Anionic Cyclocarbosiloxane Ring Opening Polymerization

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This paper presents a study of the reactivity new carbosiloxane cyclic structures in anionic ring opening polymerization reactions in the presence of catalyst potassium siloxanolate. For this purpose, 2,2,5,5-tetramethyl-3,4-diphenyl-1-oxa-2,5-disilacyclo-pentane, 2,2,5,5-tetramethyl-3,3-diphenyl-1,4-dioxa-2,5-disilacyclopentane, 2,2,7,7-tetra-methyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane and bis-[1,4-bis-(dimethylsiloxanyl)-dihydronaphthalene] were used. The evolution of the polymerization reaction was observed through measurements of the reaction mixture inherent viscosity at various temperatures. The obtained results were processed in order to obtain the influence of the chemical structures on the processes conditions of development and kinetic parameters related to the transformation of the cycles to linear compounds.

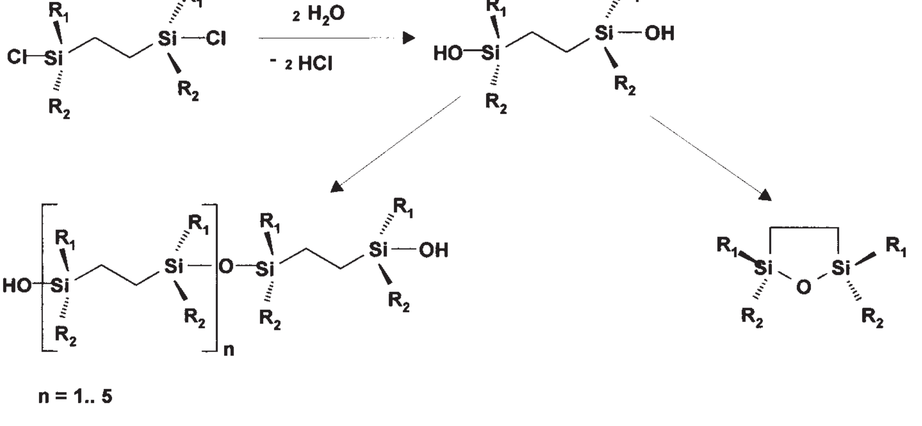
Keywords: cyclocarbosiloxanes, siloxanes, anionic polymerization, ring opening polymerization, organo-silicon compounds.

The siloxane copolymers are well known due to their capability of preserving the physico-chemical properties over wide temperature ranges as a result of the optimal thermal stability-flexibility relationship [1-6]. The synthesis of these macromolecular structures is performed generally through copolymerization reactions between suitable siloxane and organic partners. Better results could be obtained when it is necessary to obtain a perfectly alternate distribution of the segments within the final copolymer by using a different approach. This method is based on polymerization of a specific class of cyclic oligomers with a hybrid siloxane-organic structure generically named cyclocarbosiloxanes [7-9].

Cyclocarbosiloxanes could be obtained starting from disiladihalogenated compounds through similar reaction procedures as those used for their siloxane homologous and especially through intramolecular hydrolytic condensation (1) [10]:

The carbosiloxane ring opening could be done by anionic or cationic mechanism depending on the cycle reactivity and yields.

Howerer, as for the cyclosiloxane case, for the anionic polymerization of the cyclocarbosiloxanes could be used as catalysts KOH, CsOH, $(CH_3)_4NOH$, potassium siloxanolate, potassium, but their reactivity is significantly different. Therefore, in a formal series obtained by replacing of the siloxane oxygen atoms with methylene groups, the polymerization rate depends especially on the methylene number [11]. Carbosiloxanes with a methylene group in the cycle easyly react at 120 °C in the presence of KOH (1.3%) leading to a liquid polymer, the cycles which enclose two methylene groups react with difficulty and low yields and those with three or more methylenes' do not polymerize. For series with one methylene in the ring, polymers with molecular weights of 2.1×10^5 and yields of



(1)

Linear carbosiloxane oligomer

Cyclocarbosiloxane

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78% were obtained. For structures with two methylene groups, only liquid polymers with yields of 60% could be prepared [12,13].

Therefore, the cyclocarbosiloxane ring opening rate in nucleophilic catalysis is strongly influenced by the presence of the methylene group which due to its proximity to the siloxane bond increases the electropositivity of the silicon atoms [14].

This work presents a study concerning the reactivity of a series of carbosiloxane cycles in anionic ring opening polymerization reactions.

Another paper [23] presented the obtaining of polycarbosiloxanes networks.

Experimental part

Reagents

Carbosiloxane cyles:

1-2,2,5,5-tetramethyl-3,4-diphenyl-1-oxa-2,5-disilacyclopentane (***DMDFE***);

2-2,2,5,5-tetramethyl-3,3-diphenyl-1,4-dioxa-2,5-disilacyclopentane (***DMDFMO***);

3-2,2,7,7-tetramethyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane (***DMTFB***);

4-Bis-[1, 4-bis-(dimethylsiloxanyl)-dihydronaphthalene] (***DMDHNF***).

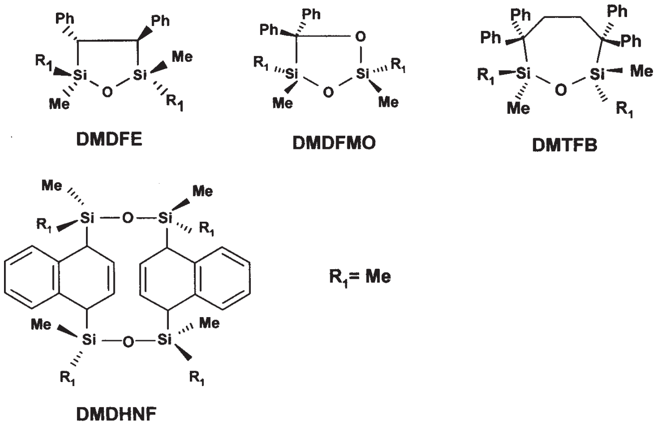


Fig. 1. Carbosiloxane cycles structures

These products were synthesized in laboratory and present the physico-chemical properties displayed in table 1 [15-17].

The spectral analyses by ^{1}H-NMR and ^{13}C-NMR are in agreement with the chemical structures.

^{1}H-NMR (80 MHz) δ (ppm, $CDCl_3$):

DMTFB, Si-CH_3 : 0.15 - 0.2, s, 6H; -CH_2-: 2.62, d, 4H; -C_6H_5 : 7.14-7.55, m, 20Har.

DMDFE, Si-CH_3 : 0.12 - 0.18, s, 6H; -CH -: 1.8-1.6, d, 2H; -C_6H_5: 7.14-7.53, m, 10Har.

DMDFMO, Si-CH_3 : 0.09 - 0.13, s, 6H; -C_6H_5 : 7.22 - 7.40, m, 10Har.

DMDHNF, Si-CH_3: 0.3-0.35, s, 12H; -$C_{10}H_8$: 7.22, m, 16Har; 6.05, d, 4H unsaturated; 2.8 (4H-saturated).

^{13}C-RMN (80 MHz) δ (ppm, $CDCl_3$):

DMDFE, Si-CH_3, 1.02...-1.75; -CH-, 42.5.

DMTFB, Si-CH_3, 1.06...-1.25; -CH_2-, 28.55; -C-, 48.31.

DMDFMO, Si-CH_3, -1.06...-2.41; -C-, 66.19.

DMDHNF, Si-CH_3, 1.52...0.02; -CH-, 43.28.

Potassium siloxanolate catalyst:

Preparation procedure [18]: a mixture of octamethylcyclotetrasiloxane and KOH powder, molecular ratio 1:3 was solved in toluene to obtain a 50% solution. This solution is charged in a reaction flask provided with mechanical stirrer, condenser and argon inlet for the water-toluene azeotrope distillation during the reaction. The system is heated to 120°C and maintained for 24 h, continuously distilling the water-toluene mixture. Finally a clear liquid is obtained (potassium siloxanolate) which is further diluted in toluene 35%.

Measurements

The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a JEOL 80 MHz spectrometer without TMS internal standard and solvent $CDCl_3$. The IR spectra were registered using a Perkin-Elmer spectrophotometer within 400-4000 cm^{-1} on KBr pellets. The molecular weights measurements through gel permeation chromatography method (GPC) were performed in chloroform solutions (~1%) at 30°C and 1cm^3/min on a Spectra Physics 8800 chromatograph equipped with two PL-gel columns and polystyrene standards (10^3 Å, 500 Å). The instrument uses a dual detection system: UV116 spectrometer and R132 differential refractometer.

General procedure

This approach is used to obtain siloxane copolymers by the cyclocarbosiloxane ring opening reaction in the presence of potassium siloxanolate catalyst (2).

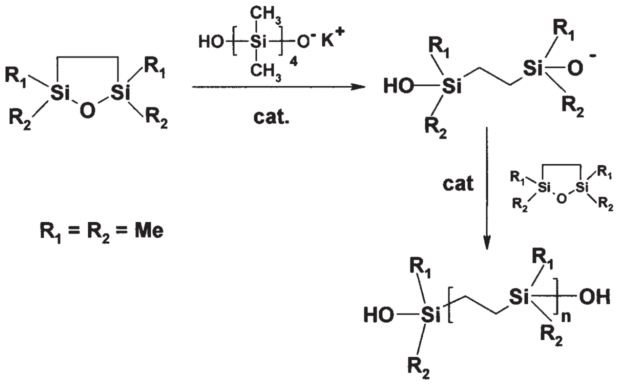
The experimental setup for study of the anionic polymerization of the carbosiloxane cycles allows measurement of the inherent viscosity of the reaction mixture at various intervals of time and temperatures. For this purpose 4 reaction flask of 25 cm^3 each were coupled to a reflux condenser using a multiple glass joint adapter. The installation is dried for 2 h in inert nitrogen atmosphere.

Each reaction flask is charged with 5 mL solution 50-60% carbosiloxane cycle in dried toluene (freshly distilled from sodium wire) and potassium siloxanolate catalyst (0.2 mole %). The temperature program is set using a thermostated bath at 50, 80°C and 100°C. At measured intervals of time one of the micro-reactors is decoupled from the installation, 1-2 drops of acetic acid are added to stop the reaction and then the mixture is cooled down to the room temperature.

Table 1

CYCLOCARBOSILOXANE PHYSICO-CHEMICAL PROPERTIES

	Mol. Weight calc./exp.	**m.p. (°C)**	**Si,(%) calc./ exp.**	**C, (%) calc./ exp.**	**H,(%) calc./ exp.**
DMDFE	418/425.2 $Si_2C_{18}H_{22}O$	124-126.5	13.39/13.25	51.67/51.81	5.26/5.35
DMDFMO	314/308 $Si_2C_{17}H_{22}O_2$	118.5-120	18.42/18.25	64.96/64.52	7.00/6.98
DMTFB	492/484 $Si_2C_{32}H_{36}O$	105.8-108	11.38/11.22	78.04/77.82	7.31/7.48
DMDHNF	520/532 $Si_4C_{28}H_{40}O_2$	143.2-144	21.53/21.38	64.61/64.42	7.69/7.82



(2)

The inherent viscosity at 25°C is measured using an Ubbelohde viscosimeter on solutions 2% in toluene. The reaction mixture is washed with water to neutral *p*H, the organic phase is dried on sodium sulfate and the solvent is vacuum distilled. The resulted rough product is solved in THF to obtain a 70% solution and then precipitated in methanol. About 2 g of solid material should be obtained. This product is weighted, then washed with isopropanol, dried and weighted again. The weight difference represents the amount of unreacted cyclic compound.

To avoid any side reactions for these experiments carbosiloxane cycles without reactive groups (-Si-H or –Si-$CH=CH_2$) were used. Also, no molecular weight regulators were added in the polymerization reactions.

Results and discussion

A study concerning the cyclocarbosiloxane reactivity in anionic polymerization reactions was made at temperatures within 50-100°C.

For this purpose the inherent viscosity of solutions, 2% in toluene, was measured.

A strong and sudden variation of the viscosity was observed during the first 2 h then, important differences concerning the evolution of the process appeared. At temperatures around 80°C, the viscosity of DMDFMO and DMDFE rises rapidly compared with that of DMTFB and DMDHNF. Further increasing of temperature leads to attenuation of these differences with the exception of DMDHNF which presents an extremely slow variation of the viscosity.

By analogy with the anionic polymerization of the cyclosiloxane in similar conditions this behaviour could be the result of the active species aggregation.

The molecular weight measurements were done by GPC analysis in chloroform solution (1.0%). The results are presented in table 2.

From this table one can see that the temperature modification within the indicated limits leads to a weak variation of the linear fraction molecular weight which has the average value close to that obtained by hydrolysis of disiladichlorosilanes.

The activation energy calculation supposes knowing of the rate constants at three different temperatures and reactant (carbosiloxane cycle) concentration variation versus time.

The graphical processing of the experimental results is shown in figure 5-7.

Two principal domains could be observed: a domain where the concentration of the cyclic monomer decreases rapidly (the initiation step and formation of low dimensional linear oligomers) and a domain where the cyclic monomer concentration varies slowly (the propagation-equilibration step). The reaction stage corresponding to this second domain proceeds with the lowest reaction rate and therefore should be considered as the determining step of the polymerization process. The reaction rate constants and activation energies were calculated for this specific stage.

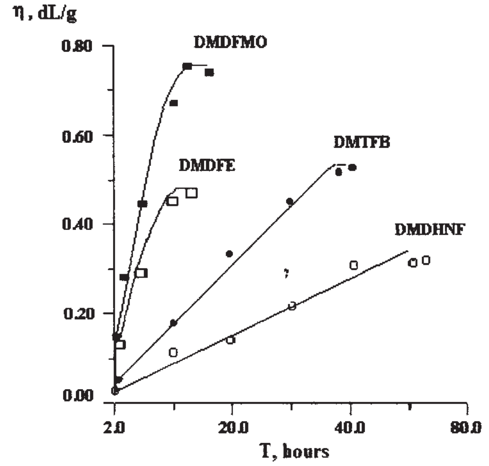


Fig. 2. Variation of the inherent viscosity at 50°C

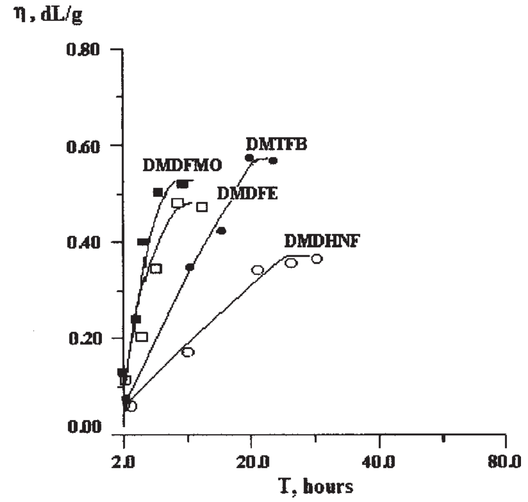


Fig. 3. Variation of the inherent viscosity at 80°C.

Table 2

EXPERIMENTAL RESULTS OF THE CARBOSILOXANE CYCLES ANIONIC POLYMERIZATION

Monomer	50 °C			80 °C			100 °C		
	t_R (h)	η (%)	Mw g.mole^{-1}	t_R (h)	η (%)	Mw g.mole^{-1}	t_R (h)	η (%)	Mw g.mole^{-1}
DMDFMO	12	80	3508	8	75	3302	5	66	3195
DMTFB	36	78	3500	18	62	3225	12	55	3005
DMDFE	14	80	4210	12	67	3506	8	59	3230
DMDHNF	-	75	2708	25	69	2601	21	62	2500

η = polymer yield
t_R = reaction time

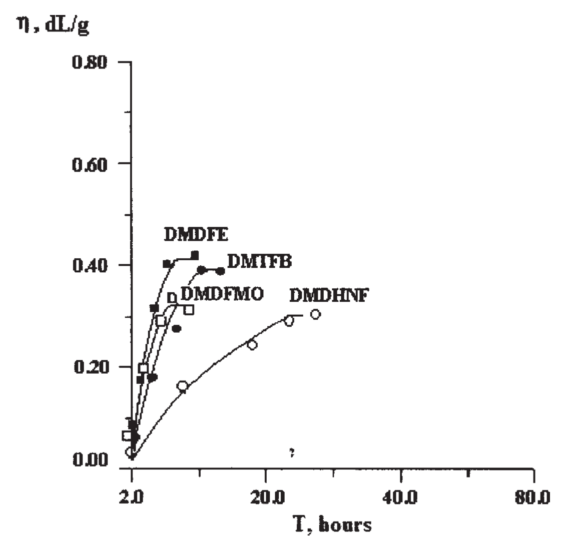


Fig. 4. Variation of the inherent viscosity at 100°C

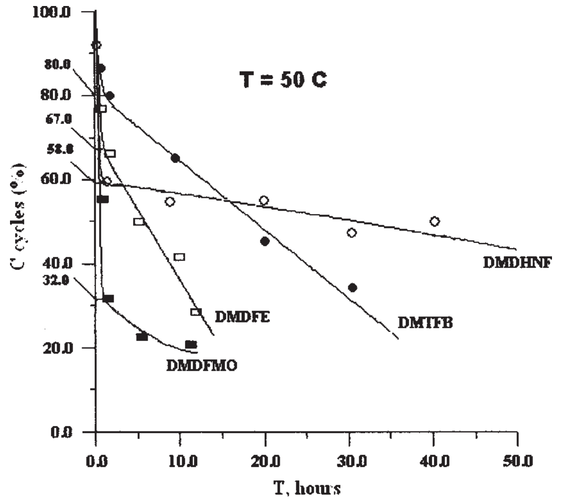


Fig. 5. Carbosiloxane cycles content versus time, C_{cycles}, at 50°C.

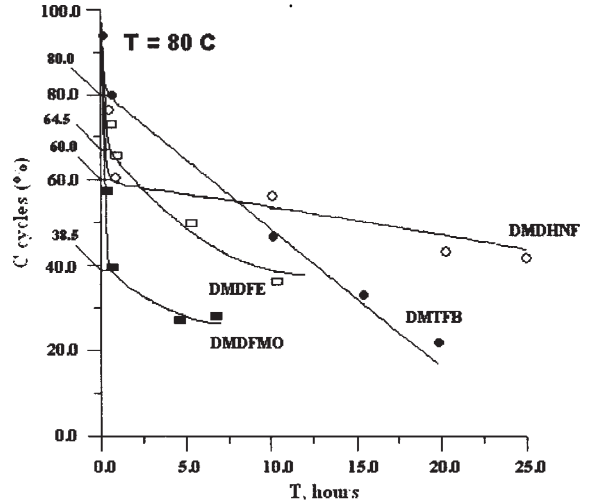


Fig. 6. Carbosiloxane cycles content versus time, C_{cycles}, at 80°C

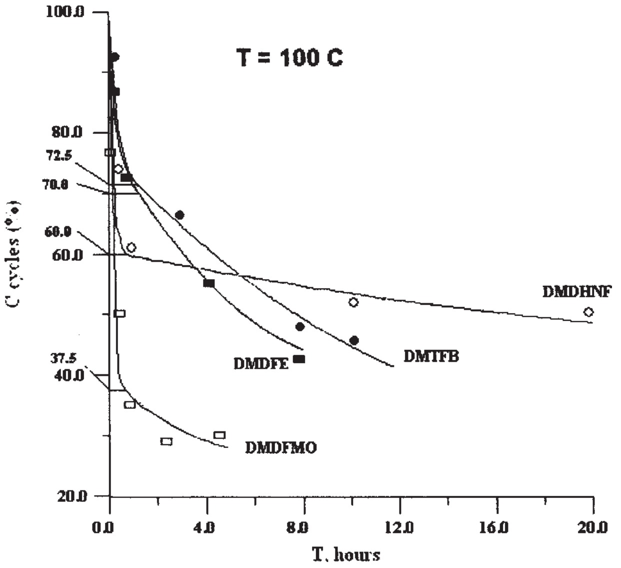


Fig. 7. Carbosiloxane cycles content versus time, C_{cycles}, at 100°C

Due to the fact that the mechanism of the anionic carbosiloxane ring opening is similar with the cyclosiloxane one, the rate constants were calculated by taking into account a first order kinetic equation:

$$k = 1/t \ln (c_1^o / c_1) \qquad (3)$$

where : k – rate constant, (s^{-1})

c_1^o- initial concentration of the carbosiloxane cycles in the cycles-linear oligomers mixture, (%); this value is marked on the c= f(t) plot for each temperature and compound.

c_1- momentary concentration of the carbosiloxane cycles in the mixture, (%); determined experimentally.

t - time,(s)

Table 3 shows the average values of the rate constants for three different temperatures.

These data confirm that compared with the siloxane cycles, the cyclocarbosiloxanes reaction rates are lower but of the same order of magnitude [19].

Knowing the reaction rates constants makes possible the calculation of the activation energies using the classical equation:

$$k = A e^{-Ea/RT} \qquad (4)$$

plotted as $\ln k = f(1/T)$ (fig. 8-11). The resulted values are presented in table 4.

These results lead to some important conclusions. First it could be observed that the reaction activation energy is of the same order magnitude as that corresponding to cyclosiloxanes. On the other hand DMDFMO and DMDFE have a reactivity closed to that of D_3 siloxane cycles (with three siloxane bonds in the molecule). This high reactivity is a consequence of a higher internal tension and less to the nature of the organic segment (normally from this point of view DMDFMO should be ranged before DMDFE due to

Table 3
AVERAGE VALUES OF THE RATE CONSTANTS AT DIFFERENT TEMPERATURES

Monomer	Temperature, °C		
	50	80	100
	k x 10^{-4}, s^{-1}	k x 10^{-4}, s^{-1}	k x 10^{-4}, s^{-1}
DMDFMO	0.77	1.06	1.41
DMDFE	0.36	0.44	0.46
DMTFB	0.14	0.27	0.35
DMDHNF	0.13	0.25	0.28

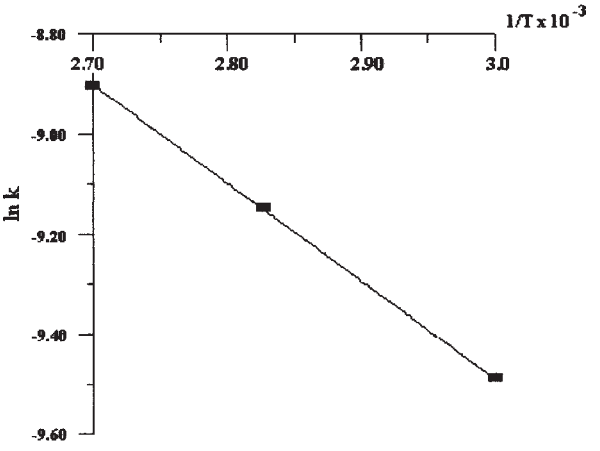


Fig. 8. Plot of ln k versus 1/T for DMDFMO

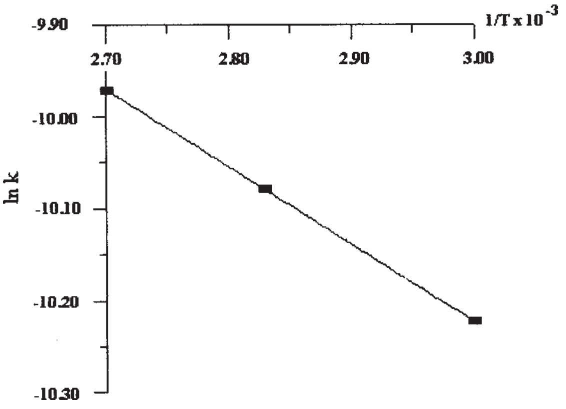


Fig. 9. Plot of ln k versus 1/T for DMDFE

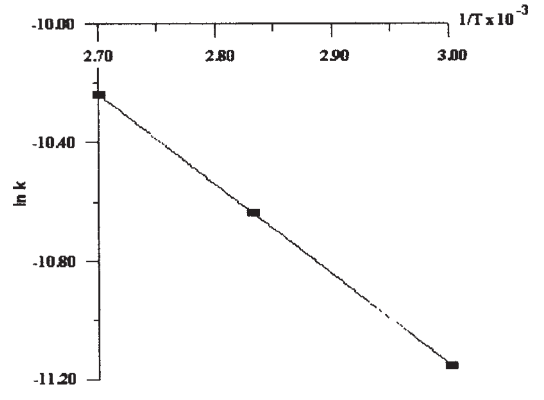


Fig. 10. Plot of ln k versus 1/T for DMTFB

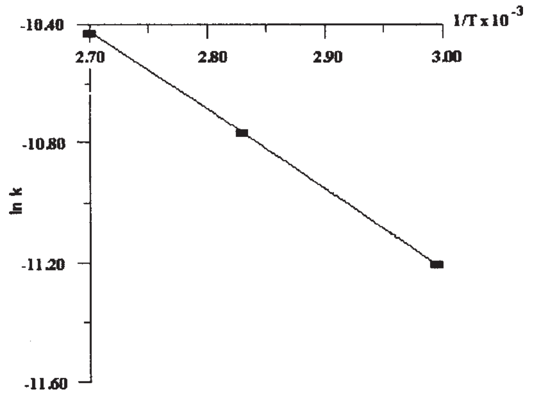


Fig. 11. Plot of ln k versus 1/T for DMDHNF

its two reactive centers that could be attacked by the nucleophile). These differences in reactivity could be also the result of the number of the methylene groups bridging the siloxane silicon atoms. Increasing of this number leads to lower intracycle tensions but the inductive +I effect which is transmitted throughout the entire ring, decreases the polarity of both the carbosiloxane bond and nucleophilic attack center (the DMTFB case). The experimental data and literature [20] show that in these cases the thermal stability in ionic medium increases strongly (comparing with the siloxanes which decompose currently above 200 °C).

Generally, it could be observed that the anionic carbosiloxane ring opening polymerization reactions with potassium siloxanolate catalyst lead to lower molecular weight oligomers.

The mechanism of the process is not different of the classical anionic polymerization of the siloxane cycles and follows the same steps. The differences should be related to the presence of the C-C bond which is more rigid than the siloxanic one. Therefore, in the initiation step dissociation reactions of the siloxanolate catalyst with formation of free ions occur (5). Then, the anionic active species is formed due to the siloxanolate anion attack at the electrophile silicon atom with opening of the carbosiloxane cycle (linearization). Latter, in the polymerization phase, increasing of the chain is achieved through addition of new cyclic molecules and formation of macroanions.

The rate determining stage of this process is the cyclic pentacovalent silicon anion re-arrangement to reactive siloxanolate anion (5).

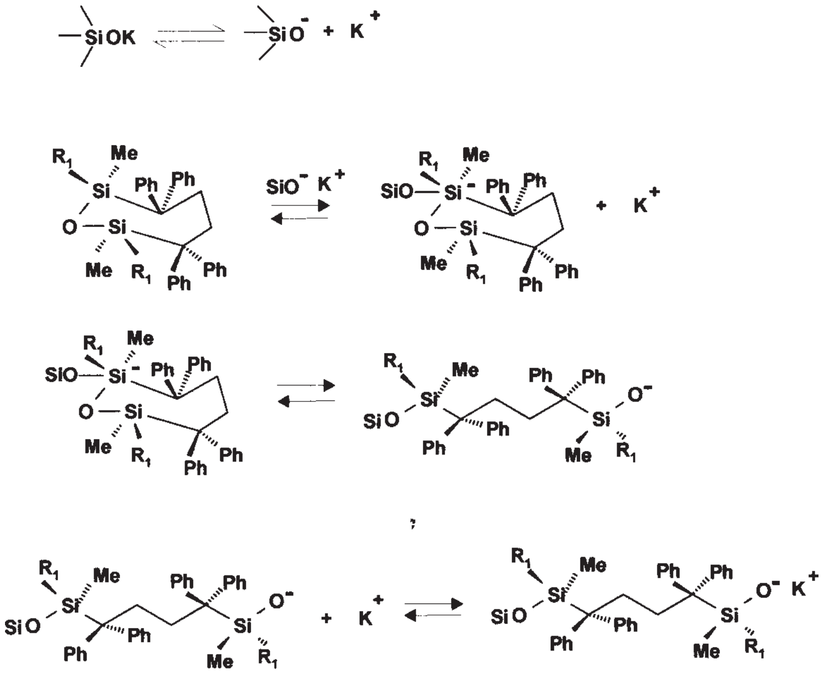
The published work [21] indicates that in the case of siloxanolate or metal hydroxides catalyst, an association of the existent ionic species occurs and this aggregation is responsible for the reaction course.

In the cyclosiloxanes case a period of acceleration of the reaction could be observed due to increasing of the concentration of the terminal reactive centers which could move closer being attached to a high flexible siloxane chain (**A**) (fig. 12).

In the carbosiloxane cycle case this happens in the first phase of the polymerization reaction when the oligomeric chain has lower dimensions. Increasing of these dimensions leads to a higher rigidity of the chain induced by the paraffin segment so that the narrowing of the reactive ends becomes less probable. Therefore, the aggregation occurs especially at intermolecular level (**B**) which leads to decreasing of the process rate.

Table 4
ACTIVATION ENERGY AND PREEXPONENTIAL FACTOR

Monomer	Activation energy, kJ/mol	Preexponential factor, s^{-1}
DMDFMO	16.62	5.5x 10^{-4}
DMDFE	6.93	4.4x 10^{-4}
DMTFB	25.76	0.15
DMDHNF	21.60	3.3x 10^{-2}



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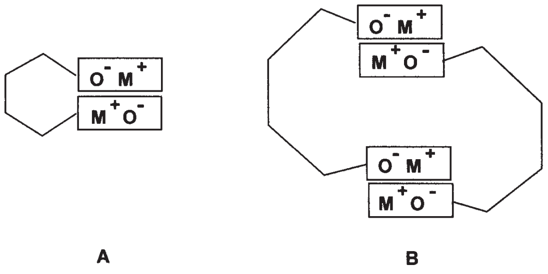
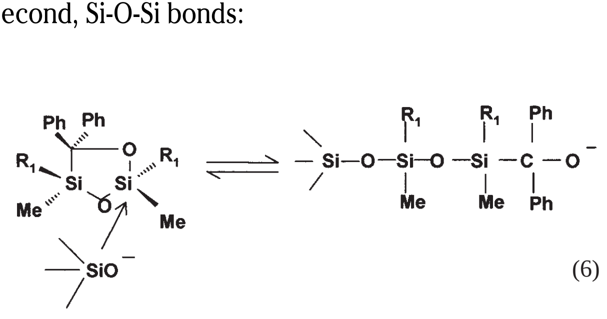


Fig. 12. Ideal aggregates types of the macroanionic species

The aggregates could be of ideal type (between the propagation centers) or hybrid (between the initiator and propagation center) [22]. The cyclocarbosiloxanes anionic polymerization reaction course suggests that the ideal type aggregates are involved mainly in the first stage of the process, when the polymerization proceeds at high rate. The hybrid aggregates which are more stable should be taken into account especially for the second stage. The presence of these specific structures could also explain the low molecular weight of the final product. All these assumptions applied identically for all the synthesized compounds excepting DMDFMO.

The nucleophile agent (the siloxanolate anion) could attack any of the two electropositive silicon atoms. According to this study, the initiation of the polymerization is done through heterolitic scission of first the Si-O-C and second, Si-O-Si bonds:



(6)

It could be assumed that the backbone of the resulted polymer should have a statistical distribution of these two types of bonds.

Conclusions

A study concerning the reactivity of some carbosiloxane cycles of different structural series was performed by anionic ring opening polymerization in the presence of potassium siloxanolate base catalyst. Measurements of the inherent viscosity variation versus time and temperature revealed the characteristics of the process compared with the homologous cyclosiloxane series. Also, the specific influence of the chemical structure of cyclocarbosiloxanes according to their structural class frame was determined. Therefore, it was observed that DMDFMO and DMDFE have reactivity similar with the D_3 cyclosiloxane and the reactivity differences should be related to the inductive effect of the methylene groups bridge which modifies the polarity of the nucleophile center. The mechanism of carbosiloxane anionic ring opening polymerization shows specific features due to the presence of the more rigid C-C bond. This affects both the reaction initiation and polymerization steps.

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