Perfluorocarbon Fluids: Universal Suspension Polymerization Media

Dong-Wei Zhu

Fluorochemical Process & Technology Center, 3M Company, 236-3C-89, St. Paul, Minnesota 55144-1000

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ABSTRACT: The use of perfluorocarbon (PFC) fluids such as perfluorinated alkanes as universal suspension polymerization media is described. PFC fluids are inert, stable, and immiscible with most organic compounds and with water. In utilization of these unusual immiscibility and stability properties, cross-linked copolymer beads bearing reactive functional groups were prepared by direct suspension copolymerization of the reactive monomer with a difunctional cross-linker in PFC fluids. Examples of functional groups include isocyanate, hydroxyl, acid chloride, carboxylic acid, aziridine, and trimethoxysilane. The suspension homopolymerization of methacrylic acid and cationic suspension polymerizations of vinyl ethers in PFC fluids were also achieved. The role of dispersants in these nonaqueous media was studied through the suspension copolymerization of styrene and divinylbenzene. The advantages of using PFC fluids in suspension polymerization over water were summarized.

Introduction

Cross-linked polymer beads bearing reactive functional groups have been used widely in organic synthesis[1] since Merrifield first reported "solid phase peptide synthesis" using chloromethylated poly(styrene−divinylbenzene) polymer beads in 1963.[2] While some of these polymer beads can be prepared by direct suspension polymerizations, others can only be obtained by multistep reactions involving suspension polymerizations followed by polymeric reactions due to difficulties in finding a suitable medium in which the reactive monomers can be suspended. For example, polymer beads bearing acid chloride functional groups were obtained by reacting polymeric carboxylic acid with $SOCl_2$,[3,4] although it is known that such a reaction is difficult to control, may change the macroporous polymer bead structure, introduces byproducts, and has relatively low functional group conversions. The alternative, direct suspension polymerization of acryloyl chloride either with or without a difunctional cross-linker, however, has not been available, since it reacts with water, and most other organic solvents dissolve it.

Nonaqueous suspension agents such as paraffin oils have been developed to polymerize polar monomers, such as acrylic acid for radical polymerizations and amino acids for condensation polymerizations, which are immiscible with these oils.[5,6] The so-called water-in-oil (w/o) suspension polymerizations (reversed phase suspension polymerizations) comprise an aqueous solution containing the hydrophilic monomer(s) and initiator(s), which are suspended in liquid paraffin oils or other nonpolar hydrocarbon media and polymerized.[7,8] Water is used to reduce the solubility of the monomer(s) in paraffin, and only monomer(s) that are insoluble in paraffin and inert to water can be polymerized. Obviously, this method is limited and will not be effective if other monomers, such as divinylbenzene, have to be incorporated. Multicomponent systems with monomers of drastically different solubility characters cannot be suspension polymerized due to the fact that it will be impossible to find a medium that can suspends all the monomers. For example, in a recent publication,[9] Vlatakis had to make his cross-linked "molecular imprints" by solution polymerization into one big chunk, followed by grinding this cross-linked polymer chunk with a mechanical mortar into the fine particles he needed.

Suspension polymerizations involving monomers or initiators with partial water solubility are also difficult to deal with since the hydrophilicity may destabilize the formed polymer beads and induce agglomeration.[10] The method of using a highly concentrated aqueous salt solution to reduce a monomer's solubility in water[11] does improve the process to a limited extent.

This paper reports our work in using perfluorocarbon (PFC) fluids in the area of suspension polymerizations. Such a suspension polymerization refers to a system in which monomers are suspended as the discontinuous phase of droplets in a continuous PFC fluid phase and polymerized. This work is an extension of our previously reported work using PFC fluids as immiscible media for organic reactions.[12]

PFC fluids are perfluorinated and saturated aliphatic compounds which include perfluoroalkanes, perfluoroalkylethers and perfluoroalkylamines (see Table 1 for boiling points, viscosity, density, water solubility, and surface tension properties of some selected PFC fluids). All three types of liquids have very similar chemical and physical properties other than boiling points (which are mainly related to their molecular weight). For example, perfluorotrialkylamines cannot be protonated by mineral acids such as HCl, do not have any odor, and are no more reactive than perfluoroalkanes under the usual reaction conditions. In fact, PFC fluids are so inert that they do not react with such reactive chemicals as Ziegler−Natta catalysts. The total substitution of fluorine has overwhelmed the structural and chemical differences of compounds. PFCs are very different from their hydrocarbon equivalents. PFCs usually have higher density, lower boiling point, lower heat of vaporization, and lower polarity than their parent hydrocarbons. Among the most important characteristics are their extremely low miscibility, excellent stability, and inertness toward organic compounds, which make them the universal suspension media unmatched by any other fluids.

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Table 1. Important Parameters of Some PFC Fluids[15−17]

PFC fluids[a]	bp, °C	density (25 °C), g/mL	viscosity (25 °C), cs	solubility in water, ppm	surface tension, mN/m
$C_5F_{11}NO$	50	1.70	0.40	14	13
C_6F_{14}	57	1.68	0.40	10	12
C_7F_{16}	83	1.73	0.55	11	13
C_8F_{18}	103	1.78	0.80	13	14
$(C_3F_7)_3N$	129	1.82	0.82		13
$(C_4F_9)_3N$	177	1.88	2.8	7.0	16
$(C_5F_{11})_3N$	215	1.94	14.0	8.0	18

[a] $C_5F_{11}NO$, perfluorinated *N*-methylmorpholine; C_6F_{14}, C_7F_{16}, and C_8F_{18}, perfluorinated hexane, heptane, and octane; $(C_3F_7)_3N$, $(C_4F_9)_3N$, and $(C_5F_{11})_3N$, perfluorinated tripropylamine, tributylamine, and tripentylamine.

Table 2. Suspension Polymerization of St−DVB in PFC Fluids

entry	dispersant	yield, %
1	none	46
2	PMAA (MW 15 000)	46
3	$C_{12}H_{25}SO_3Na$	48
4	$C_7F_{15}COONa$	66
5	FC-430	77
6	$C_{12}H_{25}C_6H_4SO_3Na$	100

Experimental Section

Materials and Characterizations. 2-Isocyanatoethyl methacrylate was obtained from Dow Chemicals, 2-aziridinylethyl methacrylate was from Chugai International Corp., and PFC fluids were from 3M Co. FC-72 (bp 56 °C, perfluorohexanes) and FC-77 (bp 97 °C, perfluorooctanes) were used in this paper.[16] All other chemicals were obtained from Aldrich and used without further purification. Standard characterizations such as elemental analysis, infrared spectra (IR) and gel permeation chromatography (GPC) were carried out by 3M analytical laboratories. The cross-linked copolymer beads were ground and KBr pellets were prepared for IR spectra.

Suspension Copolymerization of Styrene (St) and Divinylbenzene (DVB). Styrene (45.0 g) was mixed with divinylbenzene (5.0 g), AIBN (0.50 g), and FC-77 (100 mL) in a round-bottom flask equipped with a mechanical stirrer. This two-phase mixture was then polymerized at 50−55 °C for ∼8 h. Stirring speed was controlled at 250−350 rpm. The poly(St−DVB) beads were floated on top of the PFC fluid phase after polymerization, filtered, and dried at 65 °C under reduced pressure. Beads with irregular shapes, including lumps if any, were sieved out using a No. 18 sieve (1.0 mm opening) from The Murdock Co. and discarded. Cross-linked poly(St−DVB), beads which passed through the sieve (23.0 g, 46% yield), were recovered.

The above copolymerization was repeated with the addition of dispersants at 0.5 wt % of the total monomers. The types of dispersants and experimental results were summarized in Table 2.

Suspension Copolymerization of Reactive Monomers. The polymerizations, workup, and characterizations of the reactive monomers described in Table 3 were carried out under similar conditions. A typical example is the polymerization of methacryloyl chloride (10.0 g), styrene (35.0 g), and divinylbenzene (5.0 g). The monomers were mixed with AIBN (0.50 g) in a 250 mL round-bottom flask containing FC-77 (100 mL), followed by addition of sodium dodecylbenzenesulfonate (0.10 g). This two-phase mixture was suspension polymerized at 50−55 °C under nitrogen for ∼8 h. Stirring speed was controlled at 250−350 rpm. The polymer beads obtained were washed with fresh FC-77, dried under reduced pressure at 65 °C, and sieved with the No. 18 sieve described above (37 g of beads passed through; yield 74%). The IR spectrum indicated the strong absorption band of COCl at 1798 cm^{-1}. Anal. (found/calcd): C, 82.5/82.9; H, 7.4/7.1; Cl, 6.3/6.8.

Suspension Polymerization of Methacrylic Acid (MAA). Methacrylic acid (50.0 g), was mixed with AIBN (0.50 g) and FC-77 (100 mL), followed by addition of sodium dodecylbenzenesulfonate (0.10 g). This mixture was then polymerized in a round-bottom flask equipped with a mechanical stirrer at 50-55 °C under nitrogen overnight. The stirring speed was controlled at 250−350 rpm. Poly(methacrylic acid) (PMAA) suspended in FC-77 was then filtered out and dried under reduced pressure at 65 °C. Agglomerated polymers, found on the flask wall, were discarded. PMAA with very fine particles (11.0 g) was obtained. A small sample was dissolved in THF and the solution analyzed by GPC (M_w/M_n = 217000/25000 = 8.7 based on polystyrene standard).

Cationic Suspension Polymerization of Ethyl Vinyl Ether and 1,4-Bis(vinyloxy)methylcyclohexane. FC-72 (150 mL) was added to a three-necked 500 mL round-bottom flask equipped with a mechanical stirrer, a thermometer, and a condenser. The flask was kept under positive nitrogen flow and cooled by an acetone−dry ice bath. $BF_3{\cdot}Et_2O$ (1.0 g) was injected into this system when the inside temperature was at ∼−20 °C. A mixture of ethyl vinyl ether (30.0 g) and 1,4-bis(vinyloxy)methylcyclohexane (20.0 g) at room temperature was then injected slowly into the solution at ∼−50 °C. A small plastic tube was attached to the needle tip so the monomers were introduced into the solution phase directly. The solution temperature was maintained at −40 to −50 °C, and the addition took ∼30 min. The system was stirred at this temperature for another 3 h and then slowly warmed to room temperature. The suspended polymer was collected on a filter paper, washed with water to quench the catalyst and dried (31.0 g was obtained). Elemental analysis (found/calculated); C: 67.3/66.5, H: 10.6/10.2.

Results and Discussion

Choice of Dispersant. A distinctive feature of the PFC fluids is their low surface tension (12−18 mN/m; see Table 1), which is lower than that of organic monomers at 25−40 mN/m and much lower than that of water at 72 mN/m. The fact that PFCs have the lowest surface tension makes them capable of dispersing organic monomers with no additives. Thermodynamically, the higher surface energy phase disperses as droplets, and the lower surface energy phase forms the continuous phase in a two-phase system under dispersing conditions. Experimental results support the above assumption. As shown in Table 2, poly(St−DVB) beads were obtained with 46% yield by suspension polymerization in PFC fluids without using dispersants (entry 1). This would not be possible with water-based suspension polymerizations since styrene and divinylbenzene, with lower surface tension, will not disperse into droplets in water in the absence of surfactants or dispersants under normal dispersing conditions.

The role of dispersants in these PFC-based suspension polymerizations was examined with a range of compounds including a hydrocarbon polymer (PMAA, M_n = 15 000), two hydrocarbon surfactants ($C_{12}H_{25}SO_3Na$, $C_{12}H_{25}C_6H_4SO_3Na$), a fluorinated nonionic polymeric surfactant (FC-430, available from 3M Co.) and a fluorinated monomeric anionic surfactant ($C_7F_{15}COONa$). Results are summarized in Table 2. The yield in Table 2 is defined as the amount of recovered polymer beads with size smaller than 1.0 mm in diameter divided by the total monomers charged. The higher the yield is, the less polymer lumps and agglomerates of irregular sizes and shapes.

In a recent review,[17] Yuan et al. pointed out that "the presence of an organic stabilizer decreases the mean droplet size due to the reduction of interfacial tension between the dispersed and continuous phases and also due to the decrease in the rate of coalescence". Furthermore, Lewis[18] concluded, in a study of water-based suspension polymerizations, that the hydrophobic−hydrophilic balance (HLB) of the surfactant system and

Table 3. Suspension Polymerization of Reactive Monomers

polymer	feeding monomers; wt ratio	yield, %	elemental anal. theor/found	characteristic IR band, cm^{-1}
1	CH_2=C(Me)COCl:St:DVB; 20:70:10	74	C, 82.9/82.5 H, 7.1/7.4 Cl, 6.8/6.3	COCl, 1789 (s)
2	CH_2=C(Me)COCl:DVB; 90:10	56	C, 50.5/53.4 H, 5.1/5.8 Cl, 30.6/28.7	COCl, 1789(s)
3	CH_2=CHCOCl:St:DVB; 20:70:10	34	C, 81.7/81.3 H, 6.8/7.0 Cl, 7.9/7.0	COCl, 1789 (s)
4	CH_2=C(Me)$CO_2(CH_2)_2$NCO:DVB; 90:10	82	C, 58.0/54.3 H, 6.0/5.6 N, 8.1/7.3	COO, 1732 (s) NCO, 2274 (s)
5	CH_2=C(Me)COOH:DVB; 90:10	42	C, 59.4/56.3 H, 7.1/7.0	COOH, 1699 (s), 3300 (bs)
6	CH_2=C(Me)$CO_2(CH_2)_3Si(OMe)_3$:DVB; 90:10	86	C, 52.7/51.2 H, 8.8/7.5 Si, 10.2/14.7	COO, 1727 (s) Si(OMe), 1088 (s)
7	CH_2=C(Me)$CO_2CH_2CH_2OH$: DVB; 90:10	47	C, 59.0/58.3 H, 7.7/7.7	OH, 3426 (bs) COO, 1726 (s)
8	CH_2=C(Me)$CO_2(CH_2)_2$NCH_2CH_2:DVB; 90:10	98	C, 64.9/64.7 H, 8.3/8.7 N, 8.1/8.2	aziridinyl, 1150 (s) COO, 1726 (s)

its solubility in monomer and water phases determine the droplet size, droplet coagulation, and particle agglomeration for a specific agitation system. HLB values, however, are no longer applicable in these systems and hydrocarbon surfactants are not miscible in PFC fluids at all. The compatibility and solubility of these dispersants/surfactants in the monomers, therefore, become very important in these suspension polymerizations. The fact that $C_{12}H_{25}C_6H_4SO_3Na$ is a better dispersant than $C_{12}H_{25}SO_3Na$ (quantitative yield vs almost no effect; see Table 2) could possibly be explained because the former, with its additional aromatic unit, can be absorbed by the St−DVB droplets more efficiently and can thereby form a more effective stabilizing layer on the surface of droplets. Absence of any stabilization effect of PMAA (see Table 2) in this study may result from its insolubility and incompatibility in the St−DVB monomer phase due to its polar polymeric structure. In this case, PMAA could have formed a separate phase. It should be noted that the good dispersion properties of PMAA observed in some aqueous suspension polymerizations are attributed to its stabilizing effect from the aqueous suspension media since PMAA is partial soluble in water.

Both FC-430, a copolymer containing fluorocarbon and poly(ethylene oxide) tails, and $C_7F_{15}COONa$ are partially soluble in PFC fluids at the polymerization temperatures. A milky emulsion was noticed at the beginning of polymerization when FC-430 was used in the polymerization of St−DVB system. Both fluorinated surfactants improved the yields as indicated in Table 2. The fact that fluorinated surfactants are not the best dispersants in Table 2 leads us to believe that droplet coalescence and particle agglomeration are more influenced by the nature of the polymer and the dispersants/surfactants absorbed onto these surfaces than that of the suspension medium. Solubility differences between fluorinated and hydrocarbon surfactants are some other considerations. The hydrophobic tail of fluorinated surfactants is compatible with PFC fluids as the hydrophilic end of the hydrocarbon surfactants in water. Fluorinated surfactants will be, therefore, present in the interface of the PFC phase and St−DVB monomer phase with the fluorinated tails in PFC fluids, whereas hydrocarbon surfactants are not soluble in PFC fluids at all and they will be excluded from the PFC phase. The concentration of soluble fluorinated surfactants at the interface is possibly much lower compared to the layer of insoluble hydrocarbon surfactants attached only onto the surface of the polymerizing droplets.

In general, use of dispersants in PFC-based suspension polymerization may not be required but can often reduce coalescence and agglomeration and therefore improve yields. Investigation in this area is being continued in an attempt to understand the role of dispersants in both aqueous and PFC suspension polymerizations.

Suspension Polymerization of Reactive Monomers. Monomers reactive with or soluble in water were polymerized in PFC fluids in the presence of 0.5 wt % sodium dodecylbenzenesulfonate. All of them were obtained in bead form since they were cross-linked by DVB. Table 3 summarizes monomers used in this investigation, the weight ratio of the monomers charged in each copolymerization, the yields, the elemental analysis results of the copolymer beads, and their characteristic IR absorption bands.

Cross-linked copolymer beads with reactive functional groups such as acid chloride, carboxylic acid, isocyanate, trimethoxysilane, hydroxyl, and aziridine were prepared by one-step polymerization of the respective monomers in PFC fluids (Table 3). Previously, most of these functional groups could only be introduced to the polymer beads by subsequent polymeric reactions. The one-step suspension polymerization of acryloyl chloride with styrene and divinylbenzene is a typical sample of how PFC fluids can be used to suspend such reactive monomers. It would be impossible to find a common organic or inorganic fluid to suspend acryloyl chloride. The first three samples in Table 3 are cross-linked polymer beads containing COCl functional groups. Styrene was added as a diluent to separate the functional groups in polymer beads. Cross-linkers other than DVB such as di- or multifunctional acrylates were investigated, and no significant differences were observed. The percentages of cross-linker in the composition seem to affect the polymerization and final properties more than the type of cross-linkers does. The higher the cross-linker percentages, the higher the yields. A copolymer of methacryloyl chloride (copolymer **1**) yielded more uniform beads (74% yield) than that of acryloyl chloride (copolymer **3**, 34% yield) under almost

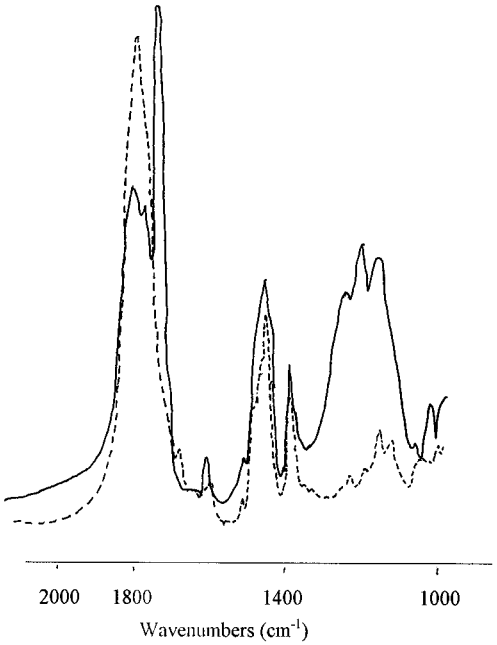

Figure 1. IR spectra of methyacryloyl chloride−DVB copolymer before (- - -) and after (—) reaction with methanol.

the same monomer ratios and reaction conditions. The higher yield could be attributed to the higher T_g of the methacryloyl chloride polymer compared to that of acryloyl chloride. This is in agreement with results from water-based suspension polymerizations of acrylate esters where higher T_g polymers usually have better yields. Lower T_g materials tend to have more agglomeration in the "sticky period", which leads lower yields. The strong IR absorption band at 1789 cm^{-1} and reasonable elemental chlorine analysis results indicated that the three copolymers retained the reactive COCl functional group. In confirming the reactivity of the polymer-supported acid chloride, copolymers **1**, **2**, and **3** were reacted with methanol. The reactions were carried out by shaking the copolymer beads with an excess amount of methanol at room temperature overnight, followed by washing with clean methanol and drying. IR spectra of the three reacted polymers showed the expected COOMe carbonyl absorption band at 1730 cm^{-1} and COOMe ether band at ~1200 cm^{-1}. Figure 1 illustrates the IR spectra of polymer **2** before and after reacting with methanol.

The cross-linked poly(MAA−DVB) was obtained in ~40% yield (polymer **5** in Table 3). The IR spectrum of this copolymer resembles that of the PMAA homopolymer with the typical strong acid broad absorption at ~3300 cm^{-1} and the carbonyl group at 1699 cm^{-1}. Uniformly dispersed copolymer beads containing carboxylic acid may be of special interest to pharmaceutical applications. A recent publication[9] reported the use of "molecular imprinting" for a drug assay, where cross-linked polymer beads containing carboxylic acid groups were used to form ionic interactions with the "print molecule" which contains amino groups.

Hydroxyethyl methacrylate (HEMA) cannot be easily suspension polymerized in aqueous medium due to its good miscibility in water, although it has been reported that it can be copolymerized with ethylene dimethacrylate in a paraffin oil dispersion and by a precipitation suspension polymerization method in an aqueous dispersion medium.[19] In the present investigation, its copolymer beads with DVB were obtained in PFC fluid

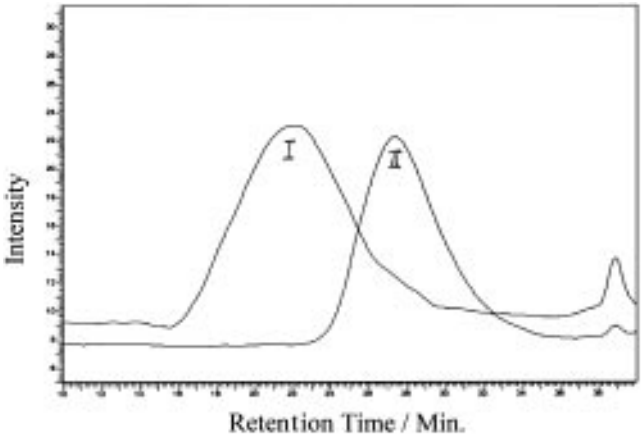

Figure 2. GPC of PMAA, derivatized with CH_2N_2: (I) prepared by suspension polymerization in PFC fluid, M_w/M_n = 224000/28500 = 7.9; (II) commercial product of 15 000 molecular weight, M_w/M_n = 19100/9000 = 2.1.

suspension in 47% yield (polymer **7**). Attempted copolymerization of hydroxyethyl acrylate (HEA) with 10% DVB produced mainly agglomerated polymer lumps. However, uniformly distributed HEA copolymer beads were obtained with 30% or more DVB in reasonable yields. Copolymers with a high percentage of HEA are too soft to be uniformly distributed under the suspension polymerization conditions described.

In a demonstration of the versatility of the present suspension method, acrylates with other reactive functional groups such as isocyanate (polymer **4**), trimethoxysilane (polymer **6**), and aziridine (polymer **8**) were also prepared. All of them afforded satisfactory yields (80−90%) and retained their reactive groups, as evidenced by their characteristic IR absorption of the resulted polymer beads.

It should be emphasized that yields in Table 3 can be improved by optimizing polymerization parameters such as agitation speed and choice of dispersant for each polymerization system. It was not our priority in this investigation to optimize the yield of each polymerization. The applications of these highly reactive polymer beads in synthetic chemistry will be further evaluated.

Suspension Polymerization to Linear PMAA. The suspension polymerization to a linear polymer is much more challenging than that of the cross-linked materials. Low-T_g polymers are too tacky to be separated efficiently and therefore usually result in agglomerated polymers instead of uniformly distributed beads. The use of PFC fluids could be advantageous if the tackiness of the polymer is due to partial water solubility. Linear PMAA, in the form of fine particles, was prepared by suspension polymerization in PFC fluids. IR analysis indicated the typical absorption band of a broad carboxylic acid peak at 2800−3300 cm^{-1}. The polymer is soluble in THF and was analyzed by GPC (M_w/M_n = 217000/25000 = 8.7 based on polystyrene standard). The chromatograms of the PMAA prepared and a commercial PMAA product with M_n = 15 000 are shown in Figure 2. Both the molecular weight and polydispersity of the current PMAA are quite high and these could be attributed to the autoacceleration (Trommsdorf effect) in the early stage of polymerization due to its minibulk conditions.

Cationic Suspension Polymerizations. Suspension cationic polymerization is little known because of the difficulties in finding suitable suspension media. Water can rarely be used since most cationic initiators

such as $TiCl_4$ and $BF_3{\cdot}Et_2O$ are moisture sensitive. Furthermore, such polymerizations are normally carried out at below 0 °C. PFC fluids are ideal for cationic suspension polymerization because of their low polarity, immiscibility, high stability, and low freezing points (−86 °C for FC-72).[13] The discovery of the use of PFC fluids, therefore, opens a new and convenient route for this type of polymerization. As an example, a cross-linked copolymer of ethyl vinyl ether/1,4-bis(vinyloxy)-methylcyclohexane (60:40 by weight) was prepared by suspension polymerization using $BF_3{\cdot}Et_2O$ in FC-72. The polymerization was carried out at temperatures as low as −50 °C. Evenly distributed polymer powder was obtained after the PFC fluid was filtered. An IR spectrum of this polymer resembles that of the poly-(ethyl vinyl ether) and is characterized by the strong ether absorption band at 1099 cm^{-1}.

Summary

The use of PFC fluids has extended the scope of the suspension polymerization method to monomers and initiators that cannot be used due to their high solubility and reactivity in conventional suspension media. This has led to many novel and useful polymers such as acid chloride-containing copolymer beads which are difficult to prepare by conventional methods and often involve multistep reactions. In suspension polymerizations involving more than one monomer with significantly different solubility and reactivity properties, it is definitely an advantage to use PFC fluids since it would be otherwise very difficult to find a medium that can satisfy all the monomers. The fact that the surface energy of PFC fluids is lower than that of organic monomers makes it theoretically possible to disperse the organic monomers without using surfactants. This feature is rather attractive since polymers thus prepared would be similar to those from solution or bulk polymerization and free of surfactants. However, the yields of good beads can be increased by using the right surfactants/dispersants since these stabilizers can prevent the polymerizing droplets from coalescence during the "sticky" period of polymerization. The availability of PFC fluids in a wide range of boiling and freezing points makes the choice of a suspension medium that can be tailored to individual needs very easy. Nevertheless, PFC fluids will not replace water in suspension polymerizations if water can be used. It is actually better to use water wherever possible since water is inexpensive and it has been used as a suspension medium for decades with a lot of research already done. Table 4 briefly summarizes the comparison of PFC fluids and water in suspension polymerizations.

Table 4. PFC Fluids vs Water in Suspension Polymerization

suspension medium	water	PFC fluids
miscibility/solubility	some organic monomers/initiators	no organic monomers/initiators
reactivity	proton donor	inert
polarity	polar	nonpolar
boiling points	100 °C	wide range 52−250 °C
freezing point	0 °C	as low as −100 °C
surfactants/dispersant	required	optional

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(15) Some data included in Table 1 come from internal 3M technical reports.
(16) Commercial PFC fluids are mixtures of isomers. FC-72, for example, is a mixture of straight and branched perfluorohexanes instead of a pure component. However, the presence of isomers does not affect the application of PFC fluids as suspension polymerization media.
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