# Synthesis of Novel Fluorinated Polymers via Cyclodextrin Complexes in Aqueous Solution

**Hakan Cinar, Oliver Kretschmann, and Helmut Ritter***

*Heinrich-Heine-Universität, Institut für Organische Chemie und Makromolekulare Chemie, Lehrstuhl II, Universitätsstrasse 1, Geb. 26.33.00, D-40225 Düsseldorf, Germany*

*Received January 12, 2005; Revised Manuscript Received April 6, 2005*

ABSTRACT: Newly synthesized fluorinated monomers 4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene (**2**) and 2,3,4,5,6-pentafluorostyrene (**1**) were polymerized in water after complexation with randomly methylated $\beta$-cyclodextrin (RAMEB) without the use of any surfactants or cosolvents. The complex stoichiometries of the RAMEB/monomer complexes were investigated by NMR experiments. Kinetic studies of the homo- and copolymerization with styrene demonstrated a high reactivity of the complexed fluorinated monomers in aqueous solution. Using a semibatch polymerization technique, the use of RAMEB induced formation of stable poly(2,3,4,5,6-pentafluorostyrene) latex particles whereas without RAMEB no spherical particles could be visualized.

## Introduction

Fluoropolymers in general are an economically important class of high performance materials. Some of their features are high chemical and thermal stability, outstanding antiadhesive and oil-repellent properties, low refractive index, and low dielectric constant. They are industrially used e.g. as coatings, seals, or insulators. Further applications include the use of fluoropolymers in membranes and as lubricants in disk drives and waveguide devices.[1−3]

Because of the insolubility of fluorinated polymers in common solvents, aqueous emulsion polymerization with added surfactants is a preferred method for industrial fluoropolymer production. Additionally, polymerization in organic solvent mixtures containing chlorofluorocarbons or fluorinated surfactants is an alternative method. Even under these reaction conditions, particularly copolymerization of fluorinated monomers with hydrophilic or lipophilic comonomers often proves difficulties because of the contrary chemical nature of the fluorinated monomers. The chemical and physical characteristics of fluorinated monomers prohibit the homo- and copolymerization in water without addition of surfactants or cosolvents. This paper reports about polymerization of fluorinated monomers in aqueous phase after complexation with cyclodextrins (CDs).

It is well-known that CDs are able to enclose smaller molecules to form host/guest complexes.[4−7] Water-insoluble molecules become water-soluble by treatment with aqueous solutions of CDs without any chemical modification of the guest molecule. Randomly methylated $\beta$-CD (RAMEB), which is industrially synthesized on a large scale and readily available, displays a very high water solubility. This ability qualifies it to transfer hydrophobic guests into the water phase in a high concentration.

Our group has investigated the free radical polymerization[8] of various RAMEB-complexed monomers under surfactant-free conditions in aqueous media.[9−20] Recently, we demonstrated the homo- and copolymerization of fluorinated methacrylates in water by the use of RAMEB.[21] In this paper, we report on the first examples of free radical homopolymerization and copolymerization of 2,3,4,5,6-pentafluorostyrene (**1**) with styrene (**3**) and its derivative 4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene (**2**) in aqueous solution via the host/guest complexation with RAMEB using water-soluble initiators.

* Corresponding author: Fax +492118114788; e-mail H.Ritter@uni-duesseldorf.de.

## Experimental Section

**Materials.** 2,3,4,5,6-Pentafluorostyrene (**1**) (Aldrich) and styrene (**3**) (Riedel de Haen) were stored over $CaH_2$ and vacuum-distilled before use. 1-Adamantylamine (Aldrich), randomly methylated $\beta$-cyclodextrin (RAMEB) (CAVASOL W7 M, technical grade, Wacker), 2,2′-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride (VA44) (Wako Chemicals), 2,2′-azobis(isobutyronitrile) (AIBN) (Fluka), and potassium peroxodisulfate (Fluka) were used as received. All solvents were distilled before use.

**Measurements.** The $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (operating at 500, 125, and 470 MHz, respectively).

Size exclusion chromatography (SEC) was carried out with a Jasco PU-1580 liquid chromatograph equipped with four PL gel 5 mm mixed-C columns, a Jasco 830-RI refractive index detector, and a Perkin-Elmer LC75 UV detector. Measurements were performed in $CHCl_3$ at room temperature with a flow of 1 mL/min. Monodisperse poly(styrene) standard samples were used for calibration.

Differential scanning calorimetry measurements were performed on a Mettler DSC-30 instrument in a temperature range of −40 to 200 °C at a heating rate of 10 °C/min. For calibration, standard tin, indium, and zinc samples were used. The $T_g$ values are reported as the average of two or three measurements using the midpoint method.

Raster electron microscopy (REM) pictures were taken with a Philips XL-30 ESEM equipped with a $LaB_6$ cathode. The maximal resolution was 3 nm, and the maximal accelerating potential was 30 keV.

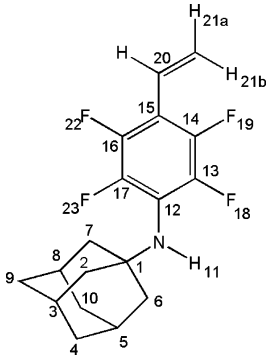
Dynamic light scattering measurements were performed on a Malvern HPPS-ET (high performance particle sizer−extended temperature) instrument equipped with a He−Ne laser and an Avalanche photodiode detector.

Kinetic measurements were carried out by high-pressure liquid chromatography (HPLC) using a Biotek Kontron Instruments System 525 equipped with a type 540 diode array detector and a LiChroCART RP-18 column. For elution,

10.1021/ma050065s CCC: $30.25 
Published on Web 05/14/2005

mixtures of acetonitril/water were used under isocratic conditions at a flow of 0.5 or 1 mL/min. Obtained data were evaluated with software Kroma Systems 2000 and plotted with Origin software.

**Synthesis of 4-(*N*-Adamantylamino)-2,3,5,6-tetrafluorostyrene (2).** Monomer **2** was synthesized following a literature procedure.[22] A mixture of 4.00 g (0.02 mol) of 2,3,4,5,6-pentafluorostyrene (**1**), 3.00 g (0.02 mol) of 1-adamantylamine, 2.76 g (0.02 mol) of anhydrous potassium carbonate, and 25 mL of DMSO was stirred and heated at 95 °C for 6 h under a nitrogen atmosphere. The mixture was cooled to room temperature and poured into ice water. The precipitate was filtered off. After drying under reduced pressure, the solid was dissolved in 500 mL of a diethyl ether/hexane mixture. After cooling, unreacted 1-adamantylamine crystallized and could be removed easily by filtration. The solvent was evaporated to afford pure **2** in 55% yield. $^1$H NMR ($CDCl_3$): $\delta$ (ppm) 1.87−2.15 (15 H, m, 1−10), 3.12 (1 H, 11), 5.48 (1 H, d, 21a), 5.90 (1 H, d, 21b), 6.53 (1 H, q, 20). $^{13}$C NMR ($CDCl_3$): $\delta$ (ppm) 28.58 (3,5,8), 35.06 (4, 9,10), 41.55 (2, 6, 7), 108.52 (15), 120.1 (20), 121.5 (21), 122.7 (12), 139.5 (13, 17), 141.5 (13, 14, 16, 17), 143.1 (13, 17), 145.1 (14, 16). $^{19}$F NMR ($CDCl_3$/$CFCl_3$): $\delta$ (ppm) −146.17 (18, 23), −151.53 (19, 22); MS (CI, *m/e*): 325 $(M + H)^+$. Calcd: C, 66.45%; H, 5.89%; N, 4.30%. Found: C, 66.15%; H, 6.04%; N, 4.44%.




**General Procedure for the Synthesis of Monomer/RAMEB Complex 1a, 2a, and 3a.** 1 mmol of monomer was added to a previously prepared 40 wt % aqueous RAMEB stock solution. The obtained monomer/RAMEB solution was stirred at room temperature until the solution became absolutely clear. In the case of **3**, 1 equiv of RAMEB was needed to encapsulate the monomer. In the case of **1** and **2**, 2 equiv of RAMEB was necessary to achieve quantitative complex formation.

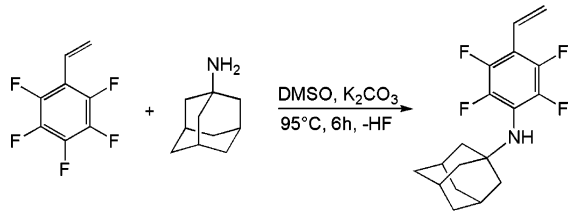
**Stoichiometry of the Complexes.** The stoichiometry of the complexes **1a**, **2a**, and **3a** was determined using the continuous variation method.[23] 3 mM solutions of monomers and RAMEB in $D_2O$ were mixed in various amounts while keeping the total concentration fixed. The products of guest molar fraction and chemical shift differences of the most significant $^1$H NMR signals of the guests were plotted against the molar fraction of the host.

**General Procedure for Polymerization in Water by Using RAMEB.** After preparing a 40 wt % aqueous RAMEB solution, the monomer was added and stirred at room temperature for 24 h followed by degassing with nitrogen for 20 min. The initiator was added, and the solution was stirred at room temperature for 90 min. After that the reaction mixture was diluted with water, and the precipitated polymer was filtered off, washed twice with methanol, and dried under reduced pressure.

**Poly(2,3,4,5,6-pentafluorostyrene) (4).** 2.00 g (10.30 mmol) of 2,3,4,5,6-pentafluorostyrene (**1**), 27.03 g (20.64 mmol) of RAMEB, 40.55 g of water, 0.070 g (0.26 mmol) of $K_2S_2O_8$, and 0.049 g (0.26 mmol) of $Na_2S_2O_5$. Yield: 1.84 g (92%).

**Poly(4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene) (5).** 0.50 g (1.54 mmol) of 4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene (**2**), 4.03 g (3.08 mmol) of RAMEB, 6.00 g of water, 0.010 g (0.038 mmol) of $K_2S_2O_8$, and 0.007 g (0.038 mmol) of $Na_2S_2O_5$. Because of the poor solubility of **2**, complexation was carried out differently. In the first step monomer **2** was grinded in a mortar to obtain a fine powder. After that small portions of the powder were added to a 40 wt % aqueous RAMEB solution and treated in an ultrasonic bath until the solution became totally clear. This procedure was repeated until the desired amount of **2** was complexed quantitatively. Polymerization was carried out as usual.

**Scheme 1. Synthesis of Monomer 2**




1 2

After polymerization the mixture was treated with a small amount of trifluoroacetic acid to force decomposition of the polymer/RAMEB complex **5a**. The precipitated polymer **5** was filtered off, washed twice with methanol, and dried. Yield: 0.44 g (88%).

**Poly(2,3,4,5,6-pentafluorostyrene-*co*-styrene) (6).** 0.40 g (2.03 mmol) of 2,3,4,5,6-pentafluorostyrene (**1**), 0.21 g (2.03 mmol) of styrene (**3**), 8.00 g (6.01 mmol) of RAMEB, 12.00 g of water, 0.027 g (0.01 mmol) of $K_2S_2O_8$, and 0.019 g (0.01 mmol) of $Na_2S_2O_5$. Yield: 0.52 g (86%).

**General Procedure for Polymerization in Organic Solvent.** The monomers were dissolved in organic solvent (toluene or benzene), and the solution was flushed with nitrogen for 20 min. The mixture was heated to 80 °C followed by addition of the initiator (2.5 mol % AIBN). After a given time, polymerization reactions were stopped by pouring the reaction mixture into cold methanol. Precipitated polymers were filtered off and washed with 50 mL of methanol, dried at 70 °C, and analyzed by SEC.

**Poly(2,3,4,5,6-pentafluorostyrene) (4′).** 4.00 g (20.6 mmol) of 2,3,4,5,6-pentafluorostyrene (**1**), 25 mL of toluene, 0.070 g (0.52 mmol) of AIBN. Yield after 4 h: 1.15 g (29%).

**Poly(4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene) (5′).** 1.00 g (3.08 mmol) of 4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene (**2**), 5 mL of toluene, 0.012 g (0.077 mmol) of AIBN. Yield after 4 h: 0.63 g (63%).

**Poly(2,3,4,5,6-pentafluorostyrene-*co*-styrene) (6′).** 2.91 g (15 mmol) of 2,3,4,5,6-pentafluorostyrene (**1**), 1.56 g (15 mmol) of styrene (**3**), 25 mL of benzene, and 0.123 g (0.75 mmol) of AIBN. Yield: 2.21 g (50%).

**Semibatch Polymerization of Poly(2,3,4,5,6-pentafluorostyrene) (7) by Use of RAMEB.** 25 mL of water was heated to 80 °C followed by addition of 0.50 g (0.38 mmol) of RAMEB. The solution was flushed with nitrogen for 20 min. Then 0.025 g (0.093 mmol) of $K_2S_2O_8$ was added under inert conditions. 4.19 g (21.59 mmol) of 2,3,4,5,6-pentafluorostyrene (**1**) was added dropwise over a period of 2 h under constant stirring at 350 rpm. After monomer addition the solution was stirred for 1 h at 80 °C. For REM images a small amount of the solution was taken and freeze-dried.

**Semibatch Polymerization of Poly(2,3,4,5,6-pentafluorostyrene) (8) without RAMEB.** Polymerization was carried out under identical conditions but without use of RAMEB.

## Results and Discussion

**Synthesis of Monomer 2.** New fluorinated monomer 2,3,5,6-tetrafluoro-4-(adamantylamino)styrene (**2**) was prepared by nucleophilic substitution starting from 2,3,4,5,6-pentafluorostyrene (**1**) and 1-adamantylamine in about 55% yield (Scheme 1).

The $^1$H NMR spectrum of **2** indicates the presence of vinylic protons (Figure 1). Furthermore, it shows a strongly deshielded multiplett between 1.61 and 2.41

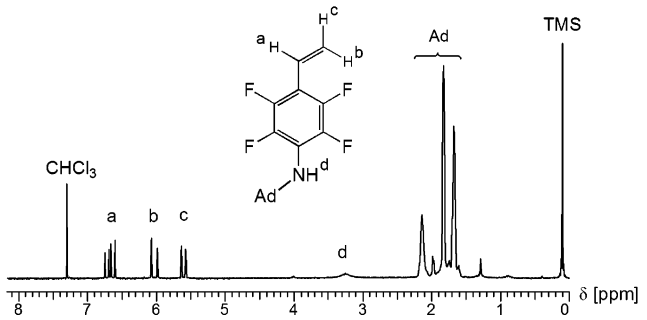



**Figure 1.** $^1$H NMR spectrum of **2** (500 MHz, $CDCl_3$,) [Ad = adamantyl].

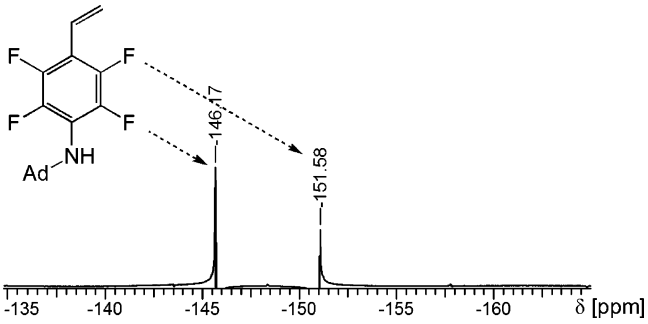



**Figure 2.** $^{19}$F NMR spectrum of **2** (470 MHz, $CDCl_3/CFCl_3$).

ppm, corresponding to the 15 protons of the adamantyl group. At a chemical shift of 3.25 ppm the proton of the amino group can be assigned.

Clear evidence for the para-substitution of the adamantylamino group at the phenyl ring in monomer **2** is obtained from the $^{19}$F NMR spectrum depicted in Figure 2. The signals of fluorine atoms imply the symmetrical para-substitution on the phenyl ring.

The aromatic ring is a good candidate for nucleophilic substitution due to the presence of electron-withdrawing fluorine substituents. The regioselective substitution in the para-position of **1** is a result of the ortho- and para-directing vinyl group in combination with a steric hindrance of the competing ortho-position.

**Formation of Host/Guest Complexes with RAMEB.** The fluorinated monomers **1**, **2**, and styrene (**3**) were complexed by RAMEB in water. The stoichiometries of the host/guest complexes were determined by NMR spectroscopy according to the Job method[23−25] (Figure 3). It was clearly shown that styrene (**3**) forms a defined 1:1 complex while the fluorinated monomers **1** and **2** are encapsulated by two RAMEB molecules. In the case of monomer **1** this result was not expected since **1** and **3** have the same molecular scaffold and molecular modeling showed that the fluorinated styrene derivative **1** is only slightly bigger than styrene itself (**3**).

**Homo- and Copolymerization of Monomers.** The RAMEB/monomer complexes **1a** and **2a** were homopolymerized in water at room temperature using the redox initiator system $K_2S_2O_8/Na_2S_2O_5$ (Schemes 2 and 3). Additionally, copolymerization of **1a** with complexed styrene (**3a**) was carried out in water (Scheme 4).

To compare our technique with traditional polymerization methods, all polymerizations were also carried out starting from the free monomers **1**, **2**, and **3** in organic solvents (toluene or benzene) at 80 °C using AIBN as initiator.

All obtained polymers were characterized by DSC and SEC, showing molecular weights up to 40 000 g/mol ($M_n$) and polydispersities up to 3 (Table 1)

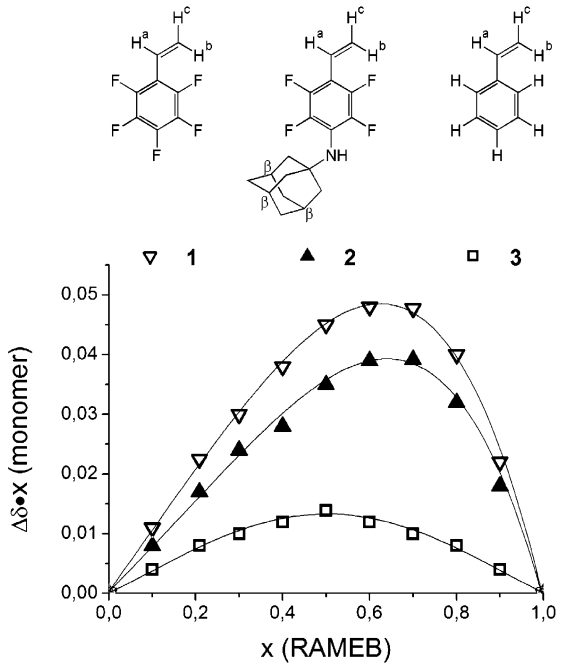
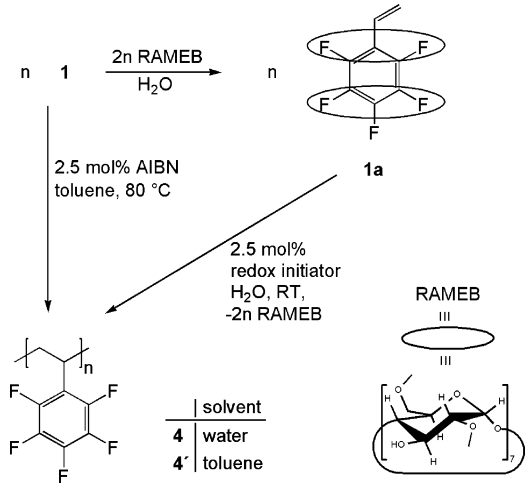



**Figure 3.** Job plots by considering the shifts of $H_c$ protons of **1**, adamantyl protons ($\beta$-position to the amino function) of **2**, and $H_c$ protons of **3** in the presence of RAMEB.

**Scheme 2. Homopolymerization of Free Monomer 1 in Organic Solution (Polymer 4′) and of 1a in Water (Polymer 4)**




In all cases almost quantitative yields of the homo- and copolymers from complexed monomers were achieved. Poly(pentafluorostyrene) (**4**) and polymer **6** could be isolated via simple filtration. Polymer **5a** was completely water-soluble due to the presence of noncovalently attached RAMEB. After treatment with trifluoroacetic acid to decompose the RAMEB ring, polymer **5** precipitated after some hours and could be isolated by filtration (Scheme 3).

In the case of polymerization in organic solvents, polymers were obtained by pouring the solution into methanol to precipitate the polymeric material. The yields of these solution polymerizations were about 40% after 2 h.

To elucidate the behavior of the new complexes **1a** and **2a**, kinetic measurements of homo- and copolymerizations in aqueous RAMEB solution were carried out by determination of monomer concentrations at various

**Scheme 3. Homopolymerization of Free Monomer 2 in Organic Solvent (Polymer 5′) and of 2a in Water Followed by Treatment with Trifluoroacetic Acid (Polymer 5)**

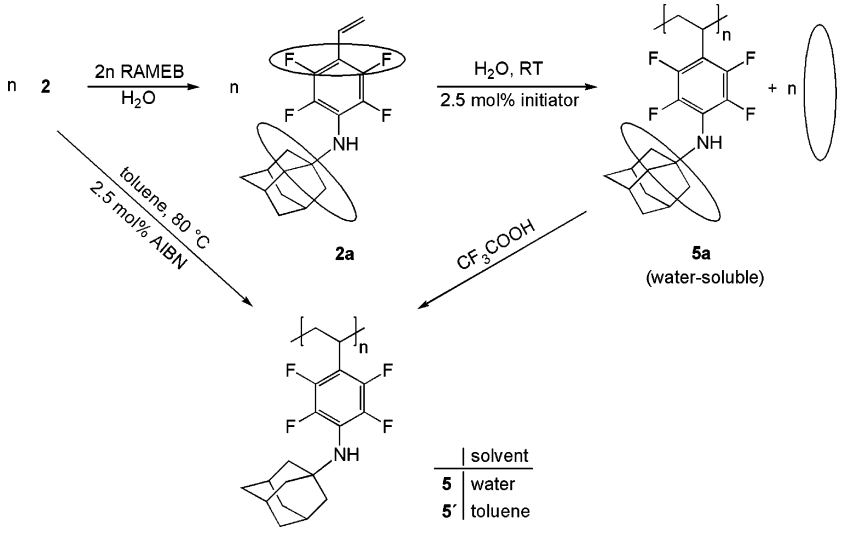
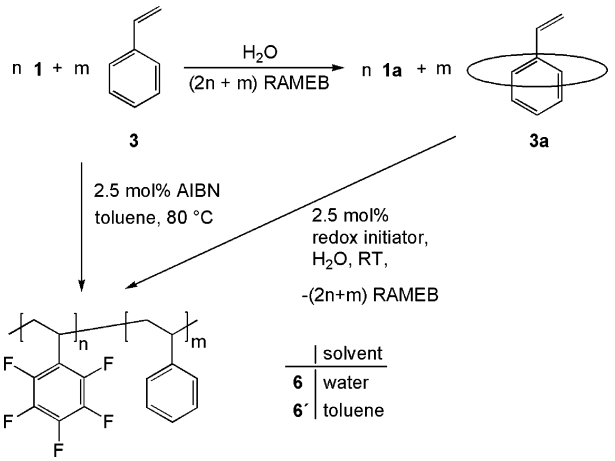



**Table 1. Characteristics of Obtained Polymers**

| polymers | monomoer | solvent | $T$ [°C] | $M_n$ | $M_w$ | PD | $T_g$ |
|---|---|---|---|---|---|---|---|
| **4** | **1a** | RAMEB/water[a] | 25 | 5 600 | 11 500 | 2.1 | 100 |
| **4′** | **1** | toluene[b] | 80 | 4 500 | 6 800 | 1.5 | 90 |
| **5** | **2a** | RAMEB/water[a] | 25 | 11 900 | 38 400 | 3.2 | |
| **5′** | **2** | toluene[b] | 80 | 12 300 | 38 400 | 3.1 | |
| **6** | **1a, 2a** | RAMEB/water[a] | 25 | 11 400 | 34 200 | 3.0 | 103 |
| **6′** | **1, 2** | toluene[b] | 80 | 4 500 | 6 800 | 1.5 | 90 |
| **7** | **1** | RAMEB/water[a] | 80 | 10 900 | 21 400 | 2.0 | 104 |
| **8** | **1** | water[c] | 80 | 38 500 | 123 000 | 3.2 | 106 |

[a] Redox initiator [b] AIBN. [c] $K_2S_2O_8$, semibatch polymerization.

**Scheme 4. Copolymerization of 1 with 3 in Toluene (Polymer 6′) and 1a with 3a in Water (Polymer 6)**



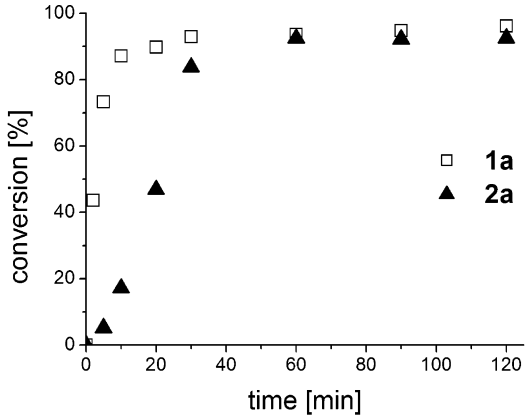




**Figure 4.** Kinetic plots of homopolymerization of RAMEB complexed 2,3,4,5,6-pentafluorostyrene (**1a**) and RAMEB complexed 4-(*N*-adamantylamino)-2,3,5,6-tetrafluorostyrene (**2a**) in water (RT, 2.5 mol % redox initiator).

reaction times via HPLC measurements. Resulting time−conversion plots of the homopolymerization reactions are shown in Figure 4.

In Figure 4 it can be seen that the complexed fluorinated monomers **1a** and **2a** are converted to polymers very fast. In both cases almost 90% yield were achieved after only 30 min of reaction time. As control experiment, polymerization of **1** and **2** was carried out in water under identical conditions but in the absence of RAMEB. Caused by the very poor solubility of **1** and **2** in aqueous solution at room temperature, no polymer could be obtained.

Additionally, **1** and **2** were homopolymerized in toluene at 80 °C. The molar concentration of the monomer was nearly identical compared to the experiment with RAMEB complexes, as described above. After 30 min, conversions of monomers **1** and **2** were about 25%. This fact indicates a high reactivity of the complexed monomers in water in comparison to classical polymerization methods. Self-evident, this comparison can only be qualitative because of the use of different solvents, initiator systems, and reaction temperatures.

The copolymerization of complexed fluorinated styrene **1a** and complexed styrene **3a** was carried out in water in comparison with copolymerization of free monomers **1** and **3** in toluene (Scheme 4). In both cases copolymerization parameters had been determined according to the method of Kelen and Tüdös.[26] In water we obtained $r_A = 45.5$ and $r_B = 0.58$, where monomer A

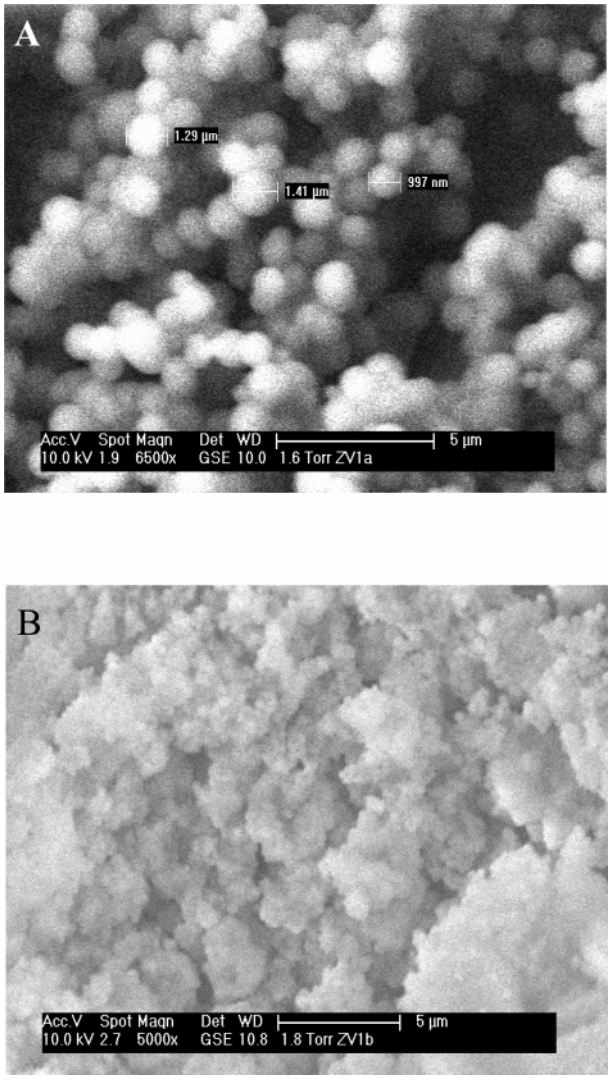



**Figure 5.** REM images of poly(2,3,4,5,6-pentafluorostyrene), synthesized by semibatch polymerization at 80 °C in aqueous RAMEB solution (A, polymer **7**) and in water in absence of RAMEB (B, polymer **8**) by using $K_2S_2O_8$ for initiation.

was RAMEB-complexed 2,3,4,5,6-pentafluorostyrene (**1a**). In toluene parameters changed to $r_A = 0.65$ and $r_B = 0.17$ (monomer A was uncomplexed 2,3,4,5,6-pentafluorostyrene (**1**)). This significant difference in the parameters demonstrates a remarkable impact of RAMEB on copolymerization kinetics. Obviously, the complexation with RAMEB causes an increasing reactivity of enclosed monomer **1a**. In contrast, the uncomplexed monomers show the expected tendency to build up alternating copolymers ($r_A < 1$ and $r_B < 1$).

**Semibatch Polymerization of Monomer 1.** A semibatch polymerization had been performed by adding monomer **1** dropwise to a 40 wt % aqueous RAMEB solution. Dynamic light scattering experiments gave no indication to the existence of micellar structures in this solution. Also, complexation of monomer **1** did not lead to the formation of big micelles. During the polymerization RAMEB acts as a single molecule solubilizer for the monomers by forming host/guest complexes.

In a control experiment monomer **1** was added gradually to water without RAMEB. The high reaction temperature of 80 °C slightly increased the solubility of free monomer **1** in water. Thus, polymerization of **1** was also possible in aqueous phase without using RAMEB. Anyway, in this case conversion was very low (<5%). REM images of the obtained polymers from the semibatch process are shown in Figure 5.

Significant differences in the morphology of the obtained polymers could be illustrated. Obviously, the use of RAMEB induces the formation of stable poly(2,3,4,5,6-pentafluorostyrene) latex particles with diameters between 1 and 1.5 $\mu$m consisting of polymer **7**. Without RAMEB, real spherical particles could not be visualized.

## Conclusions

From the above-described experiments it can be concluded that the CD complexation is a versatile method for the preparation of novel fluorinated polymers in water. It was demonstrated that the noncovalently attached CD rings may keep a polymer in aqueous solution. This supramolecular structure could be partially destroyed by use of a strong acid, leading to formation of uncomplexed polymer that precipitated immediately. By the way, the CD ring has a strong influence on copolymerization parameters compared to the uncomplexed monomers. Finally, the CD opens a possibility to polymerize in a semibatch process very effectively while polymer beads are formed.

## References and Notes

(1) Le, H. J.; Lee, M. H.; Oh, M. C.; Ahn, J. H.; Han, S. G. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2355−2361.
(2) Pitois, C.; Vukmirovic, S.; Hult, A.; Wiesmann, D.; Robertsson, M. *Macromolecules* **1999**, *32*, 2903−2909.
(3) Kim, J. P.; Lee, W. Y.; Kang, J. W.; Kwon, S. K.; Kim, J. J.; Lee, J. S. *Macromolecules* **2001**, *34*, 7817−7821.
(4) Szejtli, J.; Osa, T. In *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996; Vol. 3.
(5) Szejtli, J. *Cyclodextrin Technology*; Kluwer: Dordrecht, 1998.
(6) Harada, A. *Acta Polym.* **1998**, *49*, 3−17.
(7) Wenz, G. *Angew. Chem.* **1994**, *106*, 851−870.
(8) Braun, D.; Cherdron, H.; Rehahn, M.; Ritter, H.; Voit, B. *Polymer Synthesis: Theory and Practice, Fundamentals, Methods, Experiments*, 4th ed.; Springer: Berlin, 2004.
(9) Jeromin, J.; Ritter, H. *Macromolecules* **1999**, *32*, 5236−5239.
(10) Storsberg, J.; Ritter, H.; Pielartzik, H.; Groenendaal, L. *Adv. Mater.* **2000**, *12*, 567−569.
(11) Storsberg, J.; Ritter, H. *Macromol. Rapid Commun.* **2000**, *21*, 236−241.
(12) Glöckner, P.; Metz, N.; Ritter, H. *Macromolecules* **2000**, *33*, 4288−4290.
(13) Alupei, V.; Ritter, H. *Macromol. Rapid Commun.* **2001**, *22*, 1349−1353.
(14) Ritter, H.; Tabatabai, M. *Prog. Polym. Sci.* **2002**, *27*, 1713−1720.
(15) Alupei, C.; Alupei, V.; Ritter, H. *Macromol. Rapid Commun.* **2003**, *24*, 527−531.
(16) Sadowski, O.; Tepper, E.; Ritter, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 3171−3173.
(17) Theis, A.; Ritter, H. *Macromol. Chem. Phys.* **2003**, *204*, 1297−1304.
(18) Choi, S. W.; Kretschmann, O.; Ritter, H.; Ragnoli, M.; Galli, G. *Macromol. Chem. Phys.* **2003**, *204*, 1475−1479.
(19) Schwarz-Barac, S.; Ritter, H.; Schollmeyer, D. *Macromol. Rapid Commun.* **2003**, *24*, 325−330.
(20) Choi, S. W.; Ritter, H. *Macromol. Rapid Commun.* **2004**, *25*, 716−719.
(21) Storsberg, J.; Ritter, H. *Macromol. Chem. Phys.* **2002**, *203*, 812−818.
(22) Burdon, J. *Chem. Soc.* **1970**, *C*, 1271−1272.
(23) Blanda, T.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 4626−4636.
(24) Job, P. *Compet. Rend.* **1925**, *180*, 928.
(25) Connors, A. *Binding Constants, The Measurement of Molecular Complex Stability*; Wiley: New York, 1987.
(26) Kelen, F.; Tüdös, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.

MA050065S