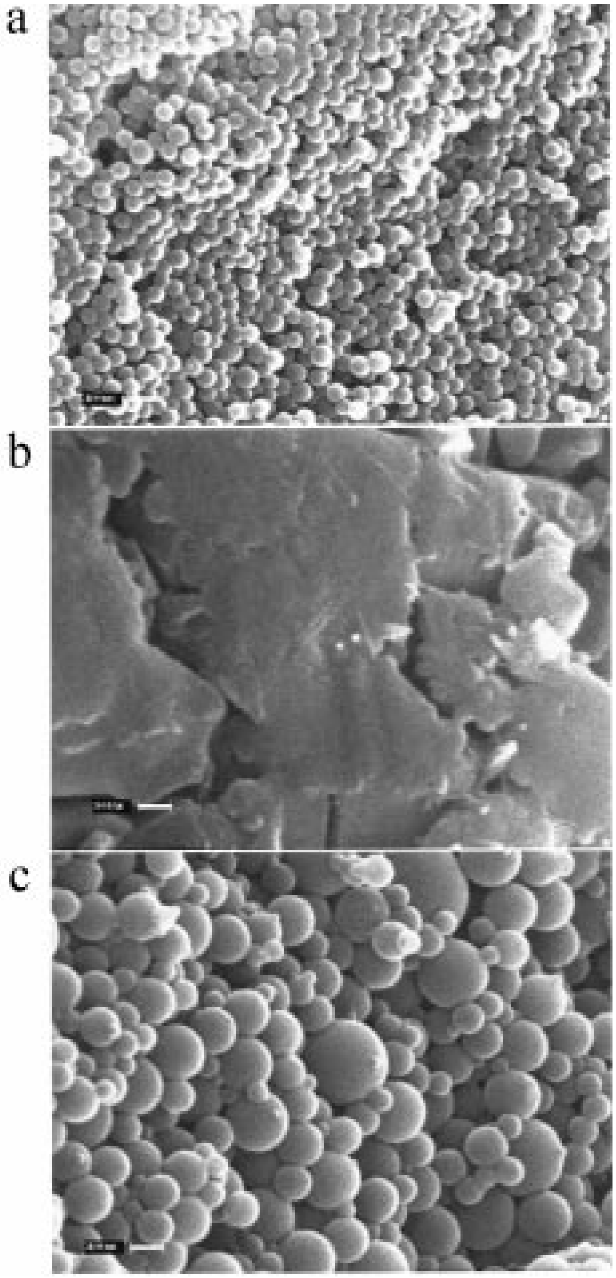

Figure 3. Scanning electron micrographs of (a) polystyrene latex obtained by conventional nonliving free-radical dispersion polymerization in 75:25 ethylene glycol−water using $PVP_{360\,000}$ (entry 1 in Table 2), (b) polystyrene synthesized by TEMPO free-radical precipitation polymerization in 75:25 ethylene glycol−water without stabilizer (entry 2 in Table 2), and (c) particles obtained by living free-radical dispersion polymerization of styrene in 95:5 ethylene glycol−water using $PVP_{360\,000}$ stabilizer. The scale-bars represent 300 nm.

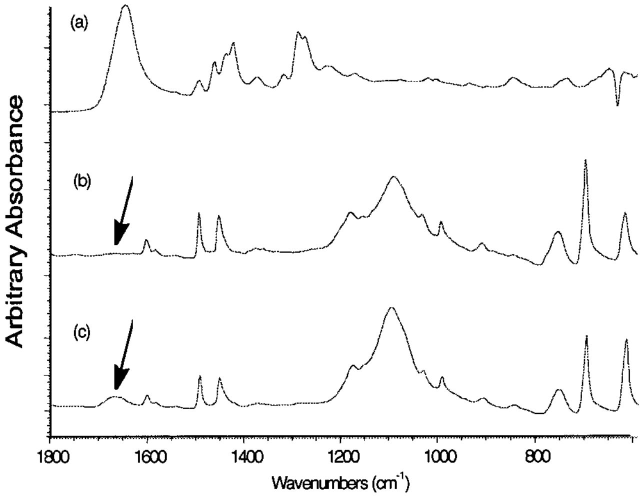

Figure 4. FTIR spectra of (a) the $PVP_{360\,000}$ stabilizer, (b) polystyrene synthesized in 75:25 ethylene glycol−water without stabilizer (entry 2 in Table 2), and (c) polystyrene latex synthesized via TEMPO-mediated dispersion polymerization in 95:5 ethylene glycol−water (entry 5 in Table 2).

the particle density, and *d* is the particle diameter. The BET diameters of the polystyrene latexes synthesized in the presence of TEMPO are all significantly larger (entries 3−6), although there is no obvious relationship between latex synthesis conditions and final particle size. Both SEM studies (see, for example, Figure 3a,c) and DCP analyses confirmed that all the latexes had very broad size distributions. In some cases bi- or multimodal distributions were observed by DCP.

The PVP stabilizer contents of all the latexes were determined by nitrogen microanalyses, taking into account the contribution from the TEMPO capping agent in each case (the polystyrene precipitate proved a useful reference material here). The stabilizer content decreased with increasing particle size, as expected. These observations were confirmed by FTIR spectroscopy, which was used to examine the composition of the polystyrene latex particles (see Figure 4).

Spectrum a is that of the $PVP_{360\,000}$ stabilizer. The most intense band is the characteristic carbonyl stretch of the amide residues at ca. 1660 cm^{-1}. As expected, this feature is not present in the IR spectrum of the polystyrene precipitate prepared in the absence of stabilizer (see spectrum b). Finally, spectrum c was obtained from a polystyrene latex prepared in 95:5 ethylene glycol−water using TEMPO (entry 5 in Table 2). A weak carbonyl feature is clearly evident in this latter spectrum, which confirmed that the PVP stabilizer is indeed adsorbed onto the polystyrene particles. This feature is more prominent in the IR spectrum (not shown) of entry 1, a polystyrene latex prepared in the absence of TEMPO. In this case, the smaller latex particle size leads to a higher specific surface area, and hence a higher proportion of stabilizer incorporated into the latex (6.8%).

The PVP stabilizer contents were combined with the BET data in order to calculate the adsorbed amount, Γ, of the PVP on the surface of the polystyrene latexes. It was envisaged that this might shed some light on whether the PVP was actually chemically grafted or merely physically adsorbed onto the polystyrene latex surface. Paine and co-workers[12] reported that PVP is grafted onto polystyrene particles prepared by conventional free-radical polymerization. In the context of the present study it was considered that such grafting might be less likely in the presence of TEMPO, since the effective concentration of free radicals is significantly reduced under these conditions.

For the PVP stabilizer adsorbed onto the polystyrene latex prepared in the absence of TEMPO, a Γ of 2.69 mg m^{-2} was calculated. This value is consistent with chemical grafting[12] of the PVP and is similar to that reported by Lascelles and Armes[10] for micrometer-sized polystyrene latexes prepared in alcoholic media. However, the Γ values calculated for the latexes prepared by TEMPO-mediated polymerization are all appreciably *higher* at 5−15 mg m^{-2}. Thus the presence of TEMPO

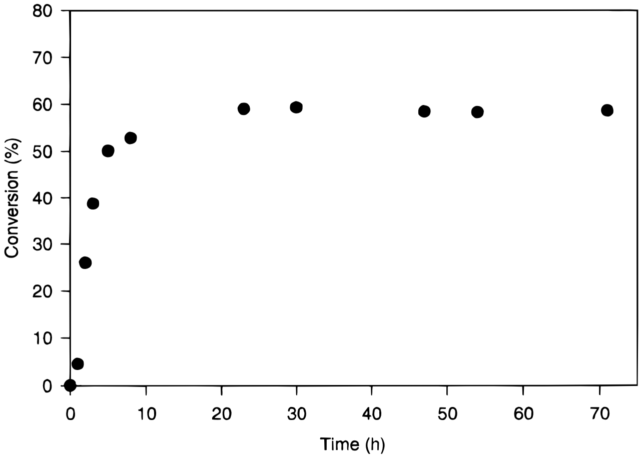

Figure 5. Plot of conversion vs time for the dispersion polymerization of styrene in 95:5 ethylene glycol–water at 124 °C using TEMPO-mediated chemistry.

apparently does not prevent efficient grafting of the PVP stabilizer. In calculating these Γ values it was assumed that all of the stabilizer was on the outside of the polystyrene particles. It is, of course, possible that a significant proportion of the PVP is located *inside* the latex. Such claims have been made by Ottewill and Satgurunathan[15] for PEG-stabilized polystyrene latexes on the basis of DSC data. In additional latex syntheses a lower molecular weight PVP stabilizer (40 000) was evaluated with similar results being obtained.

In the latex synthesis utilizing the TEMPO adduct (entry 6) a somewhat higher conversion (54%) was obtained after 24 h compared to the equivalent run (entry 5) carried out using the $K_2S_2O_8$/TEMPO system. In addition, the polystyrene molecular weight was nearly twice as high in the former case ($M_n \sim 13\,000$, compared to M_n's of 2800–7200 found using the $K_2S_2O_8$/TEMPO system). A large difference in particle size is also apparent, with much larger polystyrene particles being formed with the TEMPO adduct.

The extent of reaction was monitored for the dispersion polymerization of styrene in 95:5 ethylene glycol–water using the $K_2S_2O_8$/TEMPO initiator (entry 5 in Table 2) over a 96 h period (see Figure 5). The degree of conversion increased monotonically up to around 60% and then leveled off after 71 h. A plot of number-average molecular weight vs conversion for the same run is shown in Figure 6. A linear relationship was obtained, thus demonstrating the living nature of the TEMPO-mediated polymerization chemistry.

Conclusions

Polystyrene particles have been synthesized via living free-radical chemistry in both alcoholic and aqueous alcoholic media using PVP as a steric stabilizer. Genuine dispersion polymerization was only achieved in ethylene glycol or ethylene glycol–water mixtures. All the other alcohols investigated proved to be solvents for the low molecular weight polystyrene chains at the relatively high temperatures (112–130 °C) required for TEMPO-mediated polymerizations.

In the absence of TEMPO, near-quantitative monomer conversions, high molecular weights, broad MWDs, and submicrometer-sized latexes were obtained. The addition of TEMPO had a profound effect on the polymerization chemistry, only moderate monomer conversions (as low as 20%, with a maximum conversion of 60% obtained after 71 h) and larger, typically micrometer-sized, latexes were obtained with TEMPO-mediated syntheses. Polydispersities (M_w/M_n) as low as 1.11 were achieved in the presence of TEMPO, but only relatively low molecular weight polystyrene chains were obtained. In the absence of PVP stabilizer, low molecular weight TEMPO-capped polystyrene was obtained as a precipitate. The latexes prepared using TEMPO chemistry had a spherical particle morphology and very broad size distributions, as evidenced by SEM and DCP, respectively. The combination of average particle diameters calculated from BET data with nitrogen microanalyses allowed the calculation of surprisingly high *G* values for the PVP stabilizer. This suggests that the stabilizer is not located exclusively on the outside of the polystyrene latex particles.

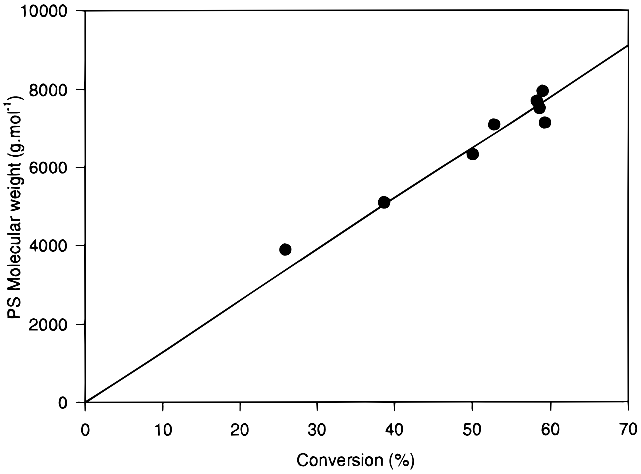

Figure 6. Molar mass as a function of conversion for dispersion polymerization of styrene in 95:5 w/w % ethylene glycol–water at 124 °C in the presence of TEMPO.

Future work will focus on examining atom transfer radical polymerization (ATRP) chemistry in order to synthesize narrower size distribution latexes comprising higher molecular weight chains.

Acknowledgment. The EPSRC is acknowledged for financial support (GR/K49232). The authors thank Dr. Julian Thorpe for his help with the SEM studies. One of the reviewers is also thanked for his/her helpful comments.

References and Notes

(1) Schwab, F. C.; Murray, J. G. Anionic Dispersion Polymerization of Styrene, in *Advances in Polymer Synthesis*; Plenum: New York, 1985.

(2) Jenkins, A. D.; Maxfield, D.; dos Santos, C. G.; Walton, D. R. M.; Stejskal, J.; Kratochvil, P. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 61–63.

(3) (a) Awan, M. A.; Dimonie, V. L.; El-Aassar, M. S. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 2633–2649. (b) Awan, M. A.; Dimonie, V. L.; El-Aassar, M. S. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 2651–2664.

(4) Gadzinowski, M.; Sosnowski, S.; Slomkowski, S. *Macromolecules* **1996**, *29*, 6404–6407.

(5) Sosnowski, S.; Gadzinowski, M.; Slomkowski, S. *Macromolecules* **1996**, *29*, 4556–4564.

(6) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66–72.

(7) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381–6382.

(8) Holderle, M.; Baumert, M.; Mülhaupt, R. *Macromolecules* **1997**, *30*, 3420–3422.

(9) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987−2988.

(10) Lascelles, S. F.; Armes, S. P. *J. Mater. Chem.* **1997**, *7*, 1339−1347.

(11) Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem.* **1986**, *24*, 2995−3007.

(12) Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* **1990**, *23*, 3104−3109.

(13) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245−5254.

(14) Baines, F. L.; Dionisio, S.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1996**, *29*, 3096−3102.

(15) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1987**, *265*, 845−853.

MA9718560