Synthesis of Polystyrene by Dispersion Polymerization in 1,1,1,2-Tetrafluoroethane (R134a) Using Inexpensive Hydrocarbon Macromonomer Stabilizers

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ABSTRACT: We describe here the use of inexpensive poly(vinyl acetate) (PVAc) macromonomer stabilizers for the free radical dispersion polymerization of styrene in 1,1,1,2-tetrafluoroethane (R134a). PVAc was identified from a wide range of polymers as being highly soluble in R134a at low pressures (<10 bar). The phase behavior of PVAc (M_w = 12 000−500 000 g/mol) in R134a was studied over a range of temperatures and pressures. It was found that PVAc exhibits LCST phase behavior in R134a. Based on the results of these solubility studies, PVAc macromonomer stabilizers were synthesized for use in dispersion polymerization. The dispersion polymerization of styrene in R134a gave rise to polystyrene microspheres (4−5 μm diameter) in good yields (up to 95%) with number-average molecular weights as high as 42 000 g/mol. The polystyrene microspheres could be redispersed in neat R134a after isolation and purification.

Introduction

We recently reported the use of a liquid hydrofluorocarbon (HFC), 1,1,1,2-tetrafluoroethane (R134a, T_c = 101.1 °C, P_c = 40.6 bar), as an environmentally benign solvent for the synthesis of cross-linked polymer microspheres by dispersion polymerization.[1] It was demonstrated that low molecular weight perfluoropolyether (PFPE) stabilizers could be used to form stable dispersions consisting of uniform polymer microspheres in the size range 1.5−3.0 μm. A key advantage of this approach is that reaction pressures are moderate (15−40 bar) in comparison with similar processes involving supercritical CO_2 ($scCO_2$), where pressures tend to be in the range 170−350 bar.[2−6] A disadvantage is that the PFPE stabilizers[7] are expensive. Moreover, it was found that these PFPE carboxylic acid stabilizers were not effective in the synthesis of *linear*, non-cross-linked polymers (e.g., PMMA, polystyrene) by dispersion polymerization in R134a.[1]

Dispersion polymerization was developed to prepare polymer particles in the micron size range for use in the surface coating industry.[8] Phase behavior in dispersion polymerization is characterized by initially homogeneous conditions (i.e., the monomer and initiator are soluble in the continuous phase). Primary nuclei are formed in the early stages of polymerization, as indicated by a deep yellow or red color caused by light scattering. As the polymerization proceeds, an opaque white latex is formed. Agglomeration of the polymer latex particles is prevented by the addition of a suitable steric stabilizer.

Motivated by the need for economic and environmental alternatives to the toxic organic solvents used in polymer chemistry, supercritical carbon dioxide ($scCO_2$) has emerged as a viable solvent alternative.[9−16] CO_2 is nontoxic and nonflammable and is available in high-purity from a number or sources. Most high molar mass polymers are insoluble in CO_2 at readily accessible temperatures and pressures (T < 100 °C, P < 350 bar), the main exceptions being certain amorphous fluoropolymers and polysiloxanes.[12,17] A variety of amphiphilic steric stabilizers and surfactants have been developed, all of which contain a "CO_2-philic" segment based upon amorphous fluoropolymers or polysiloxanes.[2−6,9,10] The discovery of less expensive CO_2-soluble polymers is an important challenge associated with extending the use of CO_2 as a solvent medium. Beckman has shown that it is possible to design CO_2-soluble *hydrocarbon* polymers, but only by achieving a precise balance of chemical and physical properties.[18,19]

R134a is nontoxic and nonflammable and is widely regarded as having zero ozone depletion potential.[1,20] R134a has found widespread use as a CFC replacement in refrigeration and auto air conditioning systems. In addition, the low toxicity has led to approval for use in metered dose inhalers.[21] Roth[22] and DiNoia et al.[23] suggested that HFC solvents could be viable candidates for supercritical fluid applications. For example, HFC solvents have been evaluated in applications such as electrochemistry,[24] particle formation,[25,26] extraction/fractionation,[27] and polymer foaming.[28] The global warming potential for R134a is estimated to be 1300 times that of CO_2, but a widely held view is that HFCs will have a very small impact on overall climate change, which will arise mostly from the accumulation of CO_2 in the atmosphere from the burning of fossil fuels.[20,29] R134a is more expensive than CO_2, and any HFC-based process would likely require effective recycling of the solvent.[30] Energy-efficient recycling of R134a may be practical since it was developed originally as a refrigerant.

An important chemical difference between R134a and CO_2 is the degree of polarity: CO_2 is symmetrical and has no permanent dipole moment (although it does possess a substantial quadrupole moment), while R134a is moderately polar and has a significant dipole moment (2.1 D).[23,31] An important advantage associated with the

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use of SCFs is the fact that the solvent properties (i.e., density and polarizability) can be varied with pressure. The solvent properties of R134a can also be varied with pressure, even in the liquid state. Just as for CO_2, product isolation is simplified by the subambient boiling point of R134a (−26.5 °C), although one would expect the rate of degassing from a fluid-swollen polymer to be somewhat lower in the case of R134a. From a chemical perspective, R134a is relatively inert, although like CO_2 it can react with strong nucleophiles.[32] We have found that most common vinyl monomers are soluble (up to 20−50% v/v) in liquid R134a at room temperature and above.[1] Previous studies have shown that certain other relatively small molecules (M_w < 2000 g/mol) are soluble in R134a; examples include lipids[27] and some low molecular weight surfactants.[21] By contrast, most high molar mass hydrocarbon polymers that we have investigated are insoluble in liquid R134a under moderate conditions (T < 100 °C, P < 50 bar). Certain vinylidene fluoride polymers[23] and poly(DL-lactide)[33] materials have been shown to be moderately soluble in R134a but only at elevated pressures (>200 bar). While R134a is a poor solvent for most hydrocarbon polymers, it is a good plasticizing agent.[34] As in the case of CO_2, this should facilitate heterogeneous polymerization due to enhanced monomer diffusion into the swollen polymer phase.

The objective of this investigation was to discover hydrocarbon polymers that are highly soluble in liquid R134a at low pressures and thus to develop inexpensive steric stabilizers for the synthesis of linear polymers by dispersion polymerization. In the studies presented here, R134a was used in the *liquid* state since the reaction temperature was well below the critical temperature for R134a (101.1 °C) in all cases.

Experimental Section

A. Materials. The structures and molecular weights of poly(vinyl acetate) (PVAc), poly(methyl acrylate) (PMA), and poly(vinyl propionate) (PVPr) samples were confirmed by NMR and GPC, respectively, and found to be consistent with the information provided by the supplier (Aldrich). PMA and PVPr were received as solutions in toluene. The solvent was removed under reduced pressure at 40 °C for 12 h. Vinyl acetate (VAc, Aldrich, 99+%), styrene (St, Aldrich, 99+%), and methyl methacrylate (MMA, Aldrich, 99%) were freed from inhibitor by distillation under reduced pressure over calcium hydride. 2,2-Azobis(isobutyronitrile) (AIBN, Fisher, 97%) was recrystallized twice from methanol and dried under vacuum before use. 2-Mercaptoethanol (2ME, Aldrich, 98%), methacryloyl chloride (MAC, Aldrich, 98+%), 2-isopropoxyethanol (IPE, Aldrich, 99%), trimethylolpropane trimethacrylate (TRIM, Aldrich, technical grade), 1,1-dihydroperfluorooctyl methacrylate (FOMA, Fluorochem), and perfluoropolyether carboxylic acid (PFPE, M_n = 550 g/mol, Aldrich) were used as received. 1,1,1,2-Tetrafluoroethane (R134a, refrigeration grade) was purchased from Ineous Fluor (Runcorn, UK) and was passed over an Oxisorb catalyst (Messer Griesheim) in order to remove any traces of oxygen.

B. Characterization. Molecular weight data for the polymers were obtained by GPC using a Polymer Laboratories ELS 1000 using a 5 μm mixed PL gel column against poly(styrene) standards. ^{1}H and ^{13}C NMR spectra were collected on a Bruker Avance 400. Polymer morphologies were investigated with a Hitachi S-2460N scanning electron microscope (SEM). Samples were mounted on aluminum studs using adhesive graphite tape and sputter-coated with approximately 10 nm of gold before analysis.

C. Solubility Screening in R134a. A range of hydrocarbon polymers was screened for solubility in liquid R134a at room temperature using a 10-well Baskerville autoclave (see Supporting Information). Weighed samples were submerged in Soxhlet extraction thimbles in liquid R134a for a fixed period (1 h) before venting the R134a. The percentage of polymer extracted was determined gravimetrically for each sample.

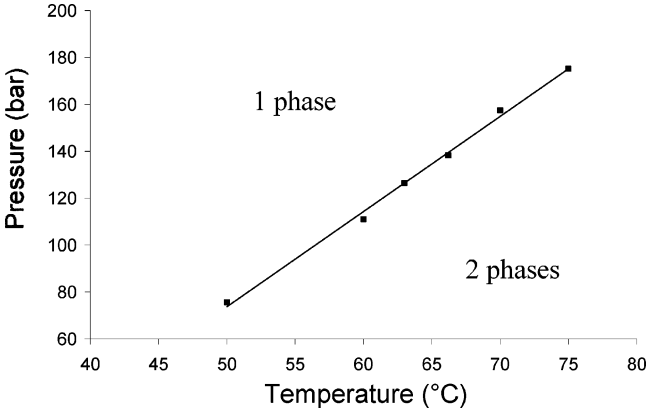

Figure 1. Cloud point behavior for PVAc in R134a (M_w = 167 000 g/mol, concentration = 0.3−0.4% w/v). Area above the line is the one-phase region.

D. Phase Behavior Measurements in R134a. i. Determination of Lower Critical Solution Temperature (LCST) for PVAc in R134a. An accurately weighed sample of polymer was added to a 10 mL fixed-volume view cell equipped with a sapphire window and a magnetic stir bar. The vessel was purged with argon followed by the addition of an accurate volume of liquid R134a (8.00 mL). Since the reactor was not completely filled with solvent, the initial pressure in the vessel was always equal to the vapor pressure of R134a at ambient temperature (~7.1 bar). The solution was stirred until a clear, homogeneous solution was obtained. All of the PVAc samples tested were found to be initially soluble under these conditions. The vessel was then heated slowly (not isobarically) until an opaque mixture was observed due to polymer phase separation (i.e., the cloud point). The cloud point was determined as the point at which the back surface of the reactor was no longer visible. The PVAc was characterized by ^{1}H NMR before and after the measurements in order to ensure that the phase separation was not due to any changes in polymer structure (e.g., hydrolysis of acetate groups).

ii. Cloud Point Determination for PVAc in R134a (M_w = 167 000 g/mol). An accurately weighed sample of PVAc (0.4 w/v %, M_w = 167 000 g/mol) was added to a 10 mL fixed-volume view cell equipped with a sapphire window and a magnetic stir bar. The system was purged with argon. Liquid R134a (8.00 mL) was added using an Isco 260D syringe pump, and the system was stirred until a clear homogeneous solution was observed. The resulting solution was then heated above the LCST for the polymer (i.e., such that the polymer precipitated from solution) to the temperature at which the cloud point would be measured. When the temperature of the view cell had stabilized, the pressure was slowly increased by the addition of liquid R134a until the polymer had redissolved to form a homogeneous, optically transparent solution. The cloud point was estimated as the pressure required to completely dissolve the polymer at a given temperature. This measurement was repeated at a number of different temperatures to construct the phase diagram shown in Figure 1.

E. Stabilizer Synthesis. i. Synthesis of PVAc Macromonomer 1a Using 2-Mercaptoethanol (2-ME) as Chain Transfer Agent. The synthesis of hydroxyl-terminated PVAc, **1**, was based on methods described previously.[35,36] To a solution of VAc (8.6 g, 100 mmol) in toluene (17.8 g, 190 mmol) containing AIBN (2% w/w with respect to VAc, 1 mmol) was added 2-mercaptoethanol (20% w/w with respect to VAc, 22 mmol). The resulting solution was deoxygenated three times by freeze−pump−thaw degassing and then heated to 60 °C for 12 h. The solvent was evaporated under reduced pressure, and the polymer, **1**, was reprecipitated into cold *n*-hexane. The

material was then dissolved in acetone and reprecipitated again. This was repeated two more times, followed by drying in vacuo at 30 °C. The structure of the resulting hydroxyl-functionalized PVAc was confirmed by ^{1}H NMR.[35,36] The methacrylate-terminated macromonomer, **1a**, was obtained by functionalizing **1** with methacryloyl chloride,[36] and the structure was confirmed by ^{1}H NMR and FTIR. The degree of methacrylate functionalization was determined to be 28% (from integration of backbone −CH groups at 4.87 ppm against the vinyl protons at 5.64 and 6.18 ppm). ν_{max} (film)/cm^{-1} 1740 (C═O); δ_H (400 MHz, $CDCl_3$), 1.65−2.19 (m, CH_3 and CH_2), 4.87 (m, CH), 5.64 and 6.18 ppm (CH_2, vinyl end groups).

ii. Synthesis of PVAc Macromonomer 2a Using Isopropoxyethanol (IPE) as Solvent and Chain Transfer Agent. The synthesis of the hydroxyl-terminated PVAc, **2**, was based on methods described previously.[37,38] VAc (8.6 g, 100 mmol) was added to IPE (30 mL, 27.1 g, 260 mmol) containing AIBN (0.33% w/w based upon monomer, 0.1 mmol). The resulting solution was deoxygenated three times by freeze−pump−thaw degassing and then heated to 60 °C for 12 h. The solvent was removed under reduced pressure, and the polymer, **2**, was reprecipitated into cold *n*-hexane. The resulting polymer was dissolved in acetone and reprecipitated again. This was repeated two more times followed by drying in vacuo at 30 °C. The methacrylate-terminated macromonomer, **2a**, was obtained by functionalizing **2** with methacryloyl chloride, and the structure was confirmed by ^{1}H NMR and FTIR. ν_{max} (film)/cm^{-1} 1740 (C═O); δ_H (400 MHz, $CDCl_3$), 1.65−2.19 (m, CH_3 and CH_2), 4.87 (m, CH). In this case, the vinyl end groups could not be observed by ^{1}H NMR due the higher molecular weight of the macromonomer, and it was not possible to quantify the precise degree of methacrylate functionalization.

iii. Synthesis of Poly(1,1-dihydroperfluorooctyl methacrylate) (PFOMA). This polymer was synthesized as described previously.[12] The molecular weight of the PFOMA was not determined due to insolubility of the polymer in all common solvents used for GPC.

F. Dispersion Polymerization in R134a. Reactions were carried out in a 10 mL stainless steel view cell equipped with a magnetic stir bar and a sapphire window to allow observation of phase behavior.[1] The monomer(s), initiator, and stabilizer (if any) were added to the reaction vessel, which was then purged four times with argon. R134a (7.80−9.10 mL, depending on the final pressure required at the reaction temperature) was added using an Isco 260D syringe pump, and the reactor was heated to 60 °C using an external heating tape. The temperature was monitored using a type-K thermocouple. Pressure changes were monitored using a miniature flush diaphragm pressure transducer. For reactions that yielded dry powders in high yields, the phase behavior was indicative of a dispersion polymerization mechanism.[2−6] In other cases where the latexes were unstable, latex collapse was observed during the latter stages of the reaction. These reactions gave rise to much lower polymer yields and lower average molecular weights. In reactions where powders were obtained, a small quantity (∼50 mg) of the polymer was washed with methanol and then analyzed by SEM. The remaining polymer was dissolved in toluene and reprecipitated twice into cold methanol. The polymer was isolated and dried under reduced pressure. Yields were determined gravimetrically.

Results and Discussion

Screening for R134a-Soluble Polymers. The factors affecting polymer solubility in compressed fluids are complex, and one must consider the interplay between the intra- and intersegmental interactions of the many segments of the polymer and the interactions of these segments with the solvent (i.e., the interchange energy).[17] The development of predictive models can be complicated by the fact that directional Lewis acid−base interactions may play a significant role in determining polymer phase behavior.[17,39] As such, the current level of predictive understanding for the phase behavior of polymer solutions in compressible fluids is limited. Polymer phase behavior in $scCO_2$ has been quite widely investigated,[17] but there is very little published information concerning the phase behavior of nonfluorinated hydrocarbon polymers in R134a.

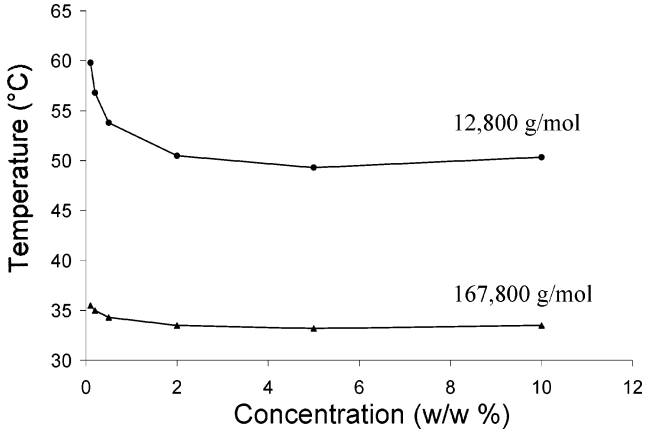

Figure 2. Effect of polymer concentration on the LCST for PVAc in R134a: circle points, M_w = 12 800 g/mol; triangle points, M_w = 167 000 g/mol. Area below curve = one-phase region. Maximum pressure during measurements = 17.9 bar.

The main objective of this study was to identify an inexpensive hydrocarbon polymer with high solubility in R134a at moderate pressures in order to synthesize effective steric stabilizers for dispersion polymerization. We adopted a rapid screening approach in order to discover candidate materials. A range of candidate polymers was selected according to some basic criteria. First, polymers with relatively low glass transition temperatures (T_g) were favored since this often indicates high flexibility and high free volume, both of which should result in a more favorable entropy of mixing.[40] Second, many of the polymers possessed specific functional groups (e.g., carbonyl groups) that might interact with the dipole moment of R134a, thus increasing solute−solvent interactions and improving the enthalpy of mixing.[17,39] Over 50 polymers were screened for solubility in R134a (25 °C, 7.1 bar, see Supporting Information). All of the polymers in this group were found to have negligible solubility (<0.2% w/v) in R134a under these conditions, apart from PVAc which was found to be highly soluble (up to 30% w/v at 12 800 g/mol, 21 °C, 7.1 bar). As a result, the phase behavior of PVAc in liquid R134a was studied in more detail.

Phase Behavior of PVAc in Liquid R134a. It was found that PVAc exhibits lower critical solution temperature (LCST) phase behavior in R134a, as indicated by the positive gradient of the cloud point curve (+4 bar/°C) shown in Figure 1. LCST behavior is common to a variety of polymer-compressed fluid systems such as poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) in CO_2,[4] PMMA in chlorodifluoromethane,[41] and poly(1,1,2,2-tetrahydrofluoroperfluorodecyl acrylate) [poly(TAN), average alkyl chain length = 9.6] in CO_2.[42]

The main reason for carrying out these solubility tests was to determine the conditions under which PVAc would be soluble at a sufficiently high molecular weight (M_w > 10 000 g/mol) in order to act as a steric stabilizer for dispersion polymerization. Figure 2 shows the dependence of the LCST on the polymer concentration for low molecular weight (12 800 g/mol) and high molecular weight (167 000 g/mol) PVAc in liquid R134a. In each case, the area below the curve represents the

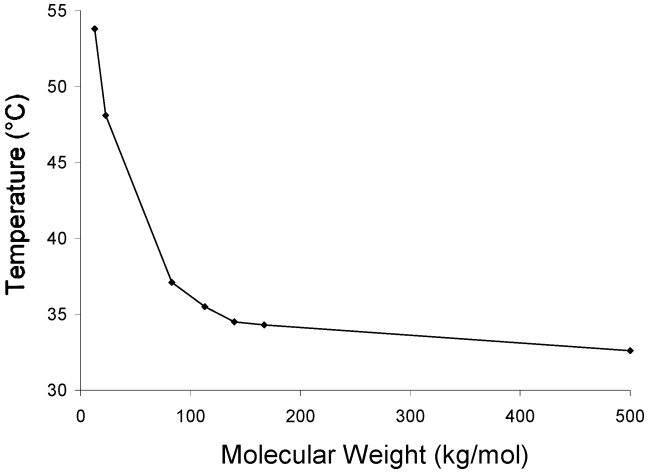

Figure 3. Effect of molecular weight on LCST for PVAc in R134a (0.5% w/w). Maximum pressure during measurements = 16.5 bar.

one-phase region while the area above the curve corresponds to the two-phase region. As might be expected, the LCST curve was found at lower temperatures for the higher molar mass PVAc. Both curves exhibit the typical shape expected for systems with LCST behavior: this is denoted by a minimum in the LCST at a certain polymer concentration. The 12 800 g/mol PVAc showed a minimum in LCST of 49.3 °C at approximately 5% w/w, while for 167 000 g/mol PVAc, the minimum LCST was found to be 33.2 °C at approximately 5% w/w. The maximum concentration in Figure 2 is 10% w/w because the 167 000 g/mol sample did not appear to be fully soluble at higher concentrations. By contrast, the 12 800 g/mol sample was found to be soluble up to at least 30% w/w at 7.1 bar and 25 °C. In these experiments, the location of the LCST was not determined isobarically (i.e., the pressure increased slightly as the solution was heated in the fixed-volume reactor). Thus, the observed phase behavior cannot be attributed solely to the effect of changing the temperature, since the pressure and the liquid density varied as well. Nonetheless, these conditions are closest in nature to the reaction conditions (i.e., a known volume of solvent is added to the reactor and the system is then heated): as such, this information was considered to be the most useful in terms of finding reaction conditions under which PVAc would remain soluble during dispersion polymerization.

Figure 3 shows the effect of polymer molecular weight on the LCST for PVAc in R134a. The polymer concentration was fixed at 0.5% w/w (based on solvent) since this corresponds approximately to the concentration of steric stabilizer that might be used in a dispersion polymerization. Figure 3 demonstrates clearly that the LCST is strongly dependent on molecular weight up to around 100 000 g/mol. At higher molar masses, the dependence on molecular weight is small. As M_w is increased from 12 800 to 83 000 g/mol, the LCST decreases by 16.7 °C. Increasing M_w from 113 000 to 500 000 g/mol decreases the LCST by only 2.9 °C.

The T_g of PVAc is moderately low (Table 1), and the polymer chain has relatively high flexibility. PVAc is polar (e.g., it is soluble in methanol) and contains carbonyl functionalities that could interact favorably with a moderately polar solvent such as R134a. This interpretation is supported by preliminary phase behavior studies carried out on structural analogues of

Table 1. Effect of Polymer Structure on LCST in R134a[a]

polymer[b]	M_w (g/mol)[c]	T_g (°C)[c]	LCST (°C)
PVAc	167 000	30	34.3
PMA	40 000	9	16.6
PVPr	34 000	10	17.0

[a] Concentration of polymer 0.5% w/w with respect to R134a (P < 15 bar). [b] PVAc = poly(vinyl acetate); PMA = poly(methyl acrylate); PVPr = poly(vinyl propionate). [c] M_w (GPC) and T_g (DSC) provided by the supplier.

Table 2. Synthesis of PVAc Macromonomers

polymer	M_n (g/mol)[c]	PDI[c,d]	yield[e]	chain transfer agent[f]	end group
1[a]	10 000	1.3	15.1	2-ME	2-hydroxyethylthio
1a[a]	10 300	1.3	~100[g]	n/a	methacrylate[g]
2[b]	16 900	1.2	27.2	2-IPE	isopropoxyethanol
2a[b]	17 000	1.2	~100[h]	n/a	methacrylate[h]

[a] Synthesized using 2-ME as chain transfer agent (section E.i). [b] Synthesized using IPE as chain transfer agent (section E.ii). [c] Measured by GPC; M_n and PDI were unchanged after methacrylate functionalization. [d] Polydispersity index = M_w/M_n. [e] Determined gravimetrically after reprecipitation. [f] 2-ME = 2-mercarptoethanol; IPE = 2-isopropoxyethanol. [g] Refers to gravimetric, isolated yield. Degree of functionalization = 28%. [h] Refers to gravimetric, isolated yield. Methacrylate end groups could not be observed by ^{1}H NMR at this molecular weight.

PVAc (Table 1). For example, poly(methyl acrylate) (PMA, 0.5% w/w, 40 000 g/mol) exhibited an LCST that is 17.7 °C lower than the LCST for PVAc (0.5% w/w, 167 000 g/mol), despite the fact that both T_g and M_w for the PMA sample were substantially lower. Poly(vinyl propionate) (PVPr) (which had T_g and M_w that were very close to those of the PMA sample) also exhibited an LCST that was significantly lower than that observed for PVAc. A possible interpretation for this difference in phase behavior is that the carbonyl groups in PMA and PVPr are less accessible to interactions with the solvent[39] (i.e., because of positional isomerism in the case of PMA and because of the more sterically bulky ethyl substituent in the case of PVPr). A similar argument has been made to rationalize the large difference in the cloud point pressures for PMA and PVAc in $scCO_2$.[17,40]

Synthesis of R134a-Soluble PVAc Macromonomers. Macromonomers can be defined as oligomers or polymers having a polymerizable functional group at one chain end. Fluorinated and siloxane macromonomers have been used as steric stabilizers for dispersion polymerization in CO_2.[5,43,44] In this study, PVAc monofunctional macromonomers were synthesized consisting of a R134a-soluble PVAc chain which was terminated with a methacrylate group. The target molecular weight for these macromonomers was in the broad range 5000−20 000 g/mol. At higher M_w (>20 000 g/mol), we expected the PVAc to be insufficiently soluble in R134a (i.e., the LCST would be too low; see Figure 3). Also, it becomes increasingly difficult to end-functionalize monohydroxyl-PVAc oligomers with a polymerizable group (e.g., a methacrylate) as the molecular weight increases (see below).[36] On the other hand, macromonomer molecular weights of >5000 g/mol were desired in order to impart efficient steric stabilization in the subsequent dispersion polymerization.[8]

Two different methods were employed to prepare monohydroxyl-terminated PVAc polymers,[35−38] and the results are summarized in Table 2. The structures of polymers **1** and **1a** (Figure 4), produced by chain

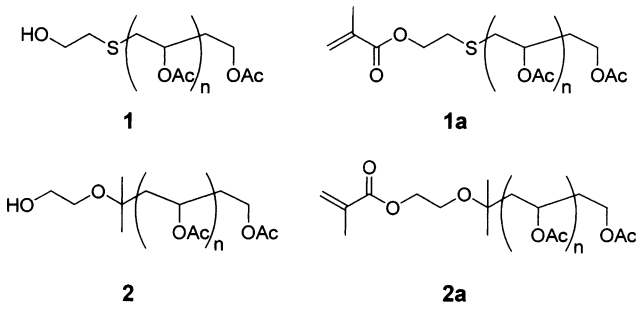

Figure 4. Structures of hydroxy- and vinyl-terminated PVAc. **1** + **1a** synthesized using 2-mercaptoethanol (2-ME) as chain transfer agent (**1** = PVAc with 2-hydroxyethylthio end group, **1a** = macromonomer after methacrylate functionalization). **2** + **2a** synthesized using isopropoxyethanol (IPE) as chain transfer agent and solvent (**2** = PVAc with hydroxyl end group, **2a** = macromonomer after methacrylate functionalization).

transfer polymerization using 2-mercaptoethanol (2ME), were confirmed by ^{1}H NMR, GPC, and FTIR. For hydroxyl-functionalized PVAc oligomers of this molecular weight, the degree of methacrylate end-capping was estimated by ^{1}H NMR to be around 28% (i.e., a significant proportion of the hydroxyl end groups remained unfunctionalized due to the comparatively high M_w of the PVAc oligomer).[36] Polymers **2** and **2a** were produced by chain transfer polymerization in neat 2-isopropoxyethanol (IPE) and were characterized in the same way. In this case, M_w was too high to observe the methacrylate end groups by ^{1}H NMR. It was not, therefore, possible to calculate the degree of methacrylate end-capping for polymer **2a**, although one might predict this to be lower than found for polymer **1a**. Nonetheless, there is clear evidence that the methacrylate-terminated species, **2a**, is active as a steric stabilizer in dispersion polymerization while the underivatized hydroxyl species, **2**, is not (see below). This suggests that a significant percentage of the hydroxyl end groups were functionalized in both cases.

Cross-Linked Polymers: Dispersion Polymerization of TRIM in Liquid R134a Using PVAc Macromonomers. PVAc macromonomer **1a** was used for the dispersion copolymerization of MMA and TRIM to produce cross-linked polymer microspheres (Table 3, entries 1−3). Figure 5 shows electron micrographs for the microspheres produced. In the absence of any stabilizer (entry 1), polymers were obtained in good yields by precipitation polymerization, although the particles were significantly agglomerated and nonspherical in shape (Figure 5a). The formation of polymer powders in good yields *without* any added stabilizer can be attributed to the rigid, cross-linked particle surface which provides an inherent barrier to agglomeration.[1,45,46] In the presence of the PVAc macromonomer, **1a**, a uniform, opaque, white latex was observed, and uniform polymer microspheres (average particle diameter = 0.91 μm) were obtained in good yield (Figure 5b). Under these reaction conditions (60 °C, 17 bar) the system was slightly cloudy at the very beginning of the reaction period; this could arise from partial insolubility of the macromonomer under these conditions. The reaction was repeated in the presence of a low molecular weight monofunctional perfluoropolyether carboxylic acid stabilizer (PFPE-CO_2H, M_n = 550 g/mol) of the type developed by Howdle for the dispersion polymerization of MMA in $scCO_2$.[7,47,48] As reported previously,[1] cross-linked microspheres were produced in high yields with spherical particle morphologies (Figure 5c). A few particles appeared to be fused together, but overall the majority existed as discrete microspheres. The cross-linked particles produced using the PVAc macromonomer, **1a**, were smaller than those produced using the PFPE-CO_2H stabilizer (0.91 μm vs 1.62 μm), perhaps suggesting that the nucleation process is more efficient due to the reactive macromonomer forming permanent chemical bonds with the microparticles. The molecular weight of the PFPE-CO_2H species (M_n = 550 g/mol) is certainly much lower than most steric stabilizers,[8] and the exact mechanism of stabilization is unclear.

Linear Polymers: Dispersion Polymerization of Styrene Using R134a-Soluble Homopolymers. In the case of cross-linked polymers, the rigid nature of these materials greatly assists in the formation of uniform spherical particles. Attempts to use PFPE-CO_2H stabilizers for the synthesis of linear polymers (e.g., PMMA, polystyrene) by dispersion polymerization proved unsuccessful and gave rise to polymers in low yields and with low molecular weights.[1] We attribute this to the fact that stable latexes were not formed (i.e., the reactions were similar to unstabilized precipitation polymerizations). In comparison with results obtained using $scCO_2$,[7,47,48] there was a large reduction in activity for these PFPE-CO_2H steric stabilizers. This could result from differences in the phase behavior of these highly fluorinated materials in CO_2 and R134a. Alternatively, the hydrogen-bonded anchoring mechanism proposed by Howdle and co-workers may be substantially weaker in the more polar hydrofluorocarbon fluid.[1]

Given that fluorinated CO_2-soluble polyacrylates (e.g., PFOA) have been used as stabilizers for the dispersion of monomers such as MMA[2,4] and styrene[49] in $scCO_2$, we first attempted to use linear R134a-soluble homopolymers in a similar fashion as steric stabilizers for the dispersion polymerization of styrene in R134a. These preliminary experiments were carried out at relatively high pressure (230 bar) in order to ensure that the homopolymer stabilizers were fully soluble in the continuous phase. Three potential stabilizers were investigated, all of which were shown to be soluble in neat R134a (i.e., PFOMA, M_w not determined; PVAc, M_w = 167 000 g/mol; PVAc, M_w = 500 000 g/mol). In each case, the yield and molecular weight of the polystyrene product were increased in the presence of the homopolymer stabilizer (Table 3, entries 4−7). The phase behavior in the reactions differed strongly; the PFOMA-stabilized system gave rise to a uniform white latex and resulted in the formation of a free-flowing polystyrene powder (74% yield, M_n = 35 500 g/mol) that consisted of partially agglomerated microspheres (see Figure 6a). By contrast, the addition of PVAc (Table 3, entries 6 + 7) did not give rise to stable latexes, and both the yields (12−20%) and the molecular weights (10 000−16 000 g/mol) in these reactions were much lower. This contrasting behavior might arise from differences in phase behavior or from the fact that PVAc is relatively polar and does not adsorb as strongly to the hydrophobic polystyrene particle surfaces.

Linear Polymers: Dispersion Polymerization of Styrene Using R134a-Soluble PVAc Macromonomers. Table 4 summarizes the results of a series of dispersion polymerizations carried out in liquid R134a using PVAc macromonomers as steric stabilizers. The presence of styrene in the reaction mixture appeared to enhance the initial solubility of the PVAc macromonomers, and all of these reactions formed clear,

Table 3. Synthesis of Cross-Linked and Linear Polymers by Dispersion Polymerization in 1,1,1,2-Tetrafluoroethane (R134a)[a]

	monomer	stabilizer[b]	stabilizer (% w/w)[c]	yield (%)[d]	M_n (g/mol)[e]	PDI[f]	pressure (bar)[g]	av particle diam (μm)[h]
1	MMA + TRIM	none	0	81.2	NA	NA	14	NA
2	MMA + TRIM	**1a**	0.5	84.7	NA	NA	17	0.91 (33)
3	MMA + TRIM	PFPE	0.5	82.4	NA	NA	19	1.62 (28)
4	styrene	none	0	10.8	6100	1.6	234	NA
5	styrene	PFOMA	5	73.6	35500	6.8	230	4.33 (40)
6	styrene	PVAc **A**	10	17.4	15600	1.5	239	NA
7	styrene	PVAc **B**	10	13.0	9900	1.3	236	NA

[a] Reaction conditions: 20% w/v total monomer concentration: cross-linked polymers (entries 1−3): 5% w/w initiator (AIBN), 6 h, 60 °C; linear polymers (entries 4−7): 1% w/w initiator (AIBN), 12 h, 60 °C. [b] PFPE = perfluoropolyether carboxylic acid (M_n = 550 g/mol); PFOMA = poly(1,1-dihydroperfluorooctyl methacrylate); PVAc **A** = poly(vinyl acetate), M_w = 167 000 g/mol; PVAc **B** = poly(vinyl acetate), M_w = 500 000 g/mol. [c] Based on monomer. [d] Determined gravimetrically after washing three times with methanol (entries 1−3) or after reprecipitation (entries 4−7). [e] Determined by GPC for linear polymers (entries 4−7). [f] Polydispersity index = M_w/M_n. [g] Initial pressure at reaction temperature (60 °C). [h] Mean particle diameter calculated from SEM images by measuring > 100 particles. Figure in parentheses = percentage coefficient of variation, CV, where CV = $(\sigma/D_n) \times 100$. σ = standard deviation in particle diameter (μm). D_n = mean particle diameter (μm); NA = agglomerated products.

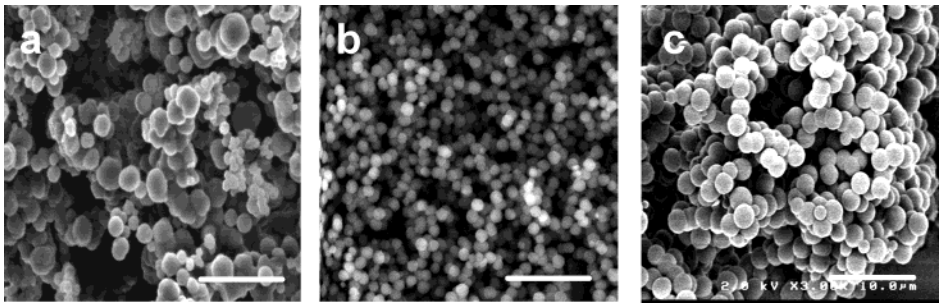

Figure 5. Electron micrographs of cross-linked polymers synthesized by dispersion polymerization in R134a (scale bar = 10 μm): (a) 14 bar, no stabilizer; (b) 17 bar, PVAc macromonomer **1a**; (c) 19 bar, PFPE carboxylic acid stabilizer.

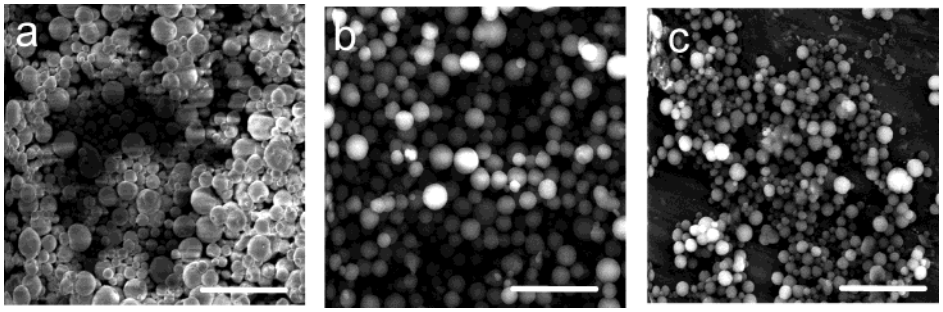

Figure 6. Electron micrographs of polystyrene synthesized by dispersion polymerization in R134a utilizing different stabilizers (scale bar = 20 μm): (a) PFOMA stabilizer, pressure = 230 bar; (b) PVAc macromonomer **2a**, pressure = 268 bar; (c) PVAc macromonomer **2a**, pressure = 14 bar.

transparent solutions at 60 °C, even those conducted at low pressures (e.g., Table 4, entries 1, 8, and 9). Similar cosolvency effects have been noted for PMMA/MMA/CO_2 systems.[50] At relatively low macromonomer concentrations (1% w/w based on styrene), neither **1a** (M_w = 10 000 g/mol) nor **2a** (M_w = 16 900 g/mol) had a very significant effect on the molecular weight or yield of the polystyrene that was produced (Table 4, entries 1−3). At this macromonomer concentration, the reaction pressure had no influence, suggesting that the amount of stabilizer present was simply insufficient to form a stable polymer latex. It should be noted that the degree of methacrylate functionalization was low (<30%): as such, it is likely that only a fraction of the added stabilizer was actually "active". Although isolated polymer yields and molecular weights were low at this stabilizer concentration, a marked difference was noted in terms of phase behavior. In particular, the higher molecular weight stabilizer (**2a**, entry 3) formed a relatively stable latex at the beginning of the reaction, although this latex was observed to collapse before the polymerization was complete. Macromonomers are known to exhibit low reactivity in many cases, particularly when the macromonomer is highly soluble in the continuous phase.[51] It is likely, therefore, that grafting of the macromonomer onto the polystyrene surface may be rather inefficient, thus requiring an excess of the stabilizer to be present.[8] When the concentration of stabilizer **2a** was increased to 8.5% w/w (entry 4), both the yield and molecular weight of the polystyrene were increased significantly. The yield could be improved further by increasing the initiator concentration, without causing a large decrease in M_n (entry 5). Indeed, M_w was *increased* at this higher initiator concentration because the molecular weight distribution became broader. Latex collapse occurred at a late stage in this polymerization to yield an agglomerated product in 82% yield. At higher stabilizer concentration (entry 6, 13.8% w/w based on styrene), the system exhibited phase behavior that is typical for dispersion polymerization

Table 4. Synthesis of Polystyrene by Dispersion Polymerization in 1,1,1,2-Tetrafluoroethane (R134a) Using PVAc Macromonomers as Stabilizers[a]

	stabilizer	stabilizer (% w/w)[b]	initiator (% w/w)[b]	yield (%)[c]	M_n (g/mol)[d]	PDI[e]	P (bar)[f]	av particle diam (μm)[g]
1	**1a**	1	1	9.4	9 000	1.3	17	NA
2	**1a**	1	1	12.3	12 400	2.5	224	NA
3	**2a**	1	1	13.3	13 800	1.4	230	NA
4	**2a**	8.5	1	63.2	31 100	4.6	224	NA
5	**2a**	8.5	2	82.3	27 000	8.2	239	NA
6	**2a**	13.8	2	94.2	42 100	2.6	268	4.94 (26)
7	**2a**	13.8	2	58.4	12 000	7.5	121	NA
8	**2a**	13.8	2	34.9	13 300	3.8	15	NA
9	**2a**	13.8	3	57.2	7 800	1.8	14	4.53 (30)
10	**2**	13.8	2	27.4	11 500	7.0	262	NA

[a] Reaction conditions: 20% w/v total monomer concentration, AIBN, 60 °C, 12 h. [b] Based on monomer. [c] Determined gravimetrically after reprecipitation. [d] Determined by GPC. [e] Polydispersity index = M_w/M_n. [f] Initial pressure at reaction temperature (60 °C). [g] Mean particle diameter calculated from SEM images by measuring > 100 particles. Figure in parentheses = percentage coefficient of variation, CV, where CV = $(\sigma/D_n) \times 100$. σ = standard deviation in particle diameter (μm). D_n = mean particle diameter (μm). NA = agglomerated polymers.

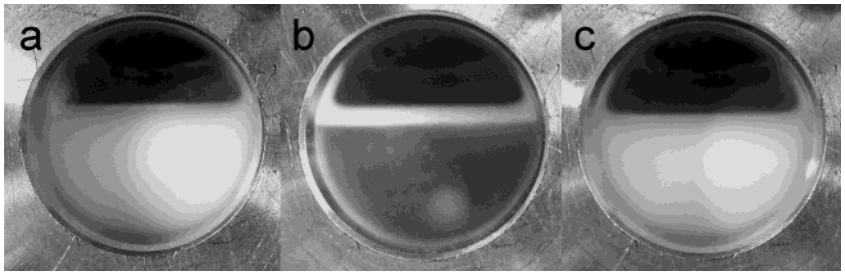

Figure 7. (a) Polystyrene latex particles (Table 4, entry 6) redispersed in R134a (149 mg polymer in 8.0 mL of R134a, 22 °C, 7.1 bar) after purification by washing with methanol. (b) Latex separation observed 15 min after stirring was stopped (note that the polymer is less dense than the R134a solvent and rises to the surface). (c) Dispersed latex after stirring is resumed.

(i.e., a homogeneous solution was formed, followed by light scattering from primary particles, followed by the formation of a stable, white latex that persisted throughout the polymerization). Both yield (>90%) and molecular weight (M_n = 42 100 g/mol) were significantly increased, and the resulting polymer was isolated from the reactor as a powder. The yield and molecular weight of this polymer are comparable with results obtained in studies on the dispersion polymerization of styrene in CO_2 using fluorinated stabilizers.[3,52,53] The polymer morphology was investigated by SEM, and the product was found to exist as discrete polymer microspheres with an average diameter of 4.94 μm (Figure 6b). The product could be redispersed in methanol to form a stable, uniform, white latex. The polymer was washed with methanol (a good solvent for PVAc and the monomer, but a nonsolvent for polystyrene) to remove any residual monomer or unreacted macromonomer, followed by centrifugation and decanting. This procedure was repeated several times. Analysis of the washed product by GPC showed a monomodal peak at 42 100 g/mol with no additional peak at 17 000 g/mol that could be assigned to the macromonomer (see Supporting Information). This confirms that the purification procedure had removed the unreacted PVAc stabilizer.

When the polymerization was repeated at lower reaction pressures (Table 4, entries 7 and 8), the polymer latex collapsed during polymerization and both yield and molecular weight were reduced. We believe that this arises from the fact that the PVAc macromonomer is close to or below its LCST (see Figure 1) at these pressures and temperatures (i.e., the PVAc chains are not sufficiently solvated to fully stabilize the latex). When the initiator concentration was increased to 3% w/w (Table 4, entry 9), a polymer latex was formed that was stable throughout the reaction. The polymer yield was increased under these conditions, but M_n was reduced considerably (7800 g/mol). A sample of the polymer was isolated in a methanol trap during venting to avoid dissolution of the polymer in residual, unreacted styrene. Characterization by SEM showed that polystyrene microspheres had been formed (Figure 6c). The phase behavior of this reaction again suggests that the anchoring of the macromonomer to the polystyrene particle surface may be a relatively inefficient process that is enhanced by increasing the initiator concentration (i.e., more stabilizer chains are grafted to the particle surface which improves latex stability, even though the degree of solvation imparted by the R134a is unchanged).[8] In support of this interpretation, only very weak signals corresponding to grafted PVAc could be detected in the ^{1}H NMR spectra of the polystyrene products (estimated <0.2% w/w PVAc based on polystyrene). Again, this suggests that the overall incorporation of the macromonomer was low, partly because of the inefficiency of the grafting process and partly because of the low degree of methacrylate end-capping (<30%) in the PVAc macromonomers.

To confirm that **2a** was indeed being grafted to the polystyrene particle surface by copolymerization through the methacrylate end groups, the reaction was repeated using the underivatized, hydroxyl-terminated species, **2**. This resulted in a dramatic decrease in yield and molecular weight (cf. entry 10 and entry 6, Table 4). The phase behavior did not indicate a dispersion polymerization mechanism and the product isolated as a hard, agglomerated solid, thus proving that the methacrylate end group was indeed essential for latex stabilization.

Redispersion of Polystyrene Latex Particles in R134a. Polymers produced by dispersion polymerization

are used extensively in the surface coatings industry.[8] For many applications, the polymers are prepared directly as stable latexes in a solvent that is suitable for application of the coatings. Alternatively, the dry, isolated latex can be redispersed in a suitable solvent prior to application. Dry, redispersible coatings are appealing since it is much less expensive to transport dry powders than it is to transport solvent-borne latexes.

The well-defined polystyrene microspheres produced in R134a (e.g., Table 4, entries 6 and 9) could be redispersed, after purification, in solvents such as methanol, which is a good solvent for PVAc but a nonsolvent for polystyrene. The particles did not redisperse in nonsolvents for PVAc (e.g., water, CO_2 (up to 300 bar), diethyl ether, and saturated hydrocarbons). This further supports the argument that permanently grafted PVAc is responsible for latex stabilization. Surprisingly, the polystyrene particles *could* be redispersed in R134a after purification (Figure 7), although the latexes thus formed were observed to separate over time in the absence of stirring (Figure 7b). Previously, Johnston and co-workers synthesized PMMA particles by dispersion polymerization in $scCO_2$ using an "ambidextrous" surfactant that allowed the dry latexes to be redispersed in water.[54] By contrast, none of the polymer latexes synthesized using SCF solvents thus far have been reported to be redispersible in the SCF continuous phase (i.e., agglomeration was irreversible when the SCF solvent was vented). We believe that this PVAc macromonomer system is the first example of a dispersion polymerization in a compressed fluid solvent where the latex particles can be redispersed in the fluid after product isolation. This suggests a number of potential applications, ranging from HFC-borne coatings to the development of aerosol calibration standards.[55]

Conclusions

Of more than 50 candidate polymers tested, PVAc alone was found to be significantly soluble in liquid R134a at room temperature and at low pressures (<10 bar). More detailed phase behavior studies showed that PVAc exhibits LCST behavior in R134a, and an approximate area of operability (i.e., points on the phase diagram where PVAc was soluble) was established. Based on this knowledge, PVAc macromonomer stabilizers were synthesized which were soluble in R134a. Under the appropriate reaction conditions, these macromonomers were effective as stabilizers in the dispersion polymerization of styrene in R134a to yield products that could be isolated directly from the reactor as dry powders in high yields (90%) and with high molecular weights (M_n = 42 000 g/mol). These products consisted of discrete, spherical microparticles in the size range 3.5−5.0 μm. The PVAc macromonomers imparted latex stability by permanently grafting onto the surface of the polystyrene microparticles, which allowed the products to be redispersed in good solvents for PVAc, such as methanol and R134a.

These results demonstrate that R134a, like CO_2, has potential as an environmentally benign solvent for polymer synthesis and processing. Moreover, polymerizations can in principle be carried out at relatively low reaction pressures (<15 bar) using hydrocarbon stabilizers that are very much less expensive than fluorinated polymers or polysiloxanes. Future work will focus on identifying second-generation hydrocarbon stabilizers that exhibit even higher solubility in R134a, thus broadening the scope of this approach and allowing reactions to be carried out at lower operating pressures over a wide range of temperatures.

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Supporting Information Available: Complete list of polymers screened for solubility in R134a and GPC elution curves for polystyrene synthesized using PVAc macromonomers. This information is available free of charge via the Internet at http://pubs.acs.org.

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