Anionic Polymerization of Phenyl Glycidyl Ether in Miniemulsion

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ABSTRACT: The anionic polymerization of phenyl glycidyl ether (PGE) in miniemulsion was investigated. Didodecyldimethylammonium hydroxide was used as an inisurf, i.e., exhibiting both surface-active properties and the ability to initiate polymerization by means of its hydroxide counterion. Stable miniemulsions were obtained by ultrasonication, and then polymerization was carried out to produce genuine α,ω-dihydroxylated polyether chains as revealed by ^{1}H NMR, FTIR, or mass spectroscopic methods. The average molecular weight could be increased by varying the initiator concentration, type and concentration of surfactants or by adding a cosurfactant (typically alcohol). In all attempts, polymer chains increased in size with conversion but remained small, with a critical polymerization degree of $DP_{max} = 8$. A mechanism was proposed to account for these results. From these observations, phenyl glycidyl ether could be used as a model monomer to investigate ionic polymerization in miniemulsion.

Introduction

The miniemulsion process has long been studied in the radical-initiated polymerization of various monomers.[1] Recently, this technique has experienced a renewed interest, mainly because it was shown possible to control ab initio the number and size of the final particles by addition of various hydrophobic species.[2] This very promising system has also been extended to other reactions, such as epoxide−amine polyaddition[3] or ring-opening emulsion polymerization of cyclosiloxanes.[4−9]

First exhaustive kinetic studies on anionic emulsion polymerization were carried out in the case of octamethylcyclotetrasiloxane (D_4).[6,7] This particular type of polymerization was shown to proceed through a fast and simple process to produce α,ω-dihydroxypoly(dimethylsiloxane) with controlled molecular weight and narrow distribution. The emergence of condensation and backbiting reactions generally observed in solution polymerization of cyclosiloxanes was delayed to 70 wt % conversion in the emulsion process.[8] Moreover, cycles D_n produced in low concentration were small enough ($n = 4-8$) to be easily removed by distillation. Studies on cationic emulsion polymerization of tetramethylcyclotetrasiloxane (D_{4H}) were found to provide similar results.[9] In both cases, polymerization appeared to strongly depend on the association between the active center and the ionic surfactant located at the interface. It was then concluded that this ionic emulsion process could be extended to the polymerization of other monomers, provided to select an appropriate surfactant.

Phenyl glycidyl ether (PGE) is generally used as a model monomer for the study of epoxy matrix hardening as its structure is close to the common reactant 2,2-bis[4-(glycidyloxy)phenyl]propane (DGEBA).[10−12] Solution polymerization of PGE has been reported in the past 40 years using anionic,[13] cationic,[14] or nucleophilic initiators.[15−17] In particular, detailed kinetic studies on the anionic polymerization of PGE were quoted mainly by Stolarzewicz[18,19] and others.[20,21] One major drawback reported by these authors is that numerous chain transfer reactions can coexist with the anionic polymerization of epoxides. Transfer reactions to the initiator[15−17] or to solvent[20] cause end-chain defects, whereas transfer to monomer[18] produces new active centers containing aliphatic double bonds and carbonyl groups. Coordination anionic polymerization was believed to provide better control of the polymer molecular weight and microstructure.[15,22] However, in most cases, cationic and coordinative anionic polymerizations simultaneously occur depending on the catalyst used.

In a previous work, anionic polymerization in miniemulsion of PGE was briefly reported.[7] It was shown that, under experimental conditions close to those used for D_4, an oligomeric polyoxide was formed, but irreversible termination reactions limited the oligomers chain length. This study aims at providing a better understanding of the miniemulsion anionic polymerization process applied to PGE polymerization.

Experimental Section

Materials. Unless otherwise stated, all reagents used in this study were purchased from Aldrich. Phenyl glycidyl ether (PGE) (purity 99%) was used as supplied. The inisurfs benzyldimethyldodecylammonium hydroxide (NOH) and didodecyldimethylammonium hydroxide (N′OH) were prepared from their bromide counterparts, according to the procedure previously reported.[6] These surfactants contain about 30% of water as revealed by Karl Fisher titration. Further drying would lead to the ammonium degradation by Hoffman reaction. Counterion exchange reaction appeared to be less easy for N′OH which is, in addition, very sensitive to degradation. Special care, such as storage at low temperature and under inert atmosphere, was required. Nonionic surfactants, i.e., poly(oxyethylene) lauryl ether Brij 30 ($n = 4$) (Aldrich), Brij 35 ($n = 23$) (Aldrich), and polyoxyethylene nonylbenzyl ether Rewopol HV25 ($n = 25$) (WITCO), were of sufficient purity (99%) to be used as received.

Measurements. Shelf stability of the PGE miniemulsion was stated as the time at which demixion started to appear. Particle size measurements were performed using a Zetasizer 4 (Malvern Instruments). ^{1}H NMR spectra were recorded on a Brüker AC 200 spectrometer at 200 MHz using $CDCl_3$ as solvent. FTIR was performed on KBr pellets using a Brüker IRTF IFS 45 apparatus.

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DCI/NH_3 mass spectra were accumulated on a triple-quadrupole tandem mass spectrometer R-30-10 NERMAG. An average of 60 scans were accumulated and retreated using the EZSCAN data system of mass evolution. The operating conditions in the source housing were as follows: electron energy, 85 eV; emission current, 100 μA; ammonia gas pressure, 10^{-4} Torr.

Size exclusion chromatography (SEC) measurements were carried out in CH_2Cl_2 using PL-Gel columns with pore sizes of 10^2, 5×10^2, 10^3, and 10^4 Å (Polymer Laboratories) and using a differential refractometer detection (Waters model R401). The oligomer mix obtained from PGE polymerization was characterized as follows. The most eluted peak was attributed to 3-phenoxy-1,2-propanediol, i.e., the diol issued from epoxide cycle opening corresponding to the DP_1 oligomer. This assignment was confirmed by co-injection of the model molecule synthesized according to ref 23. The other peaks were determined by mass spectrometry analyses (see Figure 7), from which an absolute SEC PGE calibration curve was derived in the low MW domain.

Polymerization. Miniemulsions were obtained by sonication using a 450 Branson Ultrasonics Corporation sonifier at power 7 (25 W). Sonication time was optimized to 2 min 30 s (longer sonication time would increase the local temperature and degrade the inisurf). PGE was added to the surfactant solution maintained by means of an ice bath at a temperature of 25 °C during sonication. SEC and ^{1}H NMR measurements confirmed that neither monomer degradation nor initiation occurred during sonication. The emulsion, exhibiting a pH between 11 and 13, was then transferred into the reactor.

Polymerization was carried out under thermal regulation (between 40 and 60 °C) and mechanical stirring (150 rpm). A slight nitrogen flow was maintained in the vessel, as oxygen acts as an inhibitor on the polymerization of PGE.[20] At regular time intervals, 2 mL aliquots were withdrawn and neutralized with a 5% hydrochloric acid solution in order to stop the reaction. The organic phase was separated from the aqueous one by centrifugation after adding an aluminum salt ($AlKS_2O_8 \cdot 12H_2O$) to the samples. CH_2Cl_2 was also systematically added to achieve a better phase separation and to ensure that no organic product remained in water.

The polymerization rate was followed by ^{1}H NMR and SEC measurements. ^{1}H NMR showed the decrease of the resonance at 2.5–2.7 ppm corresponding to the opening of the epoxide ring that was compared to the polyether massif around 3.8 ppm.[15–17] SEC measurements also allowed for plotting monomer conversion versus time by determining the monomer and polymer concentrations from their refractometer peak integration. No refractive index correction was necessary in this particular case.[10]

Results

Bulk Polymerization. Previous studies on cyclosiloxane anionic emulsion polymerization showed that it was possible to perform direct bulk polymerization in the presence of benzyldimethyldodecylammonium hydroxide (NOH).[24] A similar bulk reaction was conducted by mixing 3.33 g (3 mL) of PGE and 0.266 g (8 wt %/PGE) of didodecyldimethylammonium hydroxide (N′OH) at 60 °C. SEC traces of polymer withdrawn at different conversions are given in Figure 1. The polymerization is fast and complete, despite the presence of water contained in the inisurf. Small oligomer chains are first formed due to termination reactions; however, once all water molecules are consumed, molecular weights increase with conversion. The large polydispersity index obtained, 1.2–1.4, logically results from these remaining small chains. The final average molecular weight ($\bar{M}_n = 2300$ g mol^{-1}) was found to be in the same order of magnitude as in "classical" anionic polymerization initiated by methoxide anions (typically between 1500 and 3000 g mol^{-1}).[19,20] This preliminary study thus confirmed that PGE can be polymerized in a slightly aqueous environment, in the presence of the ammonium inisurf. The next step consists of polymerizing PGE in a greater amount of water, i.e., in emulsion.

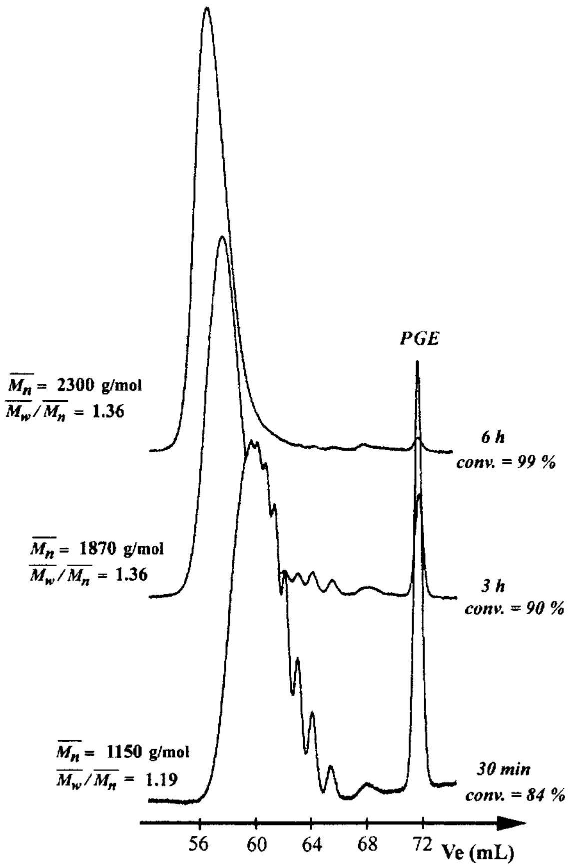

Figure 1. SEC chromatograms for samples withdrawn at different conversions from PGE bulk polymerization. Polymerization conditions: PGE, 3.33 g; N′OH, 0.266 g; 60 °C.

Conditions for Producing Stable Miniemulsions. As previously shown for D_4 miniemulsion polymerization, stable systems can be obtained when using NOH as inisurf. The monomer D_4 is indeed sufficiently hydrophobic to play the role of "costabilizer" and thus reduce Ostwald ripening partly responsible for emulsion destabilization.[25] The hydrophobicity prerequisite has also been evidenced in the epoxide/amine polyaddition in miniemulsion.[3] Moreover, the polysiloxane concentration gradually increasing inside the particles also contributes to particle stabilization.[26] The stabilization is induced by the fact that polymer cannot diffuse in the aqueous phase and force the monomer to swell it. Contrary to all expectations, the emulsification of PGE/H_2O/NOH mixture did not lead to a stable miniemulsion. This mitigated result is due to the much higher water solubility of PGE (2×10^{-3} mol L^{-1}, as revealed by partitioning measurements using UV spectrometry) compared to D_4 (2×10^{-7} mol L^{-1}).[27] Addition of a costabilizer such as hexadecanol did not favor miniemulsion formation due to its low solubility in PGE. Adding a nonionic surfactant such as Brij35 in the case of D_{4H} polymerization[9] was not shown to improve stability either.

Therefore, a systematic study on emulsion stability was carried out using mixtures of ionic (NOH or N′OH) and nonionic (Brij30) surfactants. Emulsion stability is shown to be dependent on the overall surfactant concentration but not on the ratio of ionic/nonionic surfac-

Table 1. Influence of Emulsion Recipe on the Polymerization Rate, Average Molecular Weight ($\bar{M}_n$), and Polydispersity Index ($\bar{M}_w/\bar{M}_n$)

run	[PGE] (mol L^{-1})[a]	[N′OH] (mol L^{-1})[a]	additive type	[additive] (mol L^{-1})[a]	temp (°C)	R_p ($\times 10^6$ mol L^{-1} s^{-1})	$\bar{M}_n$ (g mol$^{-1)}$	$\bar{M}_w/\bar{M}_n$
1	1.4	4.2×10^{-2}			60	31.6	580	1.25
2	1.4	4.2×10^{-2}			40	10.9	520	1.36
3	2.0	6.1×10^{-2}			40	2.8	330	1.31
4	1.0	3.2×10^{-2}			40	4.7	230	1.28
5	1.4	3.2×10^{-2}			60	6.1	410	1.33
6	1.4	6.2×10^{-2}			60	>100	690	1.21
7	1.4	4.2×10^{-2}	Brij 30	5.7×10^{-2}	60		590	1.23
8	1.4	4.2×10^{-2}	Brij 30	8.6×10^{-2}	60		475	1.27
9	1.4	4.2×10^{-2}	Rewopol HV25	7.9×10^{-3}	60	10.3	490	1.27
10	1.4	4.2×10^{-2}	Rewopol HV25	7.9×10^{-3}	40	2.8		
11	1.4	4.2×10^{-2}	Brij 35	8.6×10^{-3}	40	1.4		
12	1.4	4.2×10^{-2}	pentanol	9.9×10^{-2}	40	5.7	730	1.19
13	1.4	4.2×10^{-2}	octanol	6.7×10^{-2}	40	6.1	620	1.25
14	1.4	4.2×10^{-2}	hexadecanol	3.6×10^{-2}	40	5.2	270	1.27

[a] Calculated from the total volume of the emulsion.

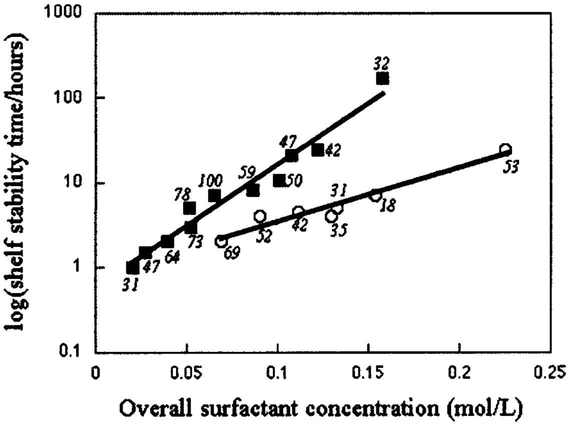

Figure 2. Semilog plot of the influence of the amount of nonionic and cationic surfactant on the miniemulsion shelf stability: (○) NOH + Brij30; (■) N′OH + Brij30. Values in italics correspond to the percentage of ionic surfactant in the overall surfactant concentration. Lines are only guides for the eyes.

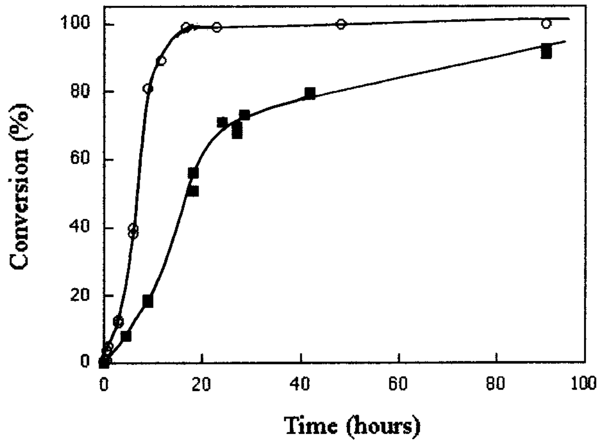

Figure 3. Conversion versus time plot for PGE polymerized in the model conditions (Table 1) at two temperatures: (○) 60 °C (run 1); (■) 40 °C (run 2).

tants, a result previously observed for siloxane emulsions[4] that remains unclear. This trend is illustrated in Figure 2, where the emulsion shelf stability is plotted against the overall surfactant concentration (the semilog plot has no physical meaning here). Basically, lower concentrations of N′OH compared to NOH are necessary to produce relatively stable miniemulsions. This observation can be related to the hydrophilic/lipophilic balance (HLB) of the surfactants. Those with a large hydrophobic tail (Brij30, N′OH) are able to stabilize the particles, whereas more polar ones (such as Brij35 and NOH) do not. In addition, N′OH exhibited from its double-tailed structure a maximum particle surface coverage, as recently demonstrated.[28] An emulsion containing only N′OH as a surfactant was chosen as the simplest recipe to study the PGE kinetics (see Table 1, runs 1 and 2). The stability of these emulsions is improved from 5 h to 3 days simply by mechanical stirring (150 rpm).

Kinetic Study on a Model System. Monomer consumption was followed by ^{1}H NMR and SEC (see experimental part) and led to similar values. Conversion versus time plots are given in Figure 3 for two temperatures, 60 and 40 °C (Table 1, runs 1 and 2, respectively). The miniemulsion polymerization rate is faster at 60 °C than at 40 °C (Figure 3 and Table 1). This effect can be indebted to differences in the propagation and termination activation energies, as well as to the higher number of polymerization loci created at 60 °C compared to 40 °C (particle diameter 200 and 240 nm, respectively). The conversion versus time curves are both S-shaped, with an acceleration occurring after 30% conversion, regardless of temperature. Kinetic studies on classical anionic solution polymerization of epoxide was shown to display a first-order behavior in monomer.[15,19,20] Miniemulsion polymerization of PGE appears to be more complex. Indeed, physicochemical parameters such as monomer concentration at the particle surface, diffusion processes, and surface properties of monomer and polymer actually complicate the analysis and thus do not actually allow for sketching a simple kinetic scheme at this point. This complex behavior could also explained the differences observed in the kinetics of D_4 anionic polymerization realized in similar miniemulsion conditions, where a constant polymerization rate was obtained up to 70% conversion.[6]

Figure 4 shows the evolution of the SEC chromatograms after 3, 9, 23, and 72 h of reaction at 60 °C. A mixture of low molecular weight polyether chains ranging from DP_1 to DP_8 were synthesized. Identification of these oligomers was confirmed by mass spectrometry (see below). The molecular weight and polydispersity index are also reported in Figure 4 at the various conversions. The average molecular weight increased with conversion, but yet, oligomers longer than DP_8 could not be attained under these conditions. In an attempt to overpass this limit, the influence on the final polymer structure of various parameters, such as initia-

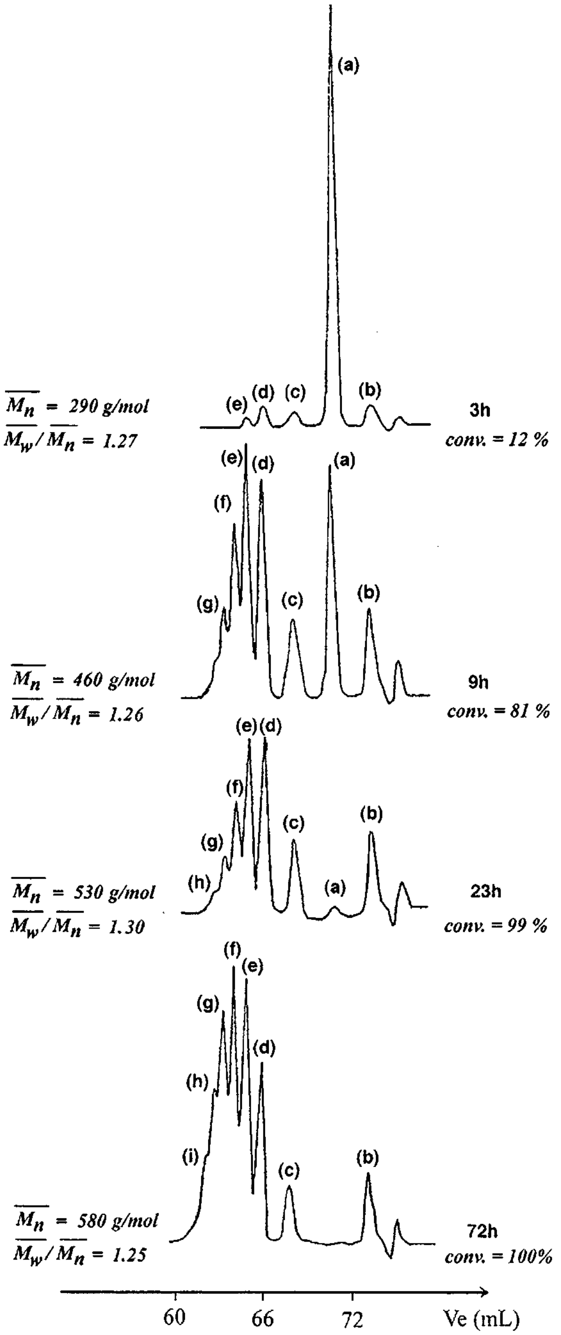

Figure 4. SEC chromatograms for samples withdrawn at different conversions from the model system polymerized at 60 °C: (a) PGE, (b) DP_1, (c) DP_2, (d) DP_3, (e) DP_4, (f) DP_5, (g) DP_6; (h) DP_7, and (i) DP_8.

tor concentration and addition of various surfactants, was investigated.

Influence of Emulsion Composition. The results are compiled in Table 1. As previously stated, both the polymerization rates and, to a lesser extent, $\bar{M}_\mathrm{n}$ varies with temperature (runs 1 and 2). In a previous work,[7] PGE was polymerized using benzyldimethyldodecylammonium hydroxide (NOH) as an inisurf and by adding nonionic surfactant to obtain stable emulsions. In these conditions, slower polymerization rate and much smaller oligomer chains ($\bar{M}_\mathrm{n} = 260$ g mol^{-1}) were obtained compared to the system using didodecyldimethylammonium hydroxide (N′OH) as reported here.

The volume ratio between water and organic phase was increased, while keeping constant the inisurf/monomer ratio (runs 2−4). The polymerization rate and molecular weights were both affected due to partial emulsion destabilization during the polymerization process, the best stability conditions being those applied to the model system.

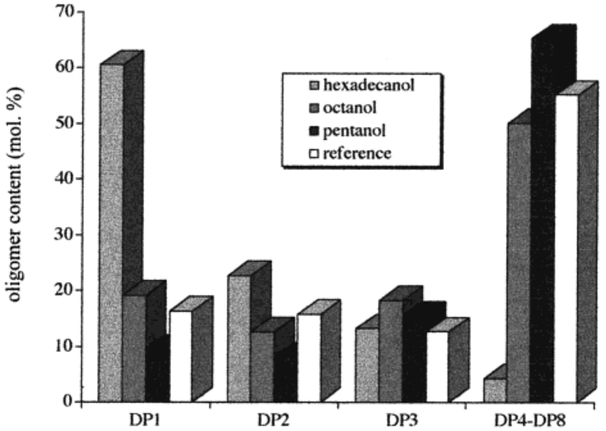

Figure 5. Influence of the alcohol chain length on the final molar composition of the polymer (runs 14, 13, 12, and 2, respectively).

The influence of the inisurf concentration on polymerization rates and average molecular weights was investigated (runs 5, 1, and 6). The polymerization rate increased with increasing inisurf concentrations, which is anticipated from previous studies showing a direct correlation between the polymerization rate and the hydroxyl concentration at the particle surface.[7] Moreover, even if the maximum DP is again equal to eight, molecular weights also increased with inisurf concentration. For a given recipe an increased polymerization rate is correlated to higher oligomer synthesis (see runs 1, 2, 5, and 6), presumably because of an increased $k_\mathrm{p}/k_\mathrm{t}$ ratio.

The addition of nonionic surfactants Brij 30, Brij 35, and Rewopol HV25 was then considered (runs 7−11). The polymerization rate decreases with increasing concentration of nonionic surfactant, whereas the oligomer molecular weight distribution is not affected. These results are consistent with competitive adsorption between nonionic and cationic surfactants on the particle surface. A reduction in hydroxyl concentration at the interface logically decreases the initiation rate, which is the limitation step in the kinetics.

Alcohols with chain length varying from $n = 5$ to 12 were added in the same weight ratio (runs 12−14 and Figure 5). Smaller alcohols (pentanol, octanol) are believed to act as cosurfactants, similarly to classical microemulsion systems, whereas longer ones (hexadecanol) should increase the miniemulsion stability (addition of an hydrophobe). The highest average molecular weight was obtained by adding pentanol. This cosurfactant is believed to decrease the number of termination events by decreasing the water solubility at the interface (see discussion part). Alcohols with longer alkyl chains (such as hexadecanol, run 14) were actually partially soluble in PGE and thus destabilized the miniemulsion, as reported earlier.

In conclusion, the numerous conditions investigated in this study affected the overall molecular weight distribution but did not permit to create polymer chains higher in length than DP_8. The consequence of this is that rather large but similar polydispersity indexes were obtained as reported in Table 1.

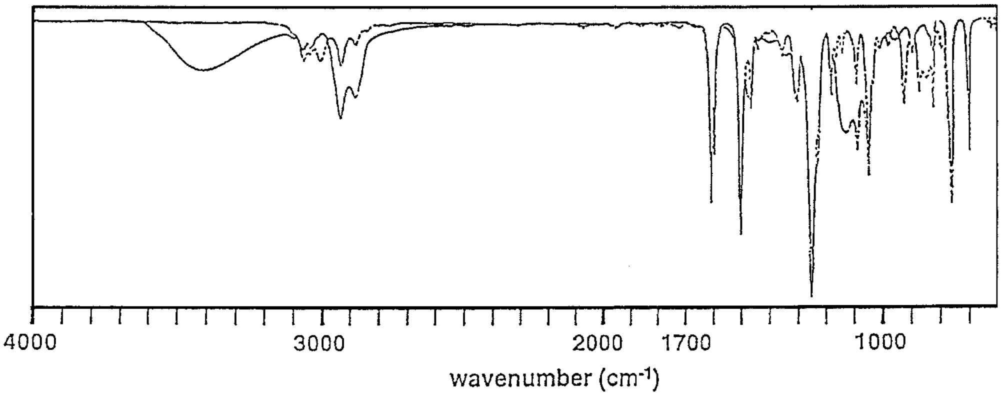

Figure 6. FTIR spectrum of (- - -) PGE and (—) poly(PGE) (Table 1, run 1).

Poly(PGE) Analyses. It has been clearly demonstrated in previous studies on solution PGE polymerization that side reactions had a nonnegligible effect on the kinetics.[18,20] Transfer to the monomer should give rise to double bonds and carbonyl groups.[13,17] Different spectroscopic analyses have been performed to show the presence of these groups. Using ^{1}H NMR, peaks located around 5.2 ppm that would indicate the presence of double bonds were not observed. Moreover, FTIR spectra[29,30] confirmed the absence of both double bonds (shoulder at 1620 cm^{-1})[15–17] and carbonyl groups (around 1730 cm^{-1})[18,20] (Figure 6). These two analyses thus confirmed the absence of transfer reactions to the monomer.

Mass spectroscopy has also been performed on the polymer synthesized using the model conditions (Table 1, run 2 and Figure 7). Oligomers ranging from DP$_1$ (not shown) to DP$_7$ were detected, the corresponding peaks being separated by a PGE unit mass (150 g mol^{-1}). Two main peaks were observed for each oligomer from cationization by H$^+$ and NH$_4$$^+$ (this latter provided by the matrix). The absolute mass values confirmed that each oligomer exhibits OH groups on both ends. This qualitative peak distribution (the DCI+ method is not quantitative up to molar mass of 700 g mol^{-1}) established as well the absence of transfer reactions that would show up as parasite peaks. Analogous α,ω-dihydroxylated polymers were obtained while polymerizing D$_4$ in emulsion, which tends to demonstrate that the same general process governs the polymerization.

Discussion and Conclusion

The anionic polymerization of PGE in miniemulsion has been investigated using didodecyldimethylammonium hydroxide (N′OH) as an inisurf. It was shown that both polymerization rate and polymer chain length obtained in bulk are very different from that observed in miniemulsion. No polymerization occur in the particle core during the miniemulsion process, as similar molecular weight to those obtained in bulk experiment would be reached: the dispersion thus play a drastic role in the polymerization of PGE. For instance, it clearly appeared in this study that modifying the interface shifts the relative proportion of various oligomers formed, from DP$_1$ to DP$_8$ ($\bar{M}_n$ varies from 230 to 690 g mol^{-1}). In particular, addition of pentanol and an increasing N′OH concentration gave the highest average molecular weight (Table 1, runs 12 and 6, respectively).

It was previously proposed[7] that the polymer chain length could be directly correlated to the lifetime of the active centers, due to irreversible termination reactions. In other words, the molecular weight would depend only on the ratio between propagation and termination rates. This reaction scheme is in contradiction with an increasing $\bar{M}_n$ with conversion. In addition, though the polymerization conditions do affect the relative proportion of oligomer chains, it does not permit to produce chains higher than DP$_8$. A more elaborate mechanism is then required to explain such discrepancies that take into account the miniemulsion specificity of this system. A general reaction scheme is proposed in Figure 8.

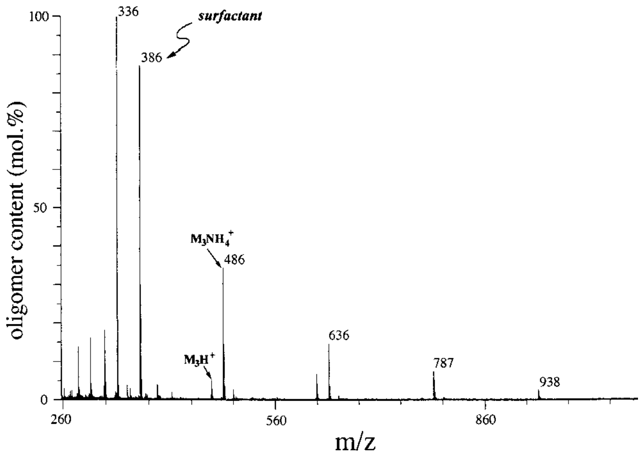

Figure 7. Positive desorption chemical ionization (DCI +) mass spectroscopy of poly(PGE) (Table 1, run 2).

The polymerization of PGE is known to proceed through four steps, namely initiation, propagation, termination, and transfer reactions.[19] Transfer reactions apparently do not occur in miniemulsion, as they could not be evidenced by various characterization methods (namely ^{1}H NMR, FTIR, and mass spectroscopy). The other three steps take place at the interface, as previously stated.[7] The polymer chains are first initiated at the surface of the particles by the hydroxyl counterions carried by N′OH. Alkoxide active centers resulted from initiation can then associate to the ammonium group of the surfactant anchored at the particle surface. These ion pairs created in situ are stable enough to permit few propagation steps to occur before chain termination by water arises.

The resulting dead oligomers seem to play an important role in the kinetics. When these chains are short enough, their affinity for the interface is undoubtedly high because of their hydroxide chain ends. These oligomers act as costabilizer, which causes an increasing PGE solubility in the interfacial layer in contrast to water, thus favoring propagation over termination. The

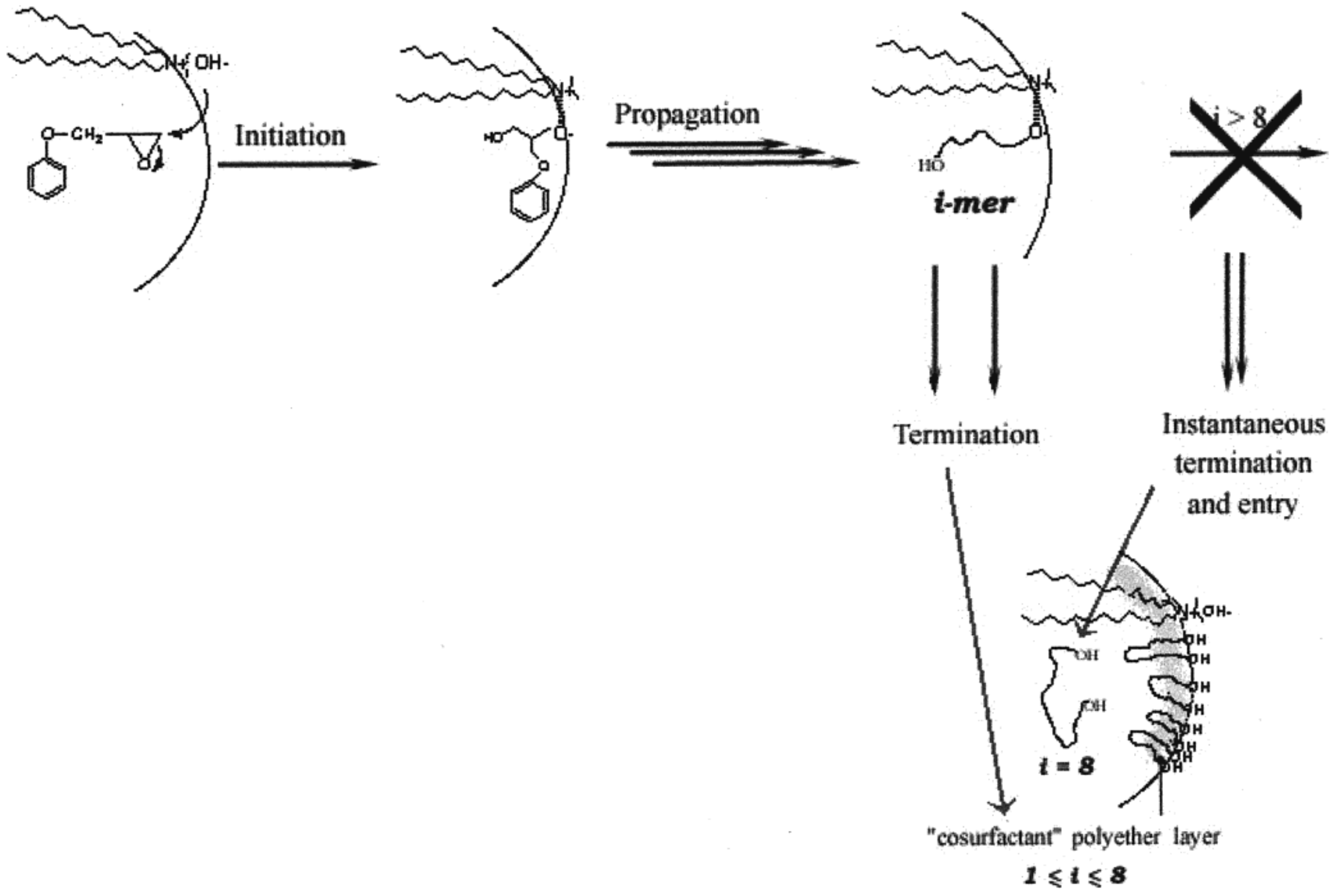

Figure 8. Proposed mechanism for PGE anionic polymerization in miniemulsion.

higher the conversion, the higher the concentration of oligomers at the interface and the longer the chains created. A similar behavior was observed for pentanol (run 12) which was shown to give the highest average molecular weight. This interpretation would account as well for the sudden increase in polymerization rate observed after 30% conversion (Figure 3) at which enough oligomer chains are present in the particles to enhance propagation reaction.

Most of the chains thus underwent termination at this stage. However, for those still propagating, another phenomenon would force the termination to occur. Once the chains attain a critical DP (set as eight in this system), they would lose their surface activity, provoking the ion pair disruption and an instantaneous termination. The "long" dead chains should thus be attracted toward the particle core and diffuse into the particles without undergoing further propagation reactions.

The interfacial locations of the various reaction steps along with the critical chain length barrier are then clearly responsible for the low molecular weight distribution. On the contrary, the absence of an interface in bulk experiment logically conducted to higher average molecular weights. This interfacial mechanism is thought to equally apply to octamethylcyclotetrasiloxane emulsion polymerization.[6,7] The main difference between D_4 and PGE systems is that in the former termination is a reversible process so that polymer chains can reinitiate and undergo further propagation. Consequently, *all* chains formed at low conversion (below 70%) are able to reach the critical size (typically $M_0 = 2500$ g mol^{-1}) at which they "enter" the particles. At higher conversions, condensation reactions occur in the bulk, which provokes an important increase in both the average molecular weight and polydispersity index.[8]

In summary, this study shows the feasibility of polymerizing anionically PGE in miniemulsion to generate α,ω-dihydroxylated polyether chains. The results depicted in this article are very promising, as the pK_a of the alkoxides (typically 14−16) should have prevented a priori any polymerization to occur in the presence of water. The mechanism proposed here suggests that the only requirement to create a relatively stable (toward termination) ion pair is to work with a meticulously chosen surfactant, which may differ from one system to another. Changing the nature of the cationic surfactant polar head should moreover modify the critical chain length at which oligomers enter the particles. Further investigations are currently in progress with phosphonium, pyridinium, and sulfonium surfactants.

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