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Kinetic Study of α,ω-dihydroxy Polydimethylsiloxane Condensation in Aqueous Emulsion

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SUMMARY: The polycondensation of α,ω-dihydroxy poly(dimethylsiloxane) (PDMS) was investigated in a cationic emulsion process, using benzyldimethyldodecylammonium hydroxide (BDDOH) as an inisurf. Studying the condensation reaction without competing redistribution and polymerization reactions remains difficult. A comparative study of the variation of $\overline{M_w}$ and $\overline{M_n}$ with conversion shows that the broadening of the molecular weight distribution is due to the short chains formed by polymerization of octamethylcyclotetrasiloxane (D_4), which is produced from back-biting reactions. Kinetic apparent constants were also determined.

Introduction

Conventional ionic ring-opening polymerizations of cyclosiloxanes[1)] are generally coupled with redistribution reactions leading to a broadening of the molecular weight distribution. Moreover, back-biting reactions produce significant amount of cyclic oligomers. In attempts to control these side reactions, Zhang[2)] studied the anionic polymerization in emulsion of D_4 using sodium hydroxide as the catalyst and benzyldimethyldodecylammonium bromide (BDDBr) as a cationic emulsifying agent. These emulsions were not found to be stable, thus Zhang proposed only a hypothetical mechanism of polymerization. More recently, Hémery and al.[3,4)] have carried out studies on the anionic polymerization of D_4 in emulsion using benzyldimethyldodecylammonium hydroxide (BDDOH) as an inisurf. This resulted in a decrease of the salt concentration in the aqueous phase, permitting stability of the emulsion throughout the reaction. The polymerization rate and the final yield were found to be higher than in a classical bulk polymerization process. Moreover, only small cyclics (D_4, D_5 and D_6), which could easily be removed by distillation, were formed. Finally, the obtained PDMS was found to be linear and α,ω-dihydroxylated. These results inferred that the different reactions are located in the interface, due to the association between the propagating silanolate species and the quaternary ammonium cation. Nevertheless, the control of the molecular weight, along with a narrow molecular weight distribution (MWD = 1.1 to 1.5), is achieved up to 70%

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conversion ($M_n \approx$ 15000 g.mol^{-1}), and lost at the end of the reaction, leading to an increased polydispersity index. This deviation was attributed to the condensation reactions of the α,ω-dihydroxylated PDMS. Indeed, experimental results and computerized simulations demonstrated a good agreement with a simultaneous polyaddition/polycondensation process. A better understanding of these condensation reactions may allow for better control of the polymerization process.

Experimental Section

In a 100 mL beaker were introduced 60 g water (3.33 mol), 30 g D_4 (0.1 mol) and 1.2 g BDDOH (3.7 10^{-3} mol). A stable emulsion was obtained by sonication in an ice bath during 6 minutes at power 7 using a sonifier 450 Branson Ultrasonics Corporation, giving an average initial particle size of 250 nm. The emulsion was then poured into an open reactor, where the polymerization proceeded under mechanical stirring at 100 rpm. The presence of a slight nitrogen flow appeared to have no influence on the polymerization. The reaction temperature was stabilized at 40°C.

In order to follow the kinetics, aliquots were regularly withdrawn during the course of the reaction and quenched with an 1N hydrochloric acid solution. The aqueous phase was then saturated in salt in order to allow for the migration of small cyclic products in the organic phase. Aliquots were frozen in liquid N_2, then the organic phase was recovered by decanting and dried over $MgSO_4$.

The α,ω-dihydroxylated PDMS used for the polycondensation study was synthesized with this process, by stopping the reaction at the time required (as determined by kinetic studies) to obtain the polymer with the appropriate molecular weight. Small cyclic products were eliminated by distillation under reduced pressure. The obtained PDMS was controlled by SEC using toluene with N,N-diisopropylethylamine (3 mL.L^{-1}) as the eluant at a flow rate of 1 mL.min^{-1}. PL Gel columns 10 µm (mixed, 500 Å and 100 Å) were calibrated with narrow polystyrene standards and low molecular weight PDMS (Waters), using a differential refractometer detector (Waters 410).

The anionic condensation of α,ω-dihydroxylated PDMS ($\overline{M_n}$ = 6000 g.mol^{-1}) was carried out under similar experimental conditions, replacing D_4 by the PDMS.

Results and Discussion

Polymerization of D_4

During the polymerization, only two reactions are responsible for the variation of the number of chains: initiation and condensation reactions which respectively create chains and reduce the number of chains. At the beginning of the reaction the D_4 concentration is important and chains are mostly formed by initiation. At about 20% conversion, the silanol concentration reaches a maximum value at which the condensation rate becomes higher than the rate of initiation. This is not in accordance with Zhang results$^{2)}$, who observed the maximum in the number of chains at about 75% conversion. After 70 hours an equilibrium is reached in the silanol and the D_4 concentrations, as the initiation rate equals the condensation rate.

The number average molecular weight $\overline{M_n}$ increases at the beginning of the reaction and stabilizes around 30000 g.mol^{-1} at 70 hours (Fig. 1). Though the number of chains remains constant, condensation and initiation reactions continue to produce respectively long chains and short chains. Chromatogram traces show that the peak shifts to longer chains, and a tail appears corresponding to shorter chains (results not shown). This is further evidenced by plotting the variation of $\overline{M_w}$ as a function of time (Fig. 1). As $\overline{M_w}$ is more sensitive to long chains than $\overline{M_n}$, it continues to increase until around 200 hours. Before the equilibrium is reached, the molecular weight distribution remains narrow, between 1 and 1.5. Then it drastically increases to stabilize around 4.5 when $\overline{M_w}$ stabilizes.

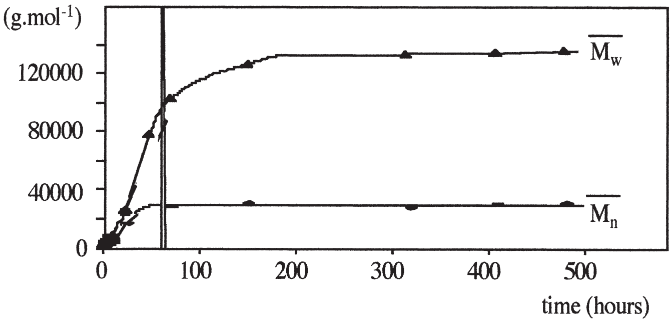

Fig. 1: Variation of the number ($\overline{M_w}$), weight ($\overline{M_w}$) average molecular weight as a function of time for the polymerization of D_4 at 40°C.

Apparent kinetic constants for initiation and condensation have been determined based on the variations in the number of chains and D_4 consumption with time$^{3)}$. A first order dependence on the initiator concentration for initiation and a second order dependence on chain ends for condensation are observed. Moreover, the ratio of the propagation rate to the condensation rate is directly linked to the ratio of D_4 to the number of chains. The number of chains rapidly increases and become high enough to account for the role of condensation in the knowledge of the system.

Condensation of α,ω-dihydroxy polydimethylsiloxane

It is difficult to study the condensation reaction in the absence of monomer. Indeed, intramolecular redistribution reactions (back-biting) take place early in the process, producing small cyclics (D_4, D_5 and D_6) in the same proportion as during the polymerization (Fig. 2). The equilibrium between cyclics and linear chains is achieved after 40 hours of reaction.

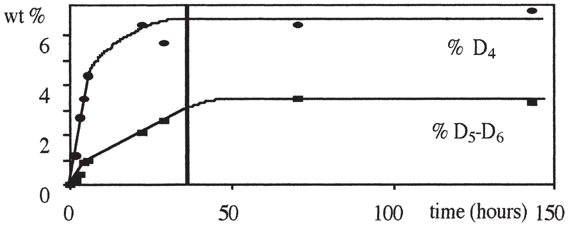

Fig. 2: Formation of D_4, D_5 and D_6 (wt%) as a function of time during the condensation of α,ω-dihydroxylated PDMS ($\overline{M_n}$ = 6000 g.mol^{-1}) at 40°C.

At the beginning of the reaction, negligeable amounts of cyclics are formed. The condensation reaction can be illustrated by the decrease in the number of chains with time (Fig. 3).

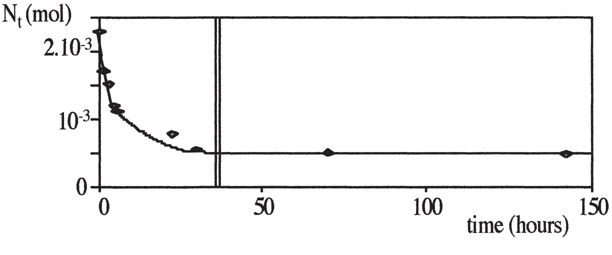

Fig. 3: Variation of the number of chains (in mol) as a function of time during the condensation of α,ω-dihydroxylated PDMS ($\overline{M_n}$ = 6000 g.mol^{-1}) at 40°C.

The initiation reaction becomes increasingly important as the reaction proceeds, as more D_4 is created. When the equilibrium between linear chains and cyclics is reached, the number of chains remains constant. Again, the rate of initiation reaction equals the rate of condensation. This equilibrium is reached for the same silanol concentration as for the polymerization process.

The increase of the number and weight average molecular weight as a function of time (Fig. 4) are similar to those observed during polymerization.

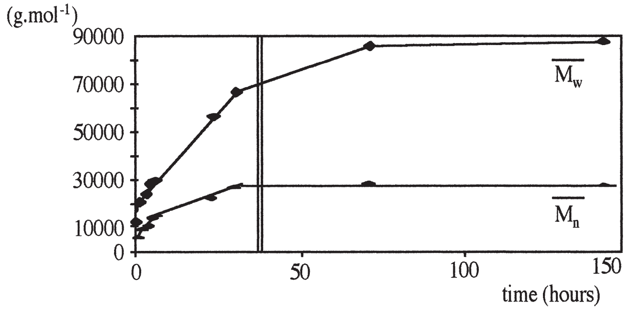

Fig. 4: Variation of the number and weight average molecular weight as a function of time for the condensation of α,ω-dihydroxylated PDMS ($\overline{M_n}$ = 6000 g.mol^{-1}) at 40°C.

$\overline{M_n}$ reaches an equilibrium around 30000 g.mol^{-1}, while $\overline{M_w}$ continues to increase after $\overline{M_n}$ stabilization, due to the simultaneous condensation reaction. The variation of the molecular weight distribution then also exhibits the same trend as the polymerization process (Fig. 5).

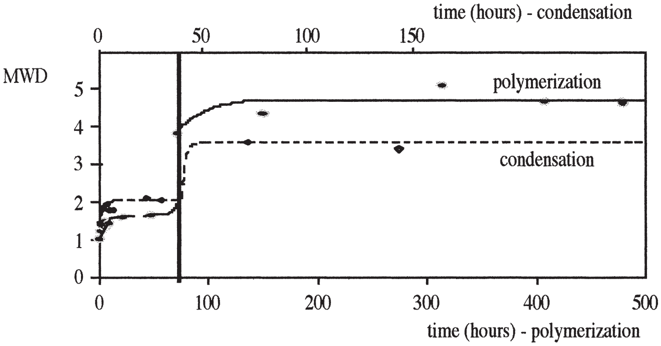

Fig. 5: Evolution of the molecular weight distribution as a function of time during the polymerization of D_4 and during the condensation of α,ω-dihydroxylated PDMS ($\overline{M_n}$ = 6000 g.mol^{-1}) at 40°C.

There are however appreciable differences between the two systems. In polycondensation, the polydispersity index increases more rapidly than during polymerization to reach a value of 2, whereas in polymerization, condensation reactions obey a statistical law. Indeed, performing condensation reactions using PDMS with molecular weight ranging from 4000 to 12000 g.mol^{-1} led to the same final distribution. Perhaps the synthesis of short chains during the polymerization process is responsible for the narrower molecular weight distribution obtained. Such a situation would be in agreement with results reported in the litterature5).

A kinetic study was realized which first confirmed the kinetic model based on the results obtained by polymerization: a second order dependence on chain ends, and an apparent condensation rate constant of 50 mol^{-1}.h^{-1}. Besides, while varying the concentration of hydroxyle ions and maintaining a constant overall surfactant concentration, a global first order dependance on hydroxyle ion concentration was observed. Finally, the activation energy obtained by varying the temperature was evaluated as 34 kJ. mol^{-1}, which is close to the value obtained for polymerization.

Conclusion

Studying the polycondensation of PDMS exhibiting a $\overline{M_n}$ superior to 4000 g.mol^{-1} led to conventional results. The condensation reaction follows a statistical law and a second order dependence on chains ends is observed. These results are in agreement with previous studies3,4). However, one question still remains: how such a narrow polydispersity index can be observed in the polymerization process when the results clearly show that condensation is important even at the beginning of the reaction? Condensation is thought to occur in a more complex way than expected, for instance by a modification of the mechanism or the location of reaction. The condensation of short dihydroxylated PDMS chains under the same experimental conditions could be studied to give more insights on the subject.

References

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