Fluorocarbon-Based Heterophase Polymeric Materials. 1. Block Copolymer Surfactants for Carbon Dioxide Applications

Zhibin Guan and J. M. DeSimone*

CB# 3290, Venable and Kenan Laboratories, Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

Received March 11, 1994; Revised Manuscript Received June 23, 1994®

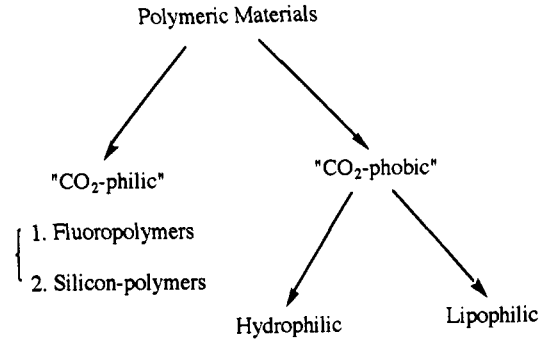
ABSTRACT: Poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) based block copolymers were synthesized for use as lipophilic/"CO_2-philic" surfactants for carbon dioxide applications. The first step was the synthesis of telechelic polystyrenes capped with the *N,N*-diethyldithiocarbamate group (TD-PS) using the iniferter method. The functionalities of the telechelic polystyrene samples were analyzed by UV/vis, ^1H NMR, and three-dimensional GPC. The 3-D GPC analysis provided detailed information on the percent functionality of end groups across the molar mass distribution. The results showed that the functionality was constant for different chain lengths. Block copolymers were synthesized by subsequent polymerization of FOA using telechelic polystyrene as a macroinitiator. The chemical composition, the glass transition temperatures, and the solubility of the block copolymers were studied.

Introduction

Recently, we have discovered that a series of amorphous fluoropolymers exhibits very high solubility in liquid and supercritical carbon dioxide. These high solubilities enabled the synthesis of a variety of acrylic and styrene fluoropolymers in supercritical carbon dioxide via homogeneous free radical polymerization methods.[1-5] We have also synthesized several statistical copolymers containing both hydrocarbon and fluorocarbon repeat units in supercritical CO_2 and found that those copolymers containing up to 50 mol % of the hydrocarbon moiety are also highly soluble in CO_2.[1,2,5]

Block copolymers can exhibit dramatically different properties than their statistical or random counterparts.[6] These differences can be attributed to the fact that the blocks of the copolymers tend to phase separate. However, the chemical bond between the blocks prevents macroscopic phase separation and microdomains are formed. When block copolymers are dissolved in solvents which are selective to one of the components but are nonsolvents for the other, micelle-like aggregates are known to form.[7,8] For ABA triblock copolymers, if the solvent preferentially dissolves the A block, the B block may aggregate to form the core of a micelle which is surrounded by a corona of solvated A blocks extending into the continuous phase.[9]

From our previous work[1,2,5] and that of others,[10,11] it is becoming clear that only a few classes of polymers have significant solubility (tens of percent) in supercritical CO_2 at relatively "mild" conditions ($T < 100$ °C, $P < 350$ bar). On the basis of the solubility in CO_2, we categorize polymers into "CO_2-philic"[12] or "CO_2-phobic" materials. Only amorphous fluoropolymers and silicon polymers are "CO_2-philic". Conventional polymers, either hydrophilic or lipophilic, are relatively insoluble in CO_2 and are termed "CO_2-phobic" polymers. The "CO_2-philic" fluoropolymers can be used to molecularly engineer surfactants specifically designed for use in CO_2:



The block copolymer portrayed in Figure 1 has a CO_2-phobic (hydrocarbon—HC) center block and CO_2-philic (fluorocarbon—FC) end blocks. The amphiphilic character of this block copolymer should lead to the formation of micelles in CO_2.[13] The copolymers may serve as surfactants for our investigations of emulsion polymerizations of lipophilic monomers in supercritical CO_2.[12]

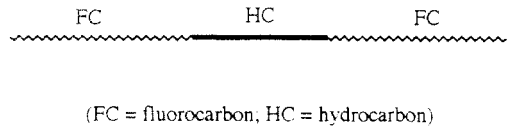
This paper will report the synthesis of the lipophilic/"CO_2-philic" surfactants by using the "iniferter" living free radical polymerization methods.[14] Due to the insolubility of most fluoropolymers in common organic solvents and some special features of the fluorinated monomers (e.g. FOA containing two acidic hydrogens on the methylene adjacent to the ester group), synthesis of these polymers by an anionic approach is difficult. Herein we report the synthesis of a telechelic polystyrene with terminal dithiocarbamate groups using the iniferter technique. The functional polystyrenes were characterized by various methods, including GPC analysis using a photodiode array UV detector to measure the percent functionality across the molar mass distribution instead of just the average functionality.

Experimental Section

Materials. Tetraethylthiuram disulfide (TD, Aldrich) was recrystallized twice from methanol, and the purity was checked by ^1H NMR. Styrene (Fisher, Certified Grade) was passed through an alumina column to remove the inhibitor. 1,1-Dihydroperfluorooctyl acrylate (FOA) was kindly provided by 3M Inc. and was passed through columns of decolorizing carbon

* To whom correspondence should be addressed.
® Abstract published in *Advance ACS Abstracts*, August 15, 1994.

0024-9297/94/2227-5527$04.50/0



(FC = fluorocarbon; HC = hydrocarbon)

Figure 1. Design of lipophilic/"CO_2-philic" surfactants for CO_2 applications.

Scheme 1. Synthesis of Telechelic Polystyrene via the "Iniferter" Method

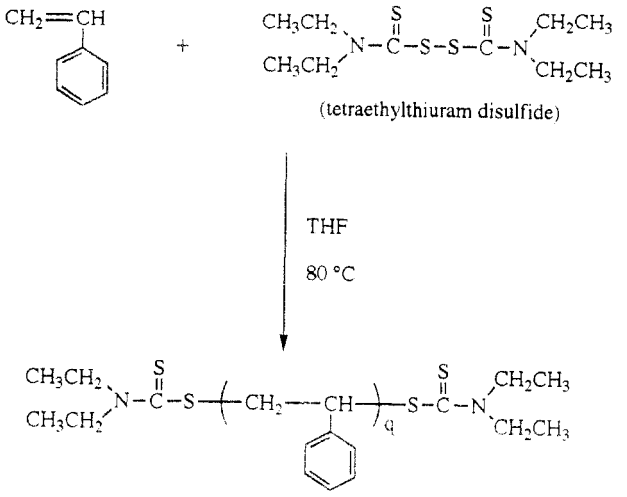


Table 1. Synthesis of Telechelic Polystyrene Using Tetraethylthiuram Disulfide as the Iniferter

sample no.	$10^{-3}M_n$[a] (g/mol)	MWD[a]	f[b]
1	3.3	1.5	1.9
2	5.6	1.8	1.8
3	8.6	2.1	2.0

[a] Data were obtained from GPC using polystyrene standards. [b] Functionalities were calculated from UV/vis and ^{1}H NMR spectra.

and alumina. Cyclohexane (Philips Petroleum) was stirred over concentrated sulfuric acid for ca. 2 weeks, decanted, and distilled under argon over sodium metal. Toluene (Fisher, Certified Grade) was distilled under argon over sodium metal. THF (Fisher, Certified Grade), $CHCl_3$, absolute ethyl alcohol, and α,α,α-trifluorotoluene (Aldrich, 99+%) were used as received. *n*-Butyl iodide (Aldrich, 99%) and sodium *N,N*-diethyldithiocarbamate trihydrate (Aldrich, 99+%) were used as received.

Synthesis of Telechelic Polystyrene (TD-PS). Telechelic polystyrene was synthesized by free radical polymerization of styrene using TD as the iniferter. The polymerizations were conducted in bulk or in solution and were stopped at an early stage (ca. 20% conversion) to ensure high functionality. One typical solution polymerization is described here: 1.0 g of TD and 15.0 mL of styrene were dissolved in 15 mL of THF. After the solution was purged with argon for ca. 10 min, the flask was immersed into a water bath at 80 °C. After polymerizing for 10 h, the polymer was recovered by precipitation of the polymerization solution into a large excess of methanol and drying. The resulting polymer was purified twice by dissolution in THF and reprecipitation into methanol. Bulk polymerizations were conducted at 65 °C for 10 h. The molar mass of the polymer was determined by gel permeation chromatography (GPC). The presence of the residual initiator and the functionality of the end groups were determined by ^{1}H NMR and by the UV analyses as described previously.[14,15]

Synthesis of the Model Compound for UV Studies. Benzyl *N,N*-diethyldithiocarbamate was synthesized by treating benzyl chloride (0.010 mol) with sodium *N,N*-diethyldithiocarbamate (0.011 mol) in 40 mL of ethanol.[16] After overnight refluxing, the solution was cooled to room temperature. The precipitated salts were filtered out, and the solvent of the filtrate was removed under vacuum. The residue was dissolved in chloroform and the solution was washed three times with water. After the organic layer was dried with sodium sulfate, the chloroform was removed

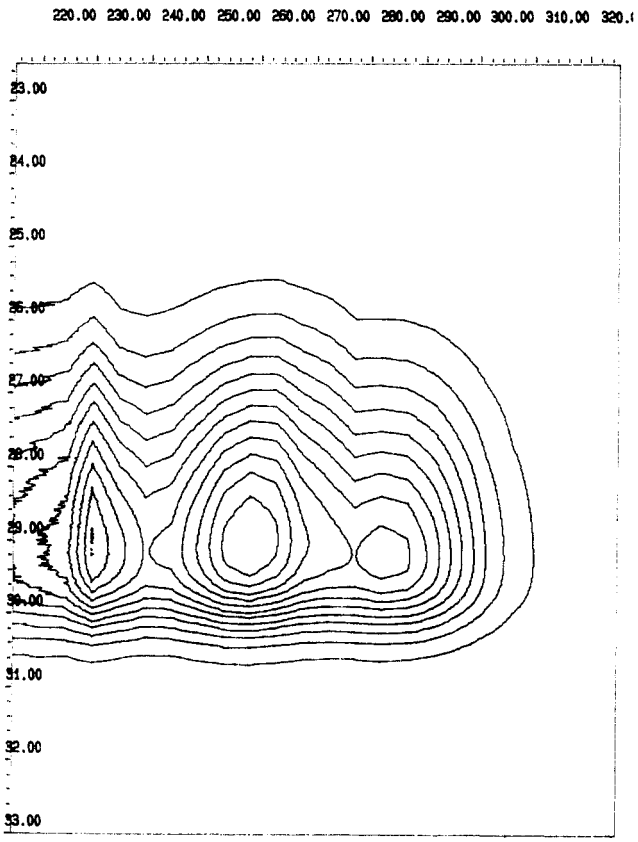


Figure 2. Contour plot of a three-dimensional GPC chromatogram.

by rotorary evaporation to give a clear oily product. Both ^{1}H and ^{13}C NMR analyses confirmed the structure of the product. ^{1}H NMR: δ 1.26 (m, 6H) ($N(CH_2CH_3)_2$), 3.70 (q, 2H) and 4.03 (q, 2H) ($N(CH_2CH_3)_2$), 4.53 (s, 2H) (Ph—CH_2—), 7.24–7.40 (m, 4H) (phenyl). ^{13}C NMR: δ 11.50, 12.38 ($N(CH_2CH_3)_2$; δ 46.61, 49.35 ($N(CH_2CH_3)_2$), δ 42.09 (Ph—CH_2—); δ 127.34, 128.45, 129.27, and 135.91 (phenyl); δ 195.10 (C=S).

Synthesis of Block Copolymers. The block copolymers were synthesized by subsequent polymerization of FOA using TD-PS as a macroinitiator. Polymerizations were conducted in a 5/1 mixed solvent of α,α,α-trifluorotoluene and THF. The reaction solution was initially cloudy, but became clear after a few hours of irradiation. A typical experimental procedure is described here: 1.0 g of a TD-PS sample was dissolved in a mixed solvent of 10 mL of α,α,α-trifluorotoluene and 2 mL of THF in a pear-shaped Pyrex flask. Upon addition of 5.0 g of FOA monomer, the solution became cloudy since FOA is a nonsolvent for polystyrene. A 140 W Hanovia medium pressure mercury lamp was set at a 10 cm distance from the reaction flask. The Pyrex glass wall of the reaction flask acts as a filter to remove the low wavelength UV light. The photopolymerization was continued for 24 h after which the polymerization solution was poured into a large excess of methanol to isolate the polymer. The unreacted polystyrene was removed by Soxhlet extraction using cyclohexane.

Characterization. ^{1}H NMR spectra were recorded on a Bruker AMX300 NMR spectrometer. UV spectra were obtained on Perkin-Elmer Lambda 6 UV/vis spectrometer. Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-7 with a heating rate of 20 °C/min. The molar mass data for the telechelic polystyrenes were obtained by running GPC on a Waters 150-C gel permeation chromatography with Ultrastyragel columns of 100, 500, 10^3, 10^4, and 10^5 Å porosities using THF as eluent. Polystyrene standards (Showa Denko) were used to determine the molar mass and molar mass distribution. The end groups were analyzed by ^{1}H NMR and UV analyses. GPC analyses were also performed on a modular Waters GPC instrument having a photodiode array UV detector (Model 996), with three Ultrastyragel columns of linear, 10^3 Å and 10^4 Å porosities. The photodioxde array detector was programmed to record one spectrum per second from from 215 to 600 nm at 32

°C using methylene chloride as the mobile phase with a flow rate of 1.0 mL/min.

Results and Discussion

Synthesis and Characterization of TD-PS. Telechelic dithiocarbamate functionalized polystyrenes of different molar masses were prepared via the iniferter technique using TD as initiator (Scheme 1). Previous studies showed that TD not only serves as a free radical initiator but also has high reactivity for chain transfer to initiator and primary radical termination.[14,17] These features assure that the polymer formed will be end-capped with two initiator fragments.[18-20]

The end groups of the TD-PS's were analyzed by ^{1}H NMR and UV/vis. The results are summarized in Table 1. These samples have functionalities close to 2, which is consistent with literature reports.[18-20] From ^{1}H NMR and UV/vis analyses, the functionality calculated is an average value of all polystyrene macromolecules having a distribution of chain lengths. We decided to employ a GPC method to calculate the percent functionality across the molar mass distribution. With a diode array UV detector, GPC is very useful for the analysis of UV sensitive end groups of functional polymers. A contour plot of a three-dimensional GPC chromatogram is shown in Figure 2 which precisely distinguishes the locations of the absorption maxima as a function of elution time. There are three absorption maxima which correspond to the phenyl ring absorption of the polystyrene backbone (λ_{max} = 225 and 258 nm) and the *N,N*-diethyldithiocarbamate end group (λ_{max} = 282 nm).

For a given elution time, the percent functionality f of the sample can be calculated explicitly by knowing the concentration of the dithiocarbamate end group and the concentration of polymer according to

$$f = \frac{\text{moles of the end group}}{\text{moles of the polymer chain}} = \frac{c_{end}}{c_{chain}} \quad (1)$$

where c_{end} and c_{chain} represent the molar concentrations of the dithiocarbamate end group and of the polymer chain, respectively. Since both the end group and polystyrene backbone have UV absorptions, their concentrations can be calculated from their UV absorbances according to Beer's law:

$$c_{end} = \frac{A_{282}}{\epsilon_{282} b} \quad (2)$$

$$c_{chain} = \frac{A_{258}}{\epsilon_{258} b} \quad (3)$$

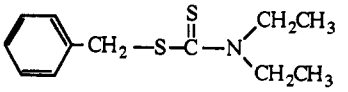
where b is the path length of the UV cell, A_{282} and ϵ_{258} are the absorbance and the molar absorptivity of the end group at 282 nm, and A_{258} and ϵ_{258} are the absorbance and the molar absorptivity of the polystyrene backbone at 258 nm. By substituting eqs 2 and 3 into eq 1, we obtain

$$f = \frac{A_{282}}{A_{258}} \frac{\epsilon_{258}}{\epsilon_{282}} \quad (4)$$

In eq 4, both A_{258} and A_{282} can be read from the 3-D GPC chromatogram, and the ϵ_{282} of the *N,N*-diethyldithiocarbamate end group was reported to be 1.05×10^4.[19] The molar absorptivity of polystrene at 258 nm (ϵ_{258}) was determined to be a linear function of molar mass, which results in the following equation of a line:[21]

$$\epsilon_{258} = 1770 + 1.6829 M_n \quad (5)$$

The absorption of the polystrene backbone does not overlap with the absorption of the dithiocarbamate end group at 282 nm since polystyrene does not absorb above 260 nm. However, it was determined that the dithiocarbamate end group absorption does overlap with the absorption of polystyrene at 258 nm, which was elucidated using benzyl *N,N*-diethyldithiocarbamate (BDC) as a model compound. BDC has the structure



and was synthesized by treating the sodium salt of *N,N*-diethyldithiocarbamic acid with benzyl chloride in ethanol. Its structure was confirmed by the ^{1}H and ^{13}C NMR

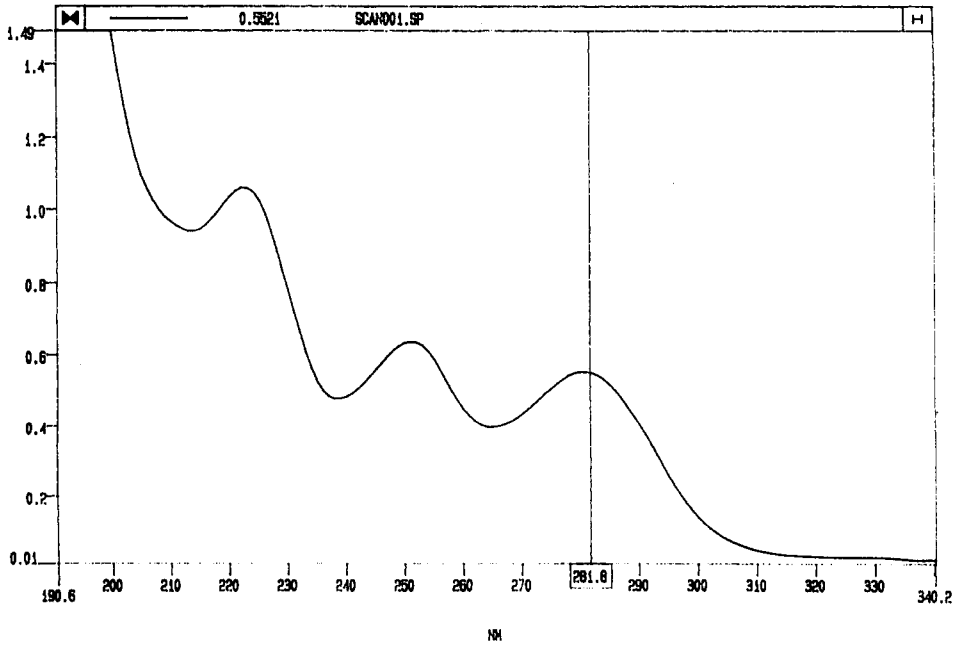


Figure 3. UV/vis spectrum of benzyl *N,N*-diethyldithiocarbamate.

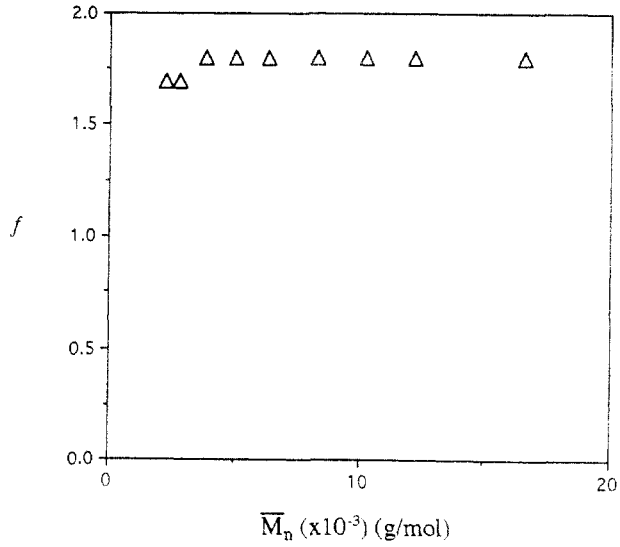


Figure 4. Percent end group functionality versus molar mass for telechelic polystyrene.

Table 2. Data for the Calculation of the Functionality of Telechelic Polystyrene Samples at Different Elution Times

elution time (min)	$10^{-3}M_n$ (g/mol)	ϵ_{258}	A_{282}	$A_{258(obsv)}$	$A_{258(corr)}$	f
30.0	2.24	5 540	0.900	1.110	0.28	1.7
29.5	2.82	6 516	1.190	1.530	0.44	1.7
29.0	3.80	8 165	1.120	1.520	0.49	1.8
28.5	5.01	10 201	0.950	1.380	0.51	1.8
28.0	6.31	12 389	0.733	1.140	0.47	1.8
27.5	8.32	15 771	0.503	0.867	0.41	1.8
27.0	10.23	18 986	0.302	0.580	0.30	1.8
26.5	12.22	21 998	0.157	0.323	0.18	1.8
26.0	16.60	29 706	0.062	0.153	0.96	1.8

spectra. Figure 3 shows the UV/vis spectrum of benzyl *N,N*-diethyldithiocarbamate which has three UV absorption bands at 282, 250, and 255 nm.

For the TD-PS UV spectra, the peak at λ_{max} = 250 nm of the end group absorption overlaps with the polystyrene backbone absorption at 258 nm. The overlap of the two peaks makes the observed A_{258} for the functionalized polystyrene larger than the actual absorption due only to the polystyrene backbone. The contribution of the absorbance due to the *N,N*-diethyldithiocarbamate end group at 258 nm must therefore be subtracted from the observed A_{258}. The absorbances of the model compound at 282 and 258 nm were ratioed to give $r = A_{258}/A_{282} = 0.91$, and the absorbance of the polystyrene backbone at 258 nm was then corrected accordingly:

$$A_{258}(\text{corr}) = A_{258}(\text{obsv}) - rA_{282} \quad (6)$$

The functionalities of the TD-PS at different elution times were calculated according to

$$f = \frac{A_{282}}{A_{258}(\text{corr})}\frac{\epsilon_{258}}{\epsilon_{282}} \quad (7)$$

The procedure for the calculation of the percent functionality across the molar mass distribution involved measuring the absorptions at 258 and 282 nm as a function of elution time. The absorbance of the polystyrene backbone at 258 nm was obtained after subtracting the contribution of the dithiocarbamate end group at the same wavelength (eq 6). The number average molar masses of the polymers corresponding to each elution time were calculated from the GPC calibration curve using polystyrene GPC standards. The ϵ_{258} of polystyrene at different molar masses was calculated from eq 5. After all the data were obtained, the percent functionality was calculated according to eq 7 and the results are summarized in Table 2.

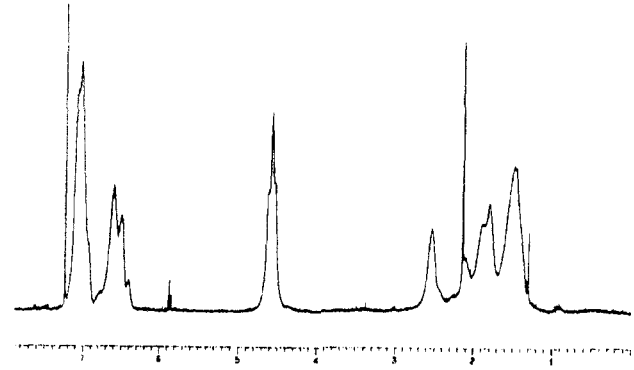
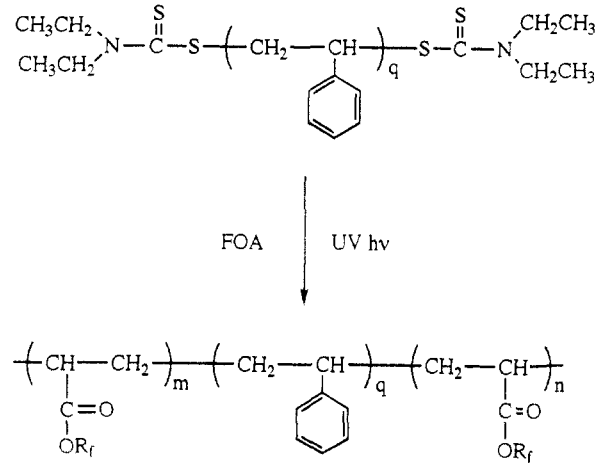


Figure 5. ^{1}H NMR spectrum of the triblock copolymer (sample 1).

Scheme 2. Photo Block Copolymerization To Make Fluorocarbon–Hydrocarbon–Fluorocarbon Triblock Copolymers



(R_f = -$CH_2CF_2CF_2CF_2CF_2CF_2CF_3$)

The percent functionality is plotted versus molar mass in Figure 4, from which we conclude that the functionalities of the TD-PS at different elution times are constant. This observation provides further support for the mechanism of the "iniferter" polymerization as proposed by Otsu et al.[19]

Synthesis and Characterization of Block Copolymers. Poly(FOA)-*b*-poly(styrene) block copolymers were synthesized by subsequent polymerization of FOA using TD-PS as a macroinitiator (Scheme 2). Upon UV irradiation, the chain ends of the TD-PS dissociate to generate polymeric radicals which initiate the polymerization of FOA. FOA is not homopolymerized by the generated dithiocarbamate radical which is not effective in initiating the polymerization of acrylate monomers.[15] We attempted to polymerize FOA using tetraethylthiuram disulfide as an initiator, but we were unsuccessful.

The block copolymers formed might be a mixture of both di- and triblock copolymers. It has been reported that the two end groups on the TD-PS have different reactivities.[16] The benzyl *N,N*-diethyldithiocarbamate end group is much more reactive than the phenylethyl *N,N*-diethyldithiocarbamate group at the other end. Therefore, it cannot be guaranteed that the polymer chains

Table 3. Synthesis of Fluorocarbon–Hydrocarbon–Fluorocarbon Triblock Copolymers[a]

	TD-PSt				block copolymer				
run	$10^{-3}M_n$ (g/mol)	f	wt (g)	FOA (g)	wt (g)	yield (%)	$10^{-4}M_n$ (g/mol)	q	$m+n$
1	5.6	1.8	1.0	5.0	4.88	81	2.87	51	51
2	5.6	1.8	0.5	5.0	4.89	89	7.73	51	158
3	3.3	1.9	0.2	5.0	4.43	85	4.95	28.7	102

[a] Polymerization run overnight in trifluorotoluene/THF (5/1) mixed solvent. [b] Determined from ^{1}H NMR and the $\langle M_n \rangle$ of the prepolymer.

Table 4. DSC Analysis of the Fluorocarbon–Hydrocarbon–Fluorocarbon Block Copolymers and Poly(1,1-dihydroperfluorooctyl acrylate) and Polystyrene Homopolymers

sample[a]	T_g^1 (°C)	T_g^2 (°C)
PFOA	-10	
PSt		100
block-1	-10	97
block-2	-10	85
block-3	-6.7	67

[a] PFOA = poly(1,1-dihydroperfluorooctyl acrylate); PSt = polystyrene; block-1, -2, -3 represent the block copolymers 1–3 in Table 3.

Table 5. Solubility Characteristics of the Fluorocarbon–Hydrocarbon–Fluorocarbon Block Copolymers in Different Solvents

	solubility			
sample	THF	$CHCl_3$	Freon-113	CO_2
block-1	sol	sol	sol	insol
block-2	insol	insol	sol	sol[a]
block-3	insol	insol	sol	sol[b]

[a] At 60 °C and 380 bar with 2.5% polymer. [b] At room temperature and 220 bar with 5% polymer.

were extended from both ends during the block copolymerizations. However, both AB diblock and ABA triblock copolymers should be interfacially actively in carbon dioxide.

The block copolymers were purified by Soxhlet extraction with cyclohexane to remove any unreacted TD-PS. The purified block polymers were characterized by UV/vis, ^{1}H NMR, and DSC. UV spectra of the block copolymers still show the absorption of the *N,N*-diethyldithiocarbamate. ^{1}H NMR spectra show the resonances of both styrene and FOA repeating units (Figure 5). The signal at 4.61 ppm corresponds to the methylene of the ester group of FOA, and the aromatic resonances (6.3–7.3 ppm) correspond to the phenyl ring of styrene. On the basis of the ratio of the area of the two peaks and the molar masses of TD-PS, the chemical compositions and the molar masses were calculated and are summarized in Table 3. The DSC thermogram of the block copolymer shows two glass transition temperatures, which indicates microphase separation in the bulk (Figure 6). T_g^1 corresponds to the glass transition of poly(FOA) microdomains and T_g^2 corresponds to the glass transition of the polystyrene microdomains. The DSC data for the block copolymers together with FOA and styrene homopolymers are compared in Table 4.

The solubilities of the block copolymers in common organic solvents and in CO_2 are summarized in Table 5. Poly(FOA) homopolymer is soluble in Freon-113 and CO_2 but insoluble in common organic solvents. However, block-1 which has an equal molar amount of FOA and styrene repeating units is soluble in THF, $CHCl_3$, and Freon-113 but insoluble in CO_2. As the fluorinated block becomes larger (block-2) or the center block becomes smaller (block-3), the copolymer becomes insoluble in THF and $CHCl_3$ but becomes soluble in CO_2. The CO_2 soluble block copolymers can potentially be used as surfactants for supercritical fluid extraction of hydrocarbons and for emulsion polymerizations of lipophilic monomers in CO_2.[12]

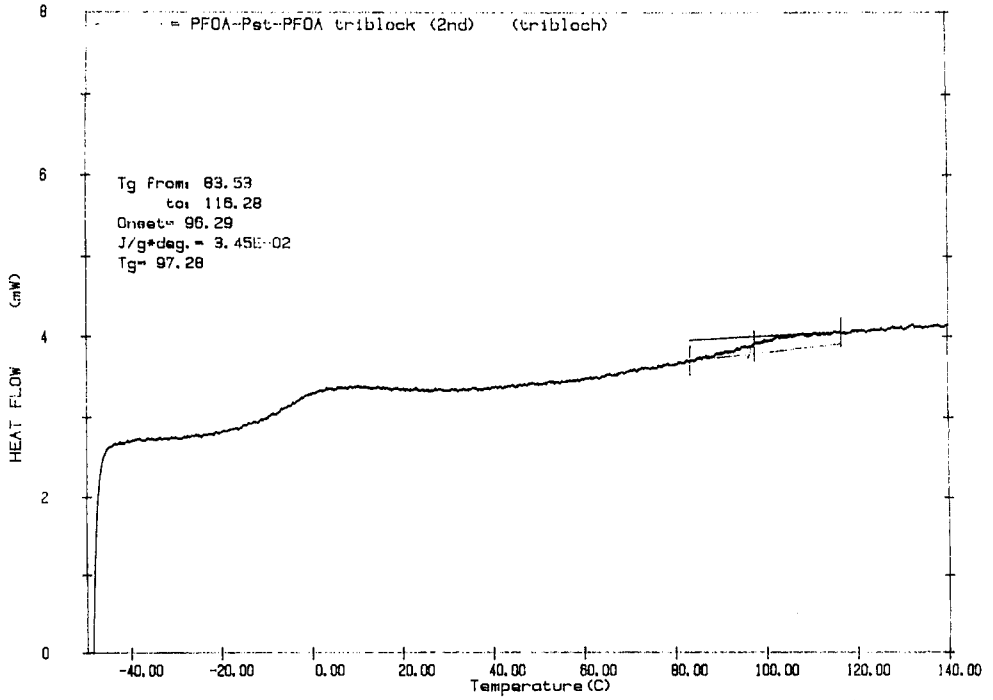


Figure 6. DSC thermogram of the triblock copolymer (sample 1).

Conclusion

Highly functionalized polystyrenes end-capped with *N,N*-diethyldithiocarbamate groups were synthesized by the iniferter method. The functionalities of the telechelic polystyrenes were characterized by UV, ^{1}H NMR, and three-dimensional GPC. 3-D GPC has proven to be a very powerful method to analyze the functionality of polymers which have UV-absorbing end groups. Unlike conventional end group analysis methods (such as UV, NMR, titration, etc.) which can only give the average value of the functionality for a whole polymer sample, this method provides information on the distribution of functionality across the molar mass distribution. This in depth information may aid in the investigation of polymerization mechanisms. The prepared TD-PS samples were useful as macroinitiators for the block copolymerization with FOA where block copolymers of different compositions were successfully prepared and characterized by ^{1}H NMR and DSC. A certain amount of "CO_2-philic" character was needed in order to impart solubility of the block copolymer in supercritical CO_2. The interfacial activity of these macromolecules in supercritical CO_2 is now under investigation.

Acknowledgment. We gratefully acknowledge the financial support from DuPont, 3M, Unilever Research, the Petroleum Research Fund, and the National Science Foundation through a Presidential Faculty Fellowship (J.M.D.: 1993–1997). We would also like to thank Chad Mistelle for his help on the GPC measurements.

Supplementary Material Available: Figures of an ϵ_{258} vs M_n plot and ^{1}H NMR and ^{13}C NMR spectra (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945.
(2) Guan, Z.; Combes, J. R.; Mencologlu, Y. Z.; DeSimone, J. M. *Macromolecules* **1993**, *26* (11), 2663–2669.
(3) Combes, J. R.; Guan, Z.; DeSimone, J. M. *Macromolecules* **1994**, *27* (3), 865.
(4) Guan, Z.; Elsbernd, C. S.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 329.
(5) Guan, Z.; Combes, J. R.; Elsbernd, C. S. and DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 447.
(6) Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1977.
(7) Price, C. In *Developments in Block Copolymers*; Goodman, I., Ed.; Elsevier Applied Science Publisher: London, 1982; Chapter 2.
(8) Vagberg, L. J. M.; Cogan, K. A.; Gast, A. P. *Macromolecules* **1991**, *24*, 1670 and references therein.
(9) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976**, *6*, 201.
(10) Consani, K. A.; Smith, R. D. *J. Supercrit. Fluids* **1990**, *3*, 51–65.
(11) Hoefling, T.; Stofesky, D.; Reid, M.; Beckman, E.; Enick, R. M. *J. Supercrit. Fluids* **1992**, *5*, 237–241.
(12) DeSimone, J. M.; Maury, E. E.; Combes, J. R.; Menceloglu, Y. *Z. PMSE Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1993**, *68*, 41. DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356.
(13) DeSimone, J. M.; Guan, Z. To be published elsewhere.
(14) Otsu, T.; Yoshida, M. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127.
(15) Turner, S. R.; Blevins, R. W. *Macromolecules* **1990**, *23*, 1856–1859.
(16) Otsu, T.; Kuriyama, A. *Polym. Bull.* **1984**, *11*, 135.
(17) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 133.
(18) Otsu, T.; Kuriyama, A. *Polym. J.* **1985**, *17* (1), 97–104.
(19) Kerckoven, C. V.; Broeck, H. V.; Smets, G.; Huybrechts, J. *Makromol. Chem.* **1991**, *192*, 101–114.
(20) Otsu, T.; Matsunag, T.; Kuriyama, A.; Yoshioka, M. *Eur. Polym. J.* **1989**, *25*, 643–650.
(21) Eight polystyrene samples, with number average molar masses of 520, 1140, 2710, 5930, 7220, 14 560, 70 000, and 172 000 g/mol, were used for determining the relationship between ϵ_{258} and the molar mass of the polymer. All samples were synthesized by standard living anionic polymerization using *sec*-butyllithium as the initiator, except the last one which was synthesized by free radical polymerization. The samples were dissolved in cyclohexane for the UV/vis measurement.