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IONIC POLYMERIZATION IN AQUEOUS EMULSION

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Abstract: A kinetic study of the anionic polymerization of octamethylcyclotetrasiloxane (D_4) in aqueous emulsion has been carried out in the presence of ionic additives. The rate of polymerization of several cyclosiloxanes has been compared, leading to additional evidence for an interfacial mechanism of polymerization.
The emulsion process has been applied to the cationic polymerization of D_4 and of tetramethylcyclotetrasiloxane (D_4^H) initiated by dodecylbenzenesulfonic acid. Very efficient for the synthesis of linear polymethylhydrogenosiloxanes (PMHS), these conditions did not seem suitable for the polymerization of D_4.
The extension of the process to other heterocyclic monomers is discussed through the anionic polymerization of phenylglycidylether.

INTRODUCTION

The ionic polymerizations of heterocyclic monomers is an important field of research in polymer synthesis. Extensive researches have been carried out and many polymers are industrially produced by this way. However, the ionic species responsible for the polymer formation are of different sensitivity to moisture leading to a modification of the reaction behaviour and/or to an absence of control. This particular aspect limits the research productivity and the reproducibility of the results. Carbanionic and carbocationic polymerizations are typical examples needing extreme purifications in order to avoid side reactions.
Organic chemists have developpped techniques allowing the synthesis of ionic species in heterophasic systems containing water (i.e. phase transfer catalysis) (Ref. 1). In such a system, ionic species can be formed in the aqueous phase or at the interface between organic material and water. After combination with an organophilic counter-ion (quaternary ammonium ion) the active species can react with a substrate in the organic phase. A large range of organic species

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can be produced by this way and such a reaction was applied with success to the polycondensation and to the chemical modification of functional polymers (Ref. 2).

Ionic polymerization of cyclosiloxanes in water dispersion was first proposed in 1959 by Hyde and Werhly (Ref. 3). Several studies of the ionic polymerization of octamethylcyclotetrasiloxane and of the polycondensation of α,ω-dihydroxypolysiloxanes have been published in the literature (Refs. 4-7).

This paper deals with new results on the mechanism of the anionic polymerization of D_4 in aqueous emulsion. An extension of the process to the cationic polymerization of functionnal cyclosiloxanes and to the anionic polymerization of glycidylphenylether is a first attempt to define the scope and limitation of the process.

EXPERIMENTAL PART

Materials

Octamethylcyclotetrasiloxane, tetramethylcyclotetrasiloxane and phenoxymethyloxirane (phenylglycidylether) were used without further purification. Chromatographic analysis indicated that less than 1 wt.-% other cyclic or linear materials are present.

Benzyldimethyldodecylammonium bromide, didodecyldimethylammonium bromide, dodecylbenzenesulfonic acid derivatives, polyoxyethylene(23)lauryl ether $C_{12}H_{25}(OCH_2CH_2)_{23}OH$ (Brij35) were purchased from Aldrich and used as received.

Benzyldimethyldodecylammonium and didodecyldimethylammonium hydroxides were prepared according to the procedure previously described (Ref. 7).

Emulsification

The monomer was added to a solution of emulsifying agent in water and the mixture was homogeneized using a sonifier 450 Branson Ultrasonics Corporation (power 7 during 6 min). During emulsification, the mixture was cooled with an ice bath in order to keep the temperature constant (~ 5°C).

Polymerization

The emulsion was transfered in a four-necked reactor and nitrogen was bubbled through the solution for five minutes and the reaction temperature was adjusted with a thermoregulated oil bath. The polymerization was carried out under a slight nitrogen flow and under mechanical stirring (100 rpm).

Aliquots were taken during the course of the polymerization and neutralized to a pH near 8 in order to stop the reaction.

Particle size measurements and polymer characterization

Particle size was determined using a Sympatec GmbH analyser or a Malvern Zetasizer Model IV after dilution at a concentration of 10-20 wt.-% in water.

The molecular weights of the polymers were measured by size exclusion chromatography using Waters Associates components (refractive index detector). The measurements were carried out in toluene or methylene chloride solution (flow rate: 1 $mL.min^{-1}$) with three µ–Styragel columns (mixt, 500, and 100 Å) calibrated with standard polystyrenes for molecular weights above 8000 and with linear trimethylsilyl terminated siloxanes for the lower molecular weights.

^{29}Si NMR spectra were recorded on a Bruker AM 500 FT-NMR spectrometer equipped with a ^{29}Si probe (10 mm diameter) at 99,3 MHz. The samples were diluted in $CDCl_3$ (10^{-2} M) containing 1 vol.-% TMS which was used as a chemical shift reference and 20 mg $Fe(acac)_3$ as relaxation agent .

RESULTS AND DISCUSSION

Anionic Polymerization of Octamethylcyclotetrasiloxane

In agreement with Xing Hua (Ref. 6), we have previously shown (Ref. 7) that anionic polymerization of octamethylcyclotetrasiloxane (D_4) initiated by benzyldimethyldodecyl-ammonium hydroxyde (NOH) in aqueous emulsion produces linear dihydroxytelechelic polysiloxanes with a narrow molecular weight distribution ($M_w/M_n \sim 1.1$ to 1.5).

For a polymer conversion lower than 70 wt.-% a zero internal order has been observed which was explained by a kinetic scheme involving the following sequence of reactions :

- continuous initiation by hydroxyde:

$$OH^{\ominus} \quad + \quad D_4 \quad \longrightarrow \quad HO\text{-}(SiO)_3\text{-}SiO^{\ominus}$$

- propagation via silanolate active species:

$$\sim\!\sim\!\sim SiO^{\ominus} \quad + \quad D_4 \quad \longrightarrow \quad \sim\!\sim\!\sim (SiO)_4\text{-}SiO^{\ominus}$$

- reversible termination (transfert to dispersing agent)

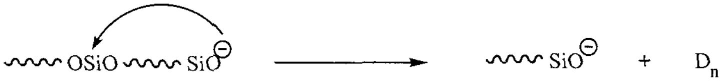
$$\sim\!\sim\!\sim SiO^{\ominus} \quad + \quad H_2O \quad \rightleftharpoons \quad \sim\!\sim\!\sim SiOH \quad + \quad OH^{\ominus}$$

All these reactions were supposed to take place at the surface of monomer particles (∅ ≈ 0.2 µm) where the active species could be ion pairs resulting from the association of the silanolate species with the quaternary ammonium emulsifying agent.

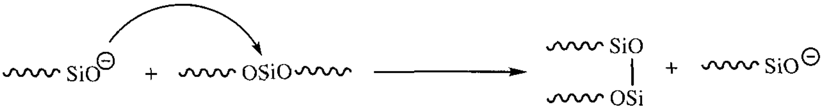
The ionic species should then mainly be located at the interface and all reactions controlled by diffusion of other molecules bearing the siloxane bond or the silanol function to be reacted.

In such an interfacial water/monomer system, thermodynamic and kinetic parameters may significantly differ from those observed in bulk or in solution, and one can expect that all reactions involving the polymeric chains, *i.e.*,

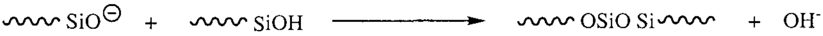
- intramolecular reaction (backbiting):



- intermolecular reaction (redistribution):



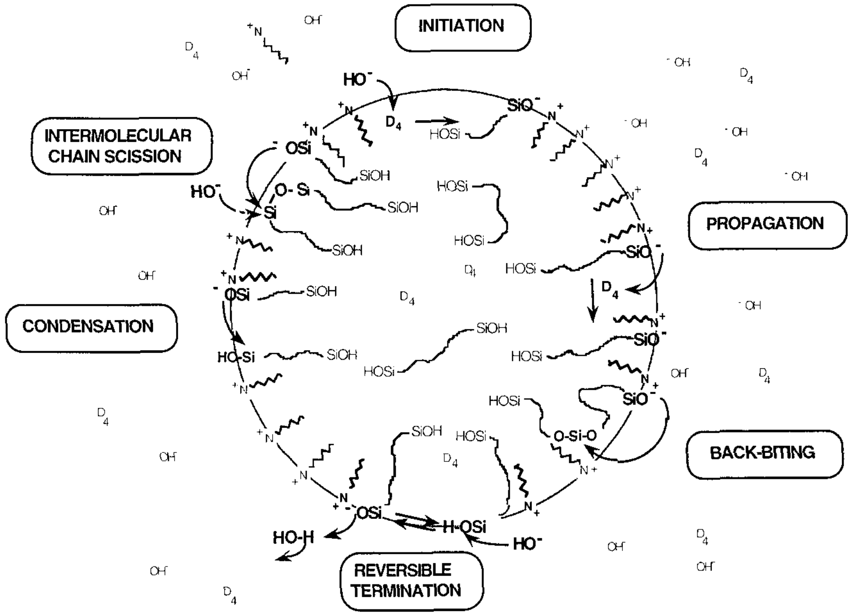
- condensation reaction:



are more affected than the reactions with the monomer molecules.

A general scheme of the process is given in Fig. 1, which describes the monomer particle in the water continuum.

Fig. 1. Schematic representation of a monomer particle for the anionic polymerization of D_4 in aqueous emulsion.



It shows the particular aspect of each reaction with its location, and the importance of the physico-chemical properties of the different molecules involved in each process. Their ionic/non-ionic character, their solubility in oil, in water and in the oil/water interphase obviously determine their reactivity and concentration, and consequently the relative rate of each particular reaction involved in the process.

Previous results have shown that the internal order in monomer and that the external order in emulsifier/initiator NOH are respectively equal to 0 and 1. A numerical simulation based on this scheme has been developped, showing an excellent agreement with the kinetic observations (Ref. 7).

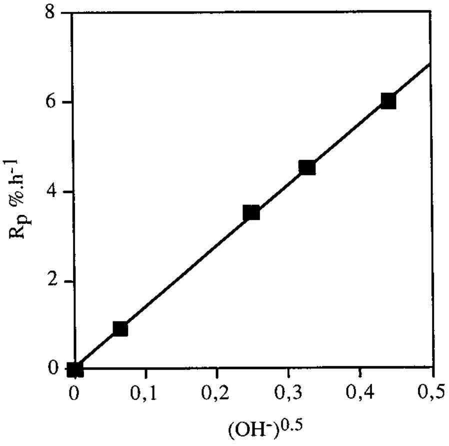
Several experiments were carried out in order to give additional arguments to this hypothetic scheme.

Kinetic order in initiator

The polymerization rate of D_4 has been determined with various amounts of initiator OH^- and with a constant amount of emulsifying agent in order to maintain the particle size at a constant value. These conditions were obtained using mixtures of an identical amount of benzyldimethyl-dodecylammonium bromide (NBr) with various concentrations of NaOH. The variation of the rate of polymerization R_p with $(OH^-)^{0.5}$ is given in Fig. 2.

For a given particle size and with an amount of OH^- lower than that of the emulsifier, the order in initiator is equal to 0.5 showing the competition between Br^- and OH^- ions at the monomer/water interface.

Fig. 2. Rate of the anionic polymerization of D_4 as a function of the square root of the initiator concentration (OH^-). T = 30°C



The explanation for the absolute value of the kinetic order is not clear, and needs additional experiments concerning the initiation reaction. However, it shows a competitive occupation of the interface by Br^- and OH^- ions. The instantaneous concentration of silanolate active centres which determines the propagation rate is a function of the number of OH^- localized at the interface (first ionic layer).

Effect of NBu_4OH

In order to estimate the role of a partially lipophilic counter-ion, kinetic experiments were carried out using various amounts of NBu_4OH in addition to the emulsifier/initiator NOH.
The results are given in Tab. 1. In these experiments NBu_4OH was added after emulsification of the medium.

Tab. 1. Rate of polymerization of D_4 in the presence of NBu_4OH. (T = 40°C)
* based on monomer

NOH mol.-%*	NBu_4OH / NOH	R_p wt.-%.h^{-1}
1.2	0	8.7
1.2	1.2	9
1.2	3.5	8.5

The polymerization rate is clearly unchanged by the addition of appreciable amounts of NBu_4OH. These results seem to give information concerning two important points:

- NBu_4OH is mainly located in the aqueous phase leading to an increase in the initiator OH^- concentration. As no modification in the kinetic of polymerization was observed, it can be concluded that the initiation reaction does not take place in the aqueous phase between the OH^- excess and the monomer. The initiation reaction is thus mainly localized at the surface of the monomer particle. Moreover, it seems that the initiation rate is not determined by the total concentration of OH^-. The effective amount of hydroxide ions leading to the initiation reaction is determined by the total area of the dispersed monomer, which depends on the amount of the emulsifier.
- Moreover, such a result could be obtained considering that the cationic layer of the emulsifying agent acts as a barrier to the NBu_4^+ ion which cannot penetrate inside the monomer particle during the polymerization reaction. The absence of effect due to the presence of NBu_4^+ species seems to show that the polymerization reaction does not take place inside the monomer particle via silanolate active species associated to NBu_4^+ as counter-ion.

A similar experiment was realized by adding an identical amount of NBu_4OH before the emulsification procedure. A slight modification of the particle size distribution was observed (apparition of a small amount of large particles) leading to a slight decrease of the rate of polymerization ($R_p \sim 7,5$ wt.-%.h^{-1}) in agreement with the reduction of the interface area. Definitively, the presence of NBu_4OH leads to a modification of the emulsion stability but has no pronounced effect on the reaction rate.

As a conclusion, an initiation reaction between hydroxide ions and water soluble monomer does not take place in the aqueous phase. Moreover, no propagation reactions being observed into the monomeric phase with NBu_4^+ as counterion, it can be supposed that this possibility remains low considering the ammonium emulsifying species. The propagation reactions are then mainly localized at the monomer /water interface.

Nevertheless, if the active species are essentially localized at the interface it can not be concluded that bimolecular reactions involving two polymeric chains (*i.e.* polycondensation and redistribution reactions) mainly take place at this location. The effects of these reaction on the molecular weight and on the distribution being observed for high conversions (>70 wt.-%) and for long reaction time, it can be also supposed that such reactions occur in the bulk between a small fraction of soluble ionic species and dihydroxy terminated PDMS chains.

Extension of the process to other cyclosiloxanes

The process having obviously an interfacial nature, the physico-chemical properties of the monomer have probably a great influence on the reaction behaviour. The rate of polymerization of several cyclosiloxanes monomers have been determined using identical experimental conditions. The results are given in Tab. 2.

Tab. 2. Rate of polymerization and molecular weight distribution M_w/M_n for the anionic polymerization of several cyclosiloxanes in aqueous emulsion.
Monomer / Water / NOH = 1 / 3 /1,2 mol.-% based on monomer. (T = 40°C).
* monomer/toluene: 1/2 wt/wt

Monomer	D_3 + Toluene*	D_5	D_4	D_4^{Vi}	D_6	D_4^{Vi} + Toluene*
R_p wt.-%.h^{-1}	100	60	10	12	< 1	< 1
M_w/M_n	≥ 2	cyclics	< 1,5	< 1,5	-	-

Hexamethylcyclotrisiloxane (D_3) being a solid monomer at r.t., it was used after dissolution in toluene in a ratio 1/2 wt/wt.

The reactivity order ($D_3 > D_5 > D_4^{Vi} \sim D_4 > D_6$) is quite different from that observed in classical anionic polymerization (Refs. 8,9). D_3 remains more reactive than D_4 but the rate of polymerization is only 100 times higher than for D_4. This ratio is significantly lower than that observed by Boileau and al. (Ref. 9) in the case of Li^+ + [211] as counter-ion in benzene solution at 20°C. Moreover emulsion polymerization of D_3 produces polydimethylsiloxanes having a broad molecular weight distribution even at low conversion, contrary to expected results as regards a conventionnal anionic process (Ref. 8).

D_5 seems to be slighlty more reactive than D_4, but leads surprisingly to the formation of low molecular weight cyclic polymer. D_6 is the less reactive monomer of the series.

For D_3, D_4, D_5 and D_6, the ionic species are probably identical and the observed differences of reactivities could be due to the interfacial properties of each monomer or to a change in the monomer concentration in the emulsifier containing layer.

The homopolymerization rates and polymer distributions were found very close in the case of pure D_4^{Vi} and D_4. The addition of 30 vol.-% of toluene as solvent has a large effect on the rate of polymerization of D_4^{Vi} which can not easily be polymerized in these conditions. This effect is in good agreement with the above mentionned results (D_3 + toluene).

In the case of D_4^{Vi} ionic species are different of those formed during the D_4 polymerization; their concentration and their reactivity seems to be greatly affected by the polymerization medium (*i.e.* pure monomer, toluene solution and interface).

The interfacial location of the reactions involved in this process seems to be established but needs to be proved by direct observations.

Cationic polymerization of cyclotetrasiloxanes

The cationic polymerization of cyclosiloxanes in aqueous emulsion was first investigated by Weyenberg et al. then by Saam and Huebner using dodecylbenzenesulfonic acid associated to its sodium salt NaDBSA (Refs. 10,11). In order to develop a comparative study with our previous results, D_4 and tetramethylcyclotetrasiloxane (D_4^H) were polymerized in appropriate conditions. Due to the presence of SiH bonds which are sensitive to nucleophilic species, D_4^H can not be polymerized by an anionic process.

The cationic polymerization of D_4^H in bulk and in solution was studied by Lasocki and al. (Ref. 12) and more recently by Sigwalt et al. (Ref. 13). When using benzenesulfonic acid as initiator, PHMS having a low molecular weight (less than 12000) were obtained, while the molecular weight reaches a value close to 100000 with triflic acid as initiator in CH_2Cl_2. In such conditions, the yields in polymer were not high (~ 35 wt.-%) and an important part of the material is probably a grafted or crosslinked product.

Using dodecylbenzenesulfonic acid as emulsifier/initiatior, a mixture of monomer/H_2O 2/1 to 8/1 vol/vol gives after emulsification a dispersed medium containing particles having a diameter in the range 250-450 nm. The addition of an ionic or of a neutral coemulsifier (dodecylbenzenesulfonic acid sodium salt (NaDBSA) or polyoxyethylene(23)lauryl ether (Brij35)) improves the stability of the emulsion, the size of the monomer particles remaining in the same order of magnitude.

The results of the polymerization of D_4 and D_4^H are summarized in Tab. 3.

Tab. 3. Cationic polymerization of D_4 and D_4^H in aqueous emulsion at 40°C.
* based on monomer

Monomer	H_2O/monomer vol/vol	DBSA mol.-%*	NaDBSA mol.-%*	Brij35 mol.-%*	Rp wt.-%.min^{-1}	M_n
D_4	2	2,7	0,7	0	0,007	20000
	8	1,98	0	0,98	0	-
D_4^H	2	2.9	0	0	>100	not soluble
	8	0.74	3;37	0	20	7400
	8	0.74	0	3.37	1.5	7400

The cationic polymerization of D_4 in the presence of small amounts of an ionic or a neutral co-emulsifier is a very slow process. The presence of Na^+ cations or of a polyethylene oxide layer at the surface of the monomer particles hinders the access of the initiating species (which could be H^+) leading to an inhibition of the polymer formation.

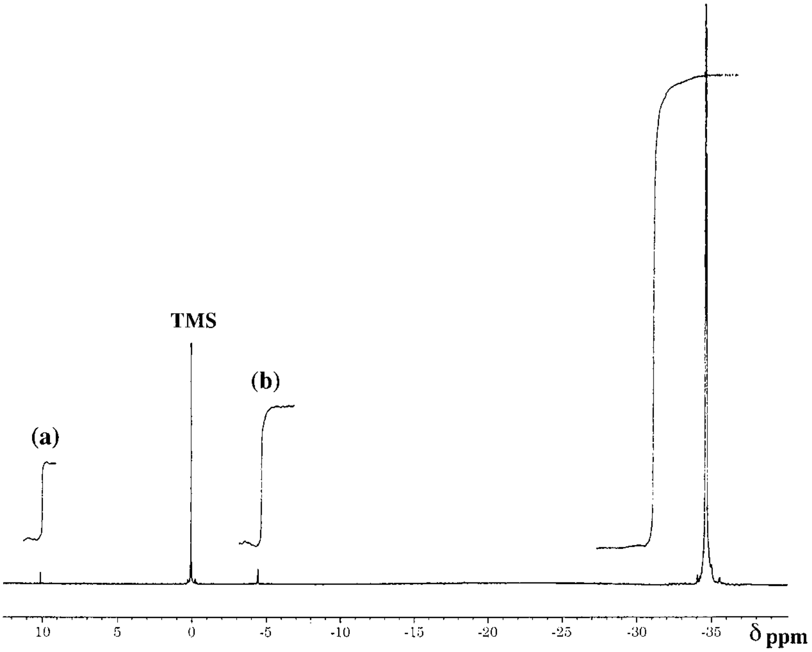
A similar behaviour was observed for the cationic polymerization of D_4^H.

With DBSA alone, a very fast reaction was observed, producing an insoluble crosslinked polysiloxane. After addition of a small amount of NaDBSA or of Brij35 the reaction of D_4^H at 40°C is greatly reduced and leads to the formation of soluble linear polymer with a yield close to 90 wt.-%. Other 10 wt.-% remaining material is exclusively composed of small cyclic products D_4^H, D_5^H and D_6^H. (Ref. 14)

The ^{29}Si NMR spectrum of the polymer is given in Fig. 3.; the absence of signal corresponding to trifunctional $CH_3\text{-}Si(O\sim\sim\sim\sim)_3$ units confirms the linearity of the polymeric chains.As no silanol end groups were detected in the spectrum, the two small peaks (a) and (b) at δ = 10,5 ppm and -4,6 ppm were respectively attributed to $\text{-}SiH(Me)_2$ and $\text{-}Si(Me)_3$ chain ends. Considering this hypothesis, the molecular ,weight calculated with the integrations is in very good agreement with that obtained by SEC measurements. The chemical nature of the terminal groups suggests that a spontaneous termination reaction takes place leading to polymeric chains unable to reinitiate a polymerization or a polycondensation reaction. For a ratio monomer/H_2O = 8, it was observed that the molecular weight of the polymer reaches very rapidly its maximum value (M_n = 7400) and does not change for long reaction time.

The molecular weight distribution ($M_w/M_n = 1.5 - 2.2$) remains broader than that observed in the case of the anionic polymerization of cyclosiloxanes.

Fig. 3. ^{29}Si NMR of PHMS synthesized by cationic polymerization of D_4^H in aqueous emulsion at 30°C.



By analogy with the anionic polymerization it is reasonnable to suppose that the main steps of the mechanism are identical (initiation, propagation, reversible termination). However, the initiator (H^+) can lead to different ionic species (*i.e.* siloxonium or silicenium cations, sulfonic acid esters) which can coexist in various proportions in the medium. Those species, having quite different reactivities and stabilities, can be responsible for a competition between a number of reaction larger than in anionic polymerization.

Anionic Polymerization of Epoxydes

As a model of anionic polymerization of epoxydes in aqueous emulsion, phenyglycidylether (PGE) was used in experimental conditions close to those used for D_4. PGE is a monomer having a low solubility in water, reducing the possibility of initiation and polymerization reactions in this medium.

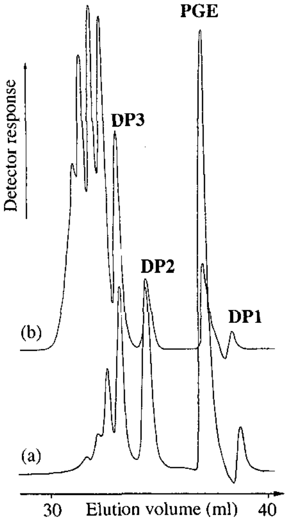
Moreover, this monomer is known for giving side reactions during its conventionnal anionic polymerization as mentionned by several authors (Refs. 15,16). Thus the molecular weights of the polymer remain generally very low in the range 2000-3000. Moreover, Stolarzewicz (Ref. 16) has shown the presence of insaturated chains ends (ethylenic and carbonyl end groups). In agreement with these observations, a mechanistic scheme was proposed, which involves transfer reactions to PGE leading to insaturated ionic species able to reinitiate the polymerization.

Using NOH as inisurf in the same conditions than D_4, the emulsions are quite stable and the main products that were obtained are the 3-phenoxy-1,2-propanediol which corresponds to the opened monomer (DP1) and a mixture of low molecular weight polyoxides (DP2-6). These results suggest a ring-opening reaction of PGE by an hydroxide ion immediately followed by a termination reaction with a water molecule. The SEC trace of the crude product is given in Fig. 4a.

A change in the nature of the inisurf for a more hydrophobic one, the didodecyl-dimethylammonium hydroxide, permitted a better emulsion stability and a mixture of oligomeric products with a DP up to 10 was obtained, as shown in Fig. 4b.

Moreover, insaturated chain ends were not detected by IR or NMR. Both analysis are in good agreement with the specific formation of pure linear α,ω-dihydroxy material.

Fig. 4. SEC traces of crude products obtained by anionic polymerization of PGE in aqueous emulsion.



In these conditions, the alcohol chain ends exhibit a very good stability. A dihydroxy terminated oligomeric polyoxide cannot reinitiate the ring-opening reaction of PGE. Thus the alcoholate active species are once formed, only by the initiation reaction of PGE and cannot be reactivated after the termination reaction. The length of the oligomeric material is then directly connected to the life-time of the active centres which can be controlled by the chemical nature of the emulsifier.

CONCLUSION

The ionic polymerization of cyclosiloxanes in aqueous emulsion is a convenient method for the synthesis of PDMS and PHMS with a good control of the structure of the polymer.

The interfacial nature of the mechanism, which seems now well-established, is responsible for the improvement of the results, probably by a non-uniform modification of main and side reactions rates. However, the efficiency depends on the monomer reactivity and also on the physico-chemical properties of the species (active centres, monomer and polymer). As a conclusion, in suitable conditions the process clearly improves the polymerization but still needs optimization in the case of selected monomers.

One of the major interest of the process is linked to its potential ability to polymerize monomer with active centres of high basicity. This was achieved in the case of phenylglycidylether, but the rate of deactivation of the alcoholate active centers with water remains too high producing low molecular weight polyoxides. However, the nature of the emulsifier containing layer is of great importance on the behaviour of the reaction and its modulation (*i.e.* control of the water content, of the location of the active centres...) is a major point of interest for future application.

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