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Anionic Polymerization of 1,3,5-Tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) in Miniemulsion

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ABSTRACT: The synthesis of poly(trifluoropropylmethyl)siloxane (PTFPMS) by anionic ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) was studied in miniemulsion using didodecyldimethylammonium bromide (DDDBr) as emulsifier and sodium hydroxide as initiator. This new process of polymerization produced well-defined α,ω-dihydroxylated polymer in very high yields and with molar masses ranging from 2000 to 30 000 g mol^{-1}. A kinetic study showed that polymerization occurs in two stages. During the first stage, which corresponds to the anionic kinetically controlled ring-opening polymerization of F_3, the maximum nonequilibrium yield is close to 100%. The second stage involves condensation and backbiting reactions. The delay between these steps offers a broad “termination window” for achieving high polymer yield.

Introduction

Only limited data have been published[1−8] on the polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) in bulk or in solution. The polymerization involves an unfavorable equilibrium between linear polymer and cyclic products formed by backbiting reactions. This equilibrium is heavily shifted toward the cyclics, F_n ($n \geq 4$), with less than 20% of linear polymer (Scheme 1).

Yuzhelevskii et al.[3−6] have studied the kinetics of the polymerization of fluoroalkylcyclosiloxanes initiated by NaOH or KOH in bulk. Their results were similar to those obtained in the octamethylcyclotetrasiloxane (D_4) polymerization initiated by KOH; namely, the kinetics are first-order with respect to monomer, and there is a square root dependence on initiator concentration. In bulk, the rate of polymerization strongly depends on the counterion of the siloxanolate active center; with KOH, NaOH, and LiOH, the relative rates are in the ratio of 900/20/1. With KOH at 120 °C, the monomer consumption rate for 1,3,5,7-tetrakis(trifluoropropylmethyl)-cyclotetrasiloxane (F_4) is approximately 3−4 times greater than for D_4. This was attributed to the increased electronegativity of the trifluoropropyl substituent and the enhanced negative induction effect on the electropositive ring silicon.

Yuzhelevskii and co-workers[3−6] also studied the effect of many promoters on F_3 polymerization. Analogous to the methylcyclosiloxanes, aprotic, polar compounds containing carbonyl or thionyl groups, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), or organic phosphates and glycol ethers, accelerate the F_3 polymerization rate by at least 2 orders of magnitude. This is due to the dissociation of ion pairs resulting from a better counterion solvation. Their results show a logarithmic dependence on rate vs activator concentration. Veith and Cohen[7] have examined in detail the effect of the DMSO/butyllithium (BuLi) activator−initiator combination on the consumption of F_3 at 40 °C. The monomer consumption rate varied by at least 4 orders of magnitude depending on the molar ratio of promoter to initiator. Furthermore, using a lithium counterion instead of sodium reduces the rate of backbiting considerably. They developed a kinetic model capable of predicting the optimum polymerization time for maximizing the polymer yield (85−90%). Nevertheless, all of these studies involved classical anionic polymerization and were therefore carried out with high-purity experimental techniques; the optimum “termination window” for high polymer yields is also narrow.

Scheme 1. Equilibrium between Polymer and Cyclic Products in Bulk or Solution Polymerization of F_3

$$F_3 \longrightarrow \underset{10\text{ to }20\ \%}{\text{Polymer}} \rightleftharpoons \underset{80\text{ to }90\ \%}{F_n\ (n \geq 4)}$$

Very few monomers have been polymerized by anionic polymerization in an aqueous emulsion. Most of these studies focus on cyclosiloxanes, including octamethylcyclotetrasiloxane[9−12] (D_4), decamethylcyclopentasiloxane[12] (D_5), and 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane (D^{Φ}_4),[13] although an epoxide, phenyl glycidyl ether (PGE), has also been reported.[14] The main advantage of the anionic polymerization in emulsion is that it is a very simple process that does not require any purification or an inert atmosphere. In the case of D_4, anionic polymerization under such conditions produces well-defined α,ω-dihydroxypoly(dimethylsiloxane)s with narrow molar mass distributions. Moreover, the evolution of the number-average molar mass is linear up to 70% conversion, which signifies good control of the polymerization.

With regard to F_3, the most important feature of the emulsion route is that the yields obtained are very high, compared to other classical polymerization methods such as bulk or solution. D_4[9−12] and D_5[12] polymerizations produced 90 and 84 wt % linear chains, respectively, with no detectable macrocyclic species. The remaining products were essentially composed of small cycles (D_4, D_5, and D_6), which can be easily removed. Side reactions should therefore be reduced in the polymerization of F_3 under emulsion polymerization conditions.

Experimental Section

Materials. 1,3,5-Tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) was kindly provided by General Electrics, and its purity

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(>99%) was assessed by NMR and SEC. Didodecyldimethylammonium bromide (DDDBr) was purchased from Acros Organics (purity 99%). Both were used as received. Water was deionized before use; nevertheless, no influence of the water purity on the polymerization was observed. NaOH solution (1.000 mol L^{-1}) was purchased from Titrinorm Prolabo.

Measurements. Steric exclusion chromatography (SEC) analyses were carried out in tetrahydrofuran (THF) eluent at a flow rate of 1 mL min^{-1} with a refractometric detector. A set of three columns from Shodex (KF 802.5L, i.e., $10^{2.5}$ Å; KF 804L, i.e., 10^4 Å; KF 805L, i.e., 10^5 Å) thermostated at 30 °C was used. Samples were prepared in THF (5 mg mL^{-1}) containing acetic acid (0.5 mg mL^{-1}) and quickly injected after dilution to avoid depolymerization. The weight fraction of the polymer in the mixture was calculated from the polymer and cyclic peak areas, taking into account the refractive indexes of each species:[3] F_3 ($n^{20}_D = 1.371$), F_4 ($n^{20}_D = 1.372$), F_5 ($n^{20}_D = 1.377$), and the polymer ($n^{20}_D = 1.382$). Number-average and weight-average molar masses were determined, using a calibration curve based on polystyrene standards provided by Viscotek (between 10^3 and 1.8×10^6 g mol^{-1}).

MALDI-TOF mass spectrometry was performed using a PerSeptive Biosystems Voyager Elite time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. The MALDI mass spectra represent averages over 256 laser shots. This instrument operated at an accelerating potential of 20 kV in both linear and reflector modes. The polymer solutions (2−5 g L^{-1}) were prepared in THF. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol), was dissolved in THF (10 g L^{-1}). The polymer solution (10 μL) was mixed with 50 μL of the matrix solution, and 10 μL of sodium iodide solution (5 g L^{-1} in THF) was added to favor ionization by cation attachment. A 1 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (peptides or porphyrin derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from PerSeptive Biosystems.

Particle size measurements were performed by dynamic light scattering using the Zetasizer-4 from Malvern at an angle of 90° and at 24 °C.

Polymerization. Stable miniemulsions were obtained by sonication using a 450 Branson Ultrasonics Corp. sonifier at power 7 (25 W) for 3 min.

The emulsion is then introduced into the polymerization reactor and continuously stirred at 100 rpm. The temperature was varied from 20 to 90 °C using an external oil bath. Usually, the temperature was 40 °C. The addition of NaOH signals the beginning of the polymerization.

At regular time intervals, aliquots were withdrawn and neutralized with a 5% hydrochloric acid solution in order to stop the reaction. Freezing in liquid nitrogen then broke the emulsion. After defrosting, the mixture was centrifuged and the organic phase decanted and dried using $MgSO_4$.

As an example, a system containing 15.4 g of F_3 (4.51×10^{-1} mol L^{-1}), 59 mL of deionized water (45.9 mol L^{-1}), 1 g of didodecyldimethylammonium bromide (DDDBr) (2.96×10^{-2} mol L^{-1}), which corresponds to 6.5 mol % based on monomer, and 1 mL of NaOH aqueous solution (10^{-3} N) (1.37×10^{-5} mol L^{-1}) produces rates of polymerization that are suitable for kinetic studies.

Results and Discussion

Setting Up of a Model Miniemulsion. As previously shown for the polymerization of D_4 in aqueous emulsion,[9–12] stable systems can be obtained with F_3 as the monomer when using didodecyldimethylammonium hydroxide as both initiator and surfactant (inisurf). Indeed, the monomer F_3 has very poor water solubility, which reduces Ostwald ripening; Ostwald ripening is partly responsible for emulsion destabilization through monomer diffusion within the particles. Nevertheless, even when stable, all systems based on this inisurf polymerize instantaneously and produce low polymer yields because of the unfavorable equilibrium between cyclic species and polymer chains. The hydroxyl ion concentration must therefore be reduced in order to obtain better control over the polymerization. Using a mixture of didodecyldimethylammonium bromide (DDDBr) and NaOH, with an NaOH concentration much lower than the concentration of DDDBr, allows good control over the polymerization. Ion exchange occurs between the bromide ion, the counterion of the surfactant, and the hydroxyl ion provided by the aqueous phase; thus, the hydroxyl ion becomes the counterion of the surfactant and is present at the surface of the emulsion particles where it can initiate polymerization.

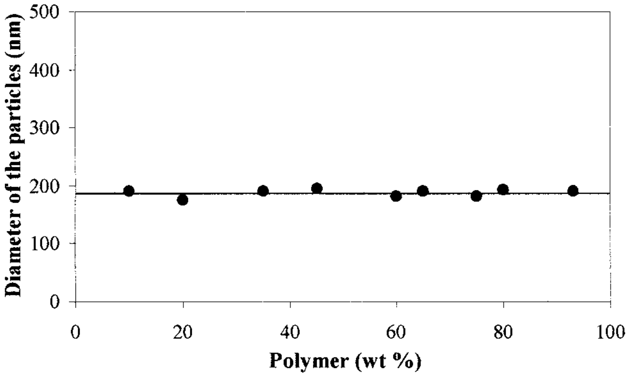


Figure 1. Evolution of the particle size as a function of polymer (wt %) for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-3} N).

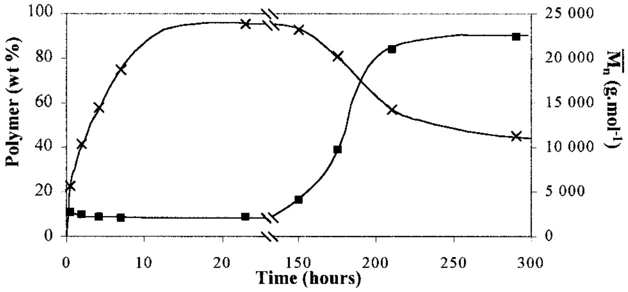


Figure 2. Kinetics of F_3 miniemulsion polymerization at 40 °C for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-3} N): (×) polymer (wt %); (■) M_n (g mol^{-1}).

The evolution of the particle size was followed throughout the reaction (Figure 1). The diameter of the particles is about 190 nm after sonication and remains quite constant with conversion. The number of particles remain unchanged, and each particle acts as an independent minireactor of polymerization. Coalescence of particles and Ostwald ripening are suppressed. The polymerization is therefore a miniemulsion process. During the emulsion polymerization of D_4 the particle size varied.[12] This was correlated with the diffusion of the monomer, which is less hydrophobic than F_3, in the aqueous phase.

The evolutions of both conversion and number-average molar mass as a function of time are shown in Figure 2. The kinetics of the polymerization of F_3 in miniemulsion can be separated into two steps: The first step, limited to about 15 h, corresponds to monomer consumption. The second step, which begins after 100 h of reaction, corresponds to the equilibration between

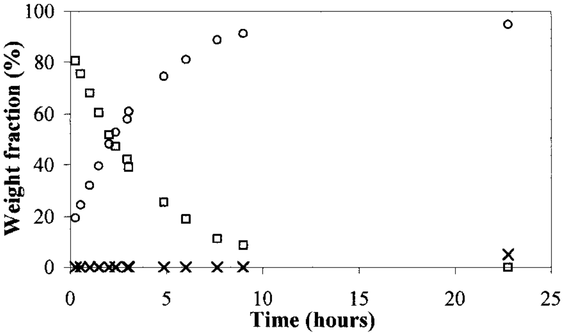


Figure 3. Kinetics of F_3 miniemulsion polymerization at 40 °C for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-3} N): (○) polymer (wt %), (□) monomer (wt %), and (×) cyclics (wt %) (F_4, F_5, F_6).

linear chains and cyclic products. Because of the very different time scales of these two steps, they have been studied separately.

First Step of the Kinetic Scheme. The kinetics of monomer consumption and the formation of linear polymer and cyclic byproducts F_n are reported in Figure 3.

Monomer consumption is complete after 15 h, although it can be varied from less than a second to several days depending on the experimental conditions, e.g., the NaOH concentration and temperature. The consumption of the monomer is directly related to the formation of polymer, with yields of more than 95% being obtained.

No cyclic byproducts were formed, which confirms the absence of backbiting reactions during this first stage of the polymerization. Indeed, in the polymerization of F_3 backbiting side products are clearly distinguishable from monomer (Scheme 1). This was not possible in the D_4 polymerization because D_4 is the main backbiting byproduct of poly(dimethylsiloxane) chains.

The miniemulsion method is therefore effective at considerably reducing the rate of backbiting.

The polymer was characterized by MALDI-TOF mass spectrometry (Figure 5). The main peaks were attributed to the oligomers $HO(F)_{3n}H$ (F represents the $(C_3H_4F_3)(CH_3)$ SiO unit). The peaks of weaker intensity correspond to the other oligomers ($HO(F)_nH$) that are formed either by intermolecular redistribution or by backbiting (Scheme 2).

Thus, the polymeric chains are apparently formed from successive monomer additions. Moreover, the chains are linear, and no macrocyclic products are detectable. All polymer chains have terminal hydroxyl groups at both chain ends.

Number-average and weight-average molar masses were determined from the SEC chromatograms. The evolution of these weighted averages with conversion is depicted in Figure 5. At the beginning of the polymerization, the number-average and weight-average molar masses were about 2500 and 3500 g mol^{-1}, respectively. Both remain fairly constant during the monomer consumption, which suggests that the condensation of the chains is reduced. Moreover, there is a slight decrease. The molar mass distribution also remains constant at around 1.3. Increasing the temperature or the initiator concentration increases the rate of polymerization but leads to the same evolution of the molar masses as a function of conversion.

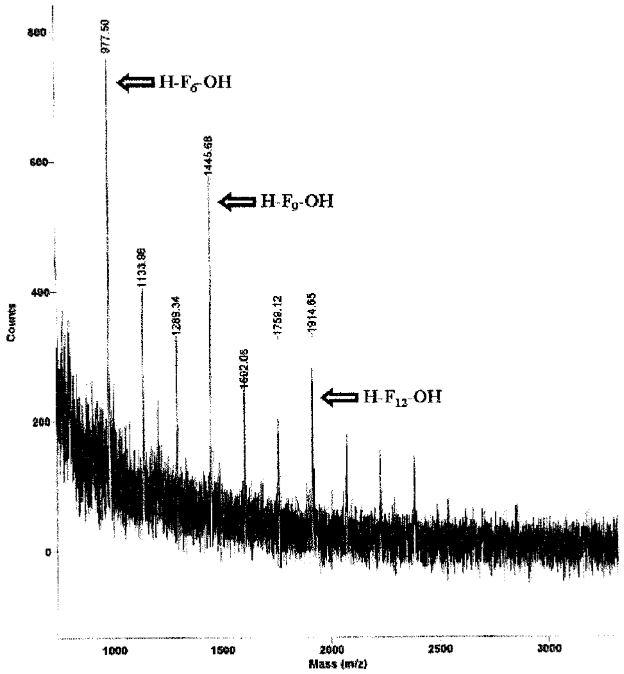


Figure 4. MALDI-TOF mass spectrum of the crude product obtained by F_3 miniemulsion polymerization at 40 °C for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-3} N) after 23 h of reaction.

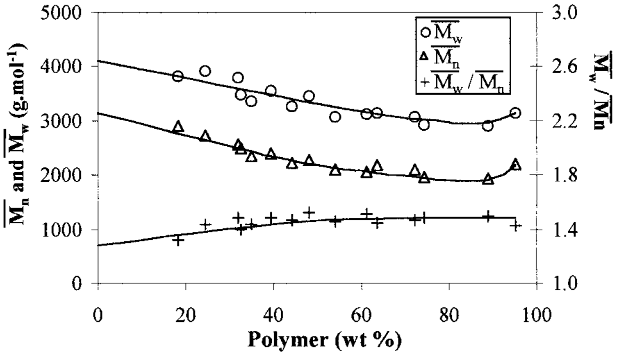
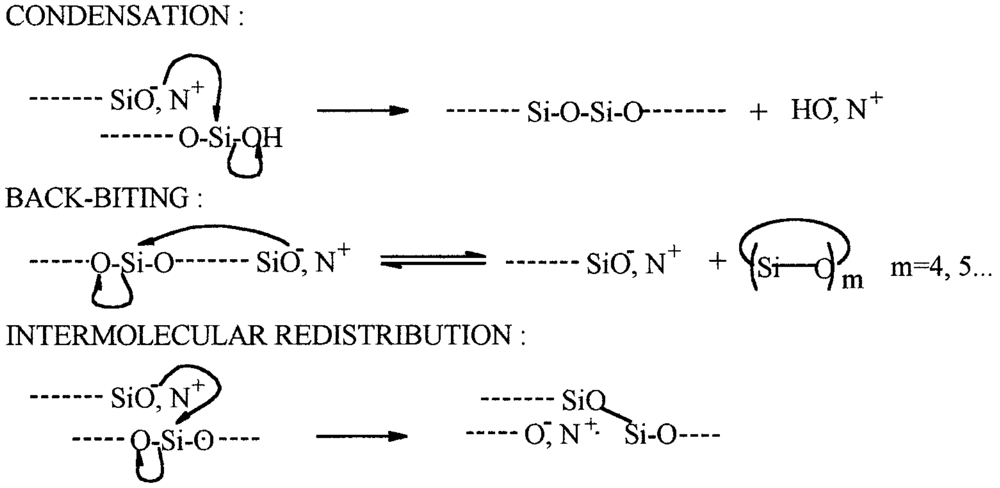


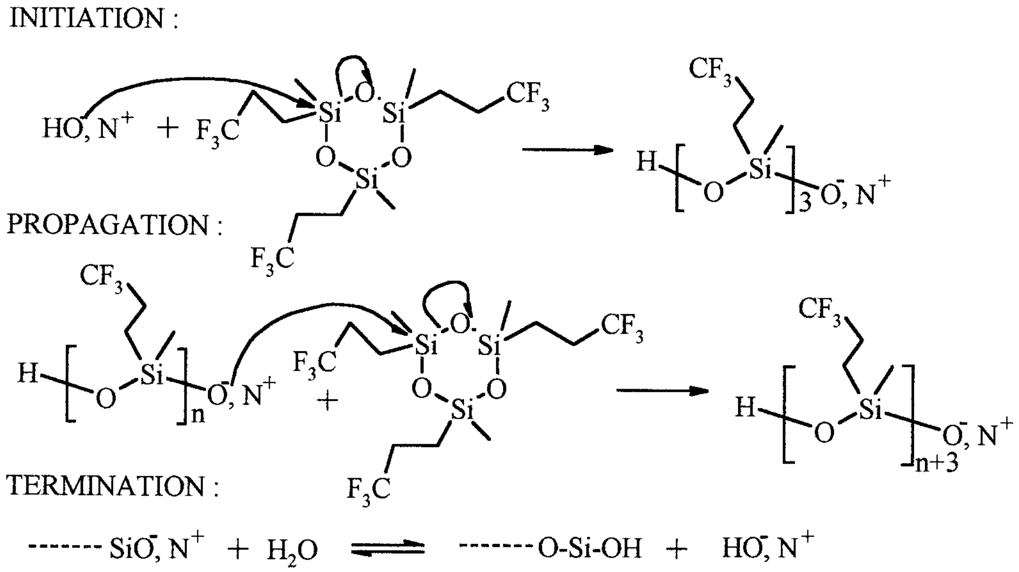
Figure 5. Average molar masses of the polymer obtained at 40 °C for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-3} N): (△) M_n (g mol^{-1}), (○) M_w (g mol^{-1}), and (+) polydispersity (M_w/M_n).

From these experimental data, the mechanism of this first stage of the polymerization can be summarized by three reactions: initiation, propagation, and termination (Scheme 3). It is useful to consider the mechanism in terms of its interfacial nature. Initiation is a continuous reaction, which takes place at the interface by attack of the hydroxyl ion (the surfactant counterion) on the monomer. Active centers thus formed are associated with the cationic surfactant as ion pairs. The ion pairs probably stay at the surface, with propagation occurring through diffusion of the monomer to the surface. First kinetic results seem to show that this propagation reaction is controlled by the diffusion of the monomer from the core of the particle to the surface (zero apparent order in monomer).[15] Then, termination with water takes place at the interface. The interfacial location of the active centers explains the decrease in the backbiting side reactions (even taking rate constants into account). During the first stage of the kinetic scheme, the polymer chain length would be directly

Scheme 2. Side Reactions Occurring during F_3 Polymerization



Scheme 3. Mechanism of F_3 Miniemulsion Polymerization



related to the rate of diffusion of the monomer to the locus of polymerization and to the local concentration of water. The slight decrease in the evolution of molar masses as a function of conversion is probably related to the decrease in the monomer concentration but could also be explained by the increase in the viscosity within the particle.

Second Step of the Kinetic Scheme. To study this stage of the polymerization in a reasonable time range, the initiator concentration was increased by 2 orders of magnitude. The rates of formation of polymer and cyclic species as well as the evolution of number-average and weight-average molar mass are shown in Figure 6.

After complete consumption of the monomer, condensation reactions clearly occur since the number-average and weight-average molar masses increase dramatically up to around 30 000 and 60 000 g mol^{-1}, respectively. Here the polydispersity approaches 2.0, which shows that condensation follows a statistical law, as observed in the case of α,ω-dihydroxylated PDMS.[11] At the same time, backbiting reactions decrease the weight fraction of polymer, until about 45 wt % of polymer. The evolution of the number of chains and of the polymer weight fraction with time is shown in Figure 7.

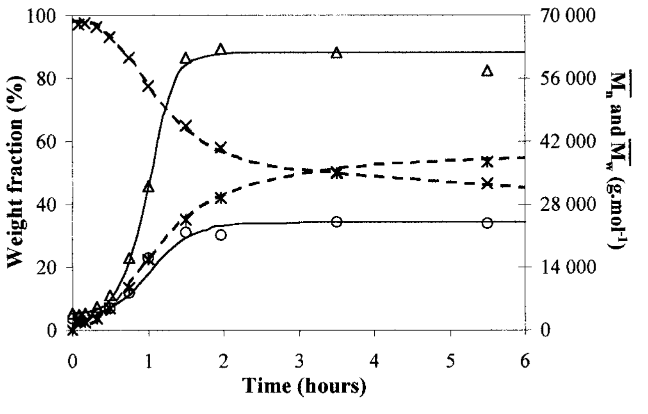


Figure 6. Kinetics of F_3 miniemulsion polymerization at 40 °C for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-1} N): (×) polymer (wt %), (∗) cyclic (wt %) (F_4, F_5, F_6, ...), (○) M_n (g mol^{-1}), (△) M_w (g mol^{-1}).

The only reaction that can be responsible for a decrease in the number of chains is condensation; the reduced conversion is directly correlated to backbiting reactions. Surprisingly, there is an induction time for the backbiting reactions. Indeed, the reduced polymer

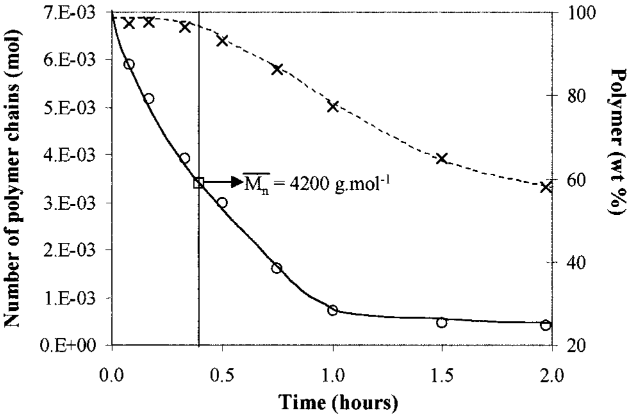


Figure 7. Evolution of the average molar masses of the polymer obtained at 40 °C for a system containing 15.4 g of F_3, 59 mL of deionized water, 1 g of DDDBr, and 1 mL of NaOH aqueous solution (10^{-1} N): (×) polymer (wt %); (○) number of polymer chains (mol).

weight fraction, indicating backbiting reactions, begins after 25 min and after the consumption of half of the polymer chains by condensation. This result seems to show that no backbiting reactions can occur below a number-average molar mass of 4200 g mol^{-1}.

After monomer consumption is complete, the active centers are reactivated, and condensation and redistribution reactions appear. Depending on the molar mass of the polymer, these reactions seem to have different locations within the particle. Below 4200 g mol^{-1}, the active centers seem to be surface active and locked in at the interface. Indeed, condensation reactions take place, but no backbiting reactions occur, probably because of steric hindrance of the surfactant molecules. Above 4200 g mol^{-1}, the active centers are being too hydrophobic to be surface active. Therefore, they diffuse inside the particle. Then, all the reactions that are usually observed in bulk can occur, including inter- and intramolecular redistribution reactions. Even after long reaction times (>90 days), the conversion is more than twice as high as the "chain-cycle" equilibrium in bulk (45% in miniemulsion vs 20% in bulk). The same was observed in D_4 polymerization under similar experimental conditions (10% of cyclic byproducts instead of 20% usually obtained in bulk). This result is still not understandable since the equilibrium should be the same as in the bulk. Even if kinetic effects are important, the equilibrium should certainly be related to the specific locations of the reactions, i.e., at the surface or in the core of the particles.

If steric hindrance of the surfactant molecules reduce backbiting reactions, the locus of the reaction also implies surface activities of the monomer and of the resulting polymer. Using a hydrophobic monomer reduces its diffusion in the aqueous phase but also modifies its local interfacial concentration. The effect of different interfacial parameters such as the nature of the surfactant, the influence of the cation, and the effect of fluorinated substituents should be studied. Indeed, the following question remains unanswered: how is it possible to vary the nonequilibrium high yield molar mass? This mass, about 3000 g mol^{-1}, is not affected by temperature or surfactant and initiator concentrations; therefore, it must be controlled by physicochemical properties of the oligomers. The specific location of each reaction suggests that a study of the influence of particle size should be interesting; for example, the microemulsion technique could be used to suppress bulk "in the core" reactions and hence favor surface active centers. Copolymerization of F_3 and D_4 will also be studied, partly as a tool to achieve a better understanding of the reactions, but also in view of the exceptional surface properties of fluorinated silicones.

Conclusions

The anionic ring-opening polymerization of 1,3,5-tris(trifluoropropylmethyl)cyclotrisiloxane (F_3) in miniemulsion using didodecyldimethylammonium bromide (DDDBr) as emulsifier and sodium hydroxide as initiator produced well-defined α,ω-dihydroxylated poly(trifluoropropylmethyl)siloxane (PTFPMS). Moreover, compared to classical anionic polymerization in bulk or in solution, the conversions were much higher, both at the maximum yield where the polymerization is almost quantitative and at the end of the reaction. A kinetic study indicated that the polymerization is clearly divided into two stages. The first stage corresponds to the kinetically controlled anionic ring-opening polymerization of F_3; backbiting and condensation reactions are delayed. Since backbiting is suppressed for F_3 compared to D_4, whereas more backbiting byproducts are obtained with D_5, the kinetic control seems to increase with the reactivity of the monomer. The high reactivity of F_3 is probably the main factor that allows initiation and propagation to be separated from condensation and backbiting. Moreover, this control is obviously related to the specific locations of the reactions. Our results indicate that initiation, propagation, and termination take place at the interface, whereas backbiting occurs in the bulk. This can be understood by the steric hindrance of the surfactant at the surface of the particles.

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