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Communications to the Editor

Polymer Synthesis Using Hydrofluorocarbon Solvents. 1. Synthesis of Cross-Linked Polymers by Dispersion Polymerization in 1,1,1,2-Tetrafluoroethane

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Introduction. This paper describes the use of 1,1,1,2-tetrafluoroethane (R134a) as a solvent for the synthesis of cross-linked polymer microspheres. Polymerizations were carried out at moderate pressures (15–40 bar) at temperatures in the range 60–90 °C. We believe this is the first example of dispersion polymerization using a hydrofluorocarbon (HFC) solvent.

There are economic and environmental reasons to explore alternatives to the range of toxic organic solvents that are currently used in polymer chemistry. Supercritical carbon dioxide (scCO₂) has been researched extensively in this context.¹ CO₂ is nontoxic and nonflammable and is widely available from a number of inexpensive, high-purity sources. Nonetheless, it is important to consider all potential economic and environmental impacts—not just the cost of the solvent. In this respect, the relatively high pressures associated with the use of scCO₂ may represent a potential problem, particularly in applications that operate substantially above the critical temperature ($T_c = 31.1$ °C) and that require liquidlike solvent densities (>0.7 g/cm³). In the short term, high pressures translate into increased capital equipment costs. In the longer

term, large pressure differentials contribute to operating costs and to overall energy consumption.²

Like CO₂, R134a is nonflammable and nontoxic and has zero ozone depletion potential. Assessment of the global warming potential (GWP) for R134a (and other HFCs) requires a detailed knowledge of both the atmospheric lifetime and the infrared absorption cross section in the “atmospheric transparency window” (8–12 μm).³ Although the precise GWP for HFCs is still the subject of debate, a widely held view is that the impact of these compounds on climate change will be a very small fraction of the total impact, which will come mainly from the accumulation of CO₂ in the atmosphere.⁴ Thus, R134a has found widespread use as a CFC replacement in refrigeration and in auto air conditioning systems. In addition, the low toxicity of R134a has led to approval as a propellant in metered dose inhalers.⁵ We have found that liquid R134a ($T_c = 101.1$ °C, $P_c = 40.6$ bar) can be used as a solvent for dispersion polymerization at much lower pressures than are possible with scCO₂. The ease of solvent separation is retained because the boiling point of R134a (–26.5 °C) is well below ambient temperature. In principle, lower pressures could equate to lower operating costs for certain processes. On the other hand, HFCs are much more expensive than CO₂, and efficient recycling of these fluids would certainly be a prerequisite for industrial-scale use.⁶ Energy-efficient solvent recycling may be practical for R134a since the fluid was originally developed as a refrigerant. Previously, HFC solvents have been evaluated in applications such as electrochemistry,⁷ particle formation,⁸ extraction/fractionation,⁹ and polymer foaming.¹⁰ To the best of our knowledge, there are only two published examples of the use of HFC solvents for polymerization, both of which involve *precipitation* polymerization in supercritical fluoroform.¹¹ We view the use of HFC solvents for polymer synthesis as a promising development that may be complementary to the use of scCO₂. Moreover, we anticipate that this research will add to the understanding of compressed fluid solvents in general.

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Table 1. Comparison of Physical Properties of CO₂, R134a, and Other HFC Solvents^a

solvent	T_m (°C) ^b	T_b (°C) ^b	T_c (°C) ^c	P_c (bar) ^c	ρ_c (g/cm ³) ^c	α (Å ³) ^c	μ (D) ^b	atm lifetime (yr) ^d	GWP at 100 yr ^d
CO ₂	-56.6	-78.6 ^e	31.1	73.8	0.47	2.65	<i>f</i>		
CH ₂ F ₂ (R32)	-136	-51.7	78.1	57.8	0.42	2.48	2.0	264	650
CHF ₃ (R23)	-155	-82.1	26.2	48.6	0.62	2.65	1.6	5.6	11700
CF ₃ CH ₂ F (R134a)	-101	-26.5	101.1	40.6	0.51	4.38	2.1	14.6	1300
CHF ₂ CF ₃ (R125)	-103	-48.5	66.2	36.3	0.57	4.56	1.6	32.6	2800

^a T_m = melting point; T_b = boiling point; T_c = critical temperature; ρ_c = critical density; α = polarizability; μ = dipole moment; GWP = global warming potential. ^b Data from *CRC Handbook of Chemistry and Physics*, 74th ed. ^c Data from refs 16 and 17. ^d Data from ref 4; GWP measured relative to CO₂. All of these HFC solvents have zero ozone depleting potential. ^e Sublimes. ^f CO₂ has no dipole moment but has a quadrupole moment of -4.3×10^{-26} erg^{1/2}cm^{5/2}.

Experimental Section. a. Materials. Methyl methacrylate (MMA, Aldrich, 99%) and trimethylolpropane trimethacrylate (TRIM, Aldrich, technical grade) were purified as described previously.¹² 2,2'-Azobis(isobutyronitrile) (AIBN, Fisher, >97%) was recrystallized twice from methanol and vacuum-dried before use. Benzoyl peroxide (BPO, Fisher, damped with 20% water) was dissolved in chloroform, reprecipitated in cold methanol, filtered, and vacuum-dried before use. Perfluoropolyether carboxylic acid (PFPE, M_n = 550 g/mol, Aldrich), perfluoroundecanoic acid (PFUA, Aldrich, 95%), penta-decafluorooctanoic acid (PDFOA, Aldrich, 98%), and poly(butyl methacrylate) (PBM, M_n = 337 000 g/mol, Aldrich) were used as received. 1,1,1,2-Tetrafluoroethane (R134a, refrigeration grade) was purchased from Ineos Fluor (Runcorn, UK) and was passed over an Oxisorb catalyst (Messer Griesheim) in order to remove any traces of oxygen.

b. Polymerizations. Reactions were carried out in a 10 cm³ stainless steel view cell, as described previously.¹² The monomers, initiator, and stabilizer (if any) were added to the reaction vessel which was then purged with nitrogen or argon. R134a was added to the reaction vessel using an Isco 260D syringe pump.

c. Characterization. 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.

Results and Discussion. From the viewpoint of a synthetic polymer chemist, the solvent properties of R134a may be thought of as somewhat similar to those of scCO₂. For example, we have found that the majority of common vinyl monomers are soluble (at least up to 20–50% v/v) in liquid R134a at room temperature and above.¹³ Similarly, most hydrocarbon polymers that we have investigated exhibit very low solubility in liquid R134a under moderate conditions ($T < 100$ °C, $P < 50$ bar) when the molecular weight is higher than a few thousand mass units.^{14,15} As such, R134a has broad potential as a solvent for precipitation polymerization or dispersion polymerization. The scope for R134a as the continuous phase for homogeneous solution polymerization or for suspension polymerization is perhaps limited to a smaller range of specific monomers. An important difference between R134a and CO₂ is solvent polarity: CO₂ is symmetrical and has no dipole moment, while R134a is moderately polar and has a significant dipole moment (2.1 D).^{16,17} From a chemical perspective, R134a is relatively inert, although like CO₂ it reacts with strong nucleophiles.¹⁸ Also, R134a contains hydrogen atoms that could participate in chain transfer reactions in free-radical polymerization. Unlike CO₂, R134a does not form significantly acidic environments when contacted with water. Table 1 gives a summary

Table 2. Synthesis of Cross-Linked PMMA by Dispersion Polymerization in 1,1,1,2-Tetrafluoroethane (R134a)^a

	temp (°C)	press. (bar)	initiator	stabilizer ^b	av particle diam (μm) ^c	yield (%)
1	60	14	AIBN	none	<i>d</i>	81
2	60	19	AIBN	PFPE	1.62 (28)	82
3	60	14	AIBN	PFUA	2.63 (11)	66
4	90	36	BPO	PFPE	2.51 (19)	94
5	90	200	BPO	none	<i>d</i>	46
6	90	200	BPO	PDFOA	1.57 (19)	84
7	90	200	BPO	PBM	2.07 (18)	86

^a Reaction conditions: 8:2 w/w MMA + TRIM, 20% w/v total monomer concentration, 5% w/v initiator, 0.5% w/v stabilizer (if added), 6 h. ^b PFPE = perfluoropolyether carboxylic acid (M_n = 550 g/mol), PFUA = perfluoroundecanoic acid, PDFOA = penta-decafluorooctanoic acid, PBM = poly(butyl methacrylate) (M_n = 337 000 g/mol). ^c Mean 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). ^d Agglomerated particles observed.

of selected physical properties for CO₂, R134a, and other common HFC solvents.

Table 2 summarizes the results of a series of dispersion polymerizations involving methyl methacrylate (MMA) and trimethylolpropane trimethacrylate (TRIM) in the proportion 8:2 w/w. Figure 1 shows electron micrographs for the cross-linked microparticles prepared by this route. Both MMA and TRIM (and mixtures thereof) are freely soluble in liquid R134a at room temperature and above, at least up to concentrations of 50% v/v. Using AIBN as the initiator, free-radical polymerization produced cross-linked powders in good yields by precipitation polymerization in the absence of any stabilizer (entry 1). The unstabilized precipitation polymers contain microparticles, some of which are spherical, but these exist in a highly agglomerated state (Figure 1a). The phase behavior was quite typical for a precipitation polymerization of this type. First, a homogeneous solution was formed; as the reaction proceeded, a red color was observed (due to light scattering from primary particles); finally, a white precipitate formed in the reaction vessel. Similar results have been obtained for the free-radical precipitation polymerization of divinylbenzene, ethylene glycol dimethacrylate (EGDMA), and TRIM in scCO₂ in the absence of any stabilizers.¹² The fact that these cross-linked systems form powders in reasonable yields by unstabilized precipitation polymerization (while, for example, the unstabilized polymerization of neat MMA does not) is due in part to the fact that the rigid, cross-linked particle surface provides an inherent barrier to agglomeration.^{12,19} The reaction was repeated in the presence of a monofunctional perfluoropolyether (PFPE) carboxylic acid stabilizer (M_n = 550 g/mol) of the type developed by Howdle for the dispersion polymerization

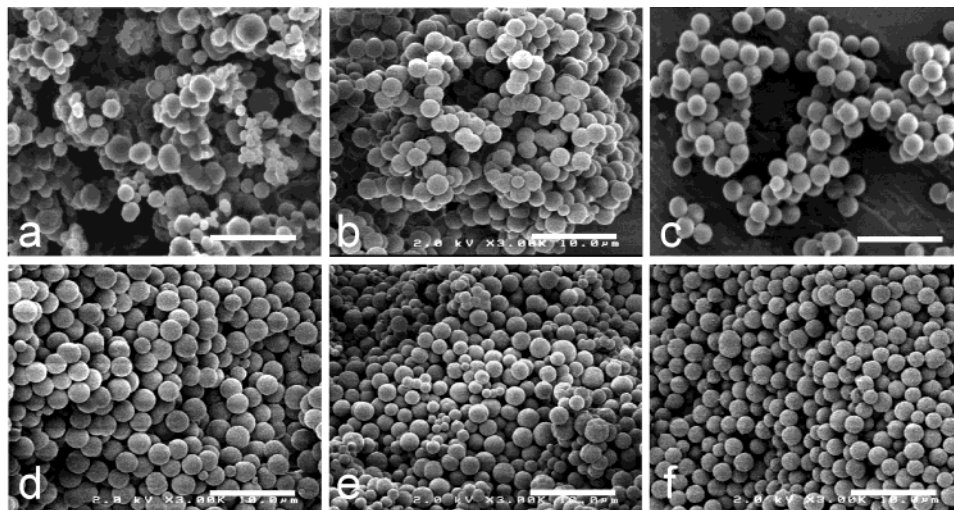


Figure 1. Electron micrographs of cross-linked polymers synthesized by dispersion polymerization in R134a (scale bar = 10 μm): (a) 60 $^{\circ}\text{C}$, 14 bar, no stabilizer; (b) 60 $^{\circ}\text{C}$, 19 bar, perfluoropolyether carboxylic acid stabilizer; (c) 60 $^{\circ}\text{C}$, 14 bar, perfluoroundecanoic acid stabilizer; (d) 90 $^{\circ}\text{C}$, 36 bar, perfluoropolyether carboxylic acid stabilizer; (e) 90 $^{\circ}\text{C}$, 200 bar, pentadecafluorooctanoic acid stabilizer; (f) 90 $^{\circ}\text{C}$, 200 bar, poly(butyl methacrylate) stabilizer.

of MMA in scCO_2 .²⁰ This stabilizer is soluble in R134a, at least at the low concentrations (0.5% w/v) used for dispersion polymerization. A uniform white latex was observed in the presence of the PFPE stabilizer, and discrete polymer microspheres were produced in good yield (entry 2, Figure 1b). The latex was observed to be stable although some particle precipitation was observed on the sapphire view window toward the end of the reaction (i.e., after a period of a few hours). These results are consistent with a dispersion polymerization mechanism, and the phase behavior is similar to that observed in comparable systems involving scCO_2 .^{12,20} PFPE stabilizers of this type are believed to anchor reversibly with the dispersed phase by hydrogen bonding to ester groups in the polymer.²⁰ Interestingly, a similar product was obtained using perfluoroundecanoic acid (PFUA), which has a molecular weight (564 g/mol) close to that of the PFPE stabilizer (entry 3, Figure 1c). Whether these relatively low molecular weight compounds act purely by steric stabilization or by some other mechanism (e.g., by lowering the surface tension between the solvent and the dispersed polymer phase) is unclear.

From a practical perspective, the most important feature of these polymerizations is the relatively low reaction pressure (typically in the range 10–20 bar at 60 $^{\circ}\text{C}$). Comparable dispersion polymerizations carried out using scCO_2 have involved much higher pressures (170–350 bar) in order to achieve reasonable solvent densities at similar temperatures.^{20,21} At even higher reaction temperatures (>80 $^{\circ}\text{C}$), the pressures required for the use of scCO_2 as a solvent may sometimes be prohibitive. Figure 1d shows the product morphology for a cross-linked polymer synthesized in R134a at 90 $^{\circ}\text{C}$ using the PFPE stabilizer and BPO as the initiator (entry 4). This sample was produced by dispersion polymerization at a pressure of 36 bar. The critical temperature for R134a is 101.1 $^{\circ}\text{C}$: thus, it is possible to carry out reactions in the liquid state at quite moderate pressures (5–50 bar) at temperatures between ambient and 100 $^{\circ}\text{C}$. Moreover, the solvent density under these conditions (for pure R134a) ranges between 0.9 and 1.3 g/cm^3 .²² This is significant because many polymerization reactions proceed at temperatures that are well above ambient. Liquid CO_2 can be used as a

solvent at relatively low pressures (<70 bar), but only for reactions occurring at temperatures below 31.1 $^{\circ}\text{C}$. In the case of the free-radical dispersion polymerization of acrylate monomers, this requires the use of low-temperature initiators that may be difficult to transport and handle.

Even in the liquid state, the solvent properties for R134a (e.g., dielectric constant and dipolarizability) can be “tuned” to some extent with pressure.^{17,22} The variation of these properties as a function of pressure increases dramatically at conditions close to and above the critical temperature. Thus, we have begun to investigate the influence of pressure on these systems (entries 6 + 7, Figure 1e,f).²³ Our first efforts to use less expensive hydrocarbon stabilizers in conjunction with R134a have been largely unsuccessful, although poly(butyl methacrylate) ($M_n = 337\,000$ g/mol) did show some activity at higher pressures and temperatures (entry 7, Figure 1f).²⁴ In this respect, the difficulties are similar to those encountered already with scCO_2 . For example, Beckman has shown that it is possible to design CO_2 -soluble hydrocarbon polymers, but only by achieving a precise balance of physical properties.²⁵ We are adopting a similar approach, taking into account the more polar nature of R134a.

Conclusions. Our results show that it is possible to synthesize cross-linked polymers using R134a as the solvent at moderate pressures. Furthermore, the polymers can be formed as uniform microspheres by addition of a suitable stabilizer. The inherently rigid nature of these cross-linked materials assists in the formation of this product morphology. Clearly, the extension of this approach to *linear* polymers would greatly broaden its scope. Preliminary attempts to polymerize MMA by these routes have resulted in relatively low yields (30–90%) and modest molecular weights ($M_n = 30\,000$ –270 000 g/mol). It has so far proved impossible to generate uniform PMMA latex particles. Reactions involving other vinyl monomers (e.g., styrene, acrylonitrile, acrylic acid) have shown broadly similar trends. In comparison with results obtained using scCO_2 ,²⁰ there appears to be a reduction in activity for the PFPE acid-terminated steric stabilizers. This may result from insufficient solubility of these materials in R134a. Alternatively, the hydrogen-bonded anchoring mecha-

nism proposed by Howdle and co-workers may be substantially weaker in the more polar hydrofluorocarbon fluid. The development of steric stabilizers suitable for the dispersion polymerization of monofunctional vinyl monomers in HFC solvents will be the subject of a future report.

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