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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Racles, Carmen , Gaina, Viorica , Marcu, Mihai , Cazacu, Maria and Simionescu, Mihaela(1997) 'Synthesis and Characterization of New α,ω -Bis(Maleimide-Ester) Substituted Siloxane Oligomers', Journal of Macromolecular Science, Part A, 34: 9, 1605 – 1617

To link to this Article: DOI: 10.1080/10601329708010030

URL: <http://dx.doi.org/10.1080/10601329708010030>

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SYNTHESIS AND CHARACTERIZATION OF NEW α,ω -BIS(MALEIMIDE-ESTER) SUBSTITUTED SILOXANE OLIGOMERS

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ABSTRACT

Organofunctional siloxane oligomers containing maleimide were synthesized by condensation reaction of α,ω -hydroxypropylsiloxane oligomers with *n*-[4-(chlorocarbonyl)phenyl]maleimide. A model compound [bis(maleimide-ester)disiloxane] was obtained to facilitate the characterization of the oligomers. Then, the heterogeneous catalyzed ring-opening cationic polymerization technique was applied to obtain an oligomer starting from the model compound and octamethylcyclotetrasiloxane.

The structures of the resulting oligomers were confirmed by elemental analysis, IR and $^1\text{H-NMR}$ spectroscopy. They were characterized by determining softening points, solubility and studying their thermal behavior by thermogravimetric (TGA and differential scanning calorimetry (DSC) measurements.

INTRODUCTION

Classic polyimides show many valuable properties such as non-combustibility, thermal and oxidative stability. However, the majority of these resins are insoluble and do not melt, which limits possible practical applications.

In order to increase the solubility, monomers with polar groups in the amine or anhydride molecules (as starting materials) were used [1].

An important path for increasing processability of polyimides is the incorporation of flexible siloxane segments into their backbone.

Poly(siloxane-imide)s impart an important class of copolymers which have a wide application in the fields of microelectronic for their unique character-

Synthesis of well-defined, novel, functionally terminated oligomers and the modification of existing structures is still one of the most active research fields in polymer chemistry. So far, the most widely utilized reactive end groups have been hydroxyl, amine, epoxy and carboxyl functionalities [3].

Bismaleimides bearing polysiloxanes were synthesized and characterized [2, 4]. They showed very good thermal stability due to both the imidic structure and ionic nature of Si-O-C bonds. However, they can be quite susceptible to hydrolytic attack depending on the conditions [3].

Organofunctionally (Si-R-X, R = aliphatic, aromatic) terminated siloxane oligomers bearing maleimides were obtained as well [5-7]. Low melting points, good solubility and heat resistance were reported.

The main objective of this paper is the synthesis and characterization of some new bismaleimide-esters bearing polysiloxanes, using N-[4-(chlorocarbonyl)phenyl]maleimide (p-CPMIC) and α,ω -hydroxypropyl-siloxane oligomers, by condensation reactions. We have also applied the relatively new procedure of obtaining siloxane oligomers by heterogeneous cationic polymerization of cyclo-siloxanes using a bismaleimide-ester disiloxane as "end-blocker" [8].

Due to their structure, the obtained oligomers can provide the starting materials for other new organofunctional oligomers, poly(siloxane-imide) copolymers, inter-penetrating networks and resin matrix for composite materials.

EXPERIMENTAL

Materials

Maleic anhydride (Fluka) was recrystallized from acetic anhydride. Thionyl chloride was purified by distillation. 4-Aminobenzoic acid (Fluka) was used as received. Triethylamine (Fluka bp 88-89°C, d_4^{20} 0.726, n_D^{20} 1.401) was dried over NaOH and freshly distilled before use. 1,4-Dioxane (Fluka, mp 10-11, bp 99.5-101.5°C, d_4^{20} 1.033, n_D^{20} 1.421) was distilled over calcium chloride. Octamethylcyclotetrasiloxane (D₄), (Fluka, 99%, mp 17.5°C, bp 175°C, n_D^{20} 1.3962, d_4^{20} 0.955) was used as received.

1,3-Bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane was supplied by Petrarch Systems Inc (bp 75°C/20 mmHg, n_D^{20} 1.4470, d_4^{20} 0.9331) and was used as received.

VIONIT CS 34-C is an ion exchanger having the following characteristics:

- granulation 0.4-0.63 mm
- porosity 39-42%
- specific surface 35 m²/g
- volumic weight 900 g/L
- exchange capacity: volumic 1.8 meq/mL; gravimetric 4.2 meq/g

In order to remove moisture, the cationite was submitted to an azeotrope distillation of toluene and dried in vacuum (20 mm Hg) at 110°C, over constant weight.

Apparatus

IR spectra were recorded on a Specord M80 spectrophotometer using KBr pellets. ¹H-NMR spectra were registered using a JEOL C-80 HL spectrometer using CDCl₃ as the solvent and TMS as internal standard. Softening points were determined by a Gallenkamp hot-block melting point apparatus. Thermogravimetric curves were obtained in air with an F. Paulik Derivatograph at a heating rate of 9°C/min. Differential scanning calorimetry (DSC) measurements were made in nitrogen using a METTLER TA Instrument DSC 12E at a heating rate of 20°C/min.

Synthesis of Hydroxypropyl Terminated Polydimethylsiloxane Oligomers

The α,ω -bis(3-hydroxypropyl)polydimethylsiloxanes were obtained through cationic ring-opening polymerization of octamethylcyclotetrasiloxane (D₄) in the presence of 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyl-disiloxane as chain transfer agent, using styrene-divinylbenzene ion exchanger with sulfonic acid groups (VIONIT CS 34-C) as catalyst [8]. Oligomers with prescribed molecular weights were prepared by the same general procedure described below (for a prescribed numerical molecular weight of 1000).

In a reaction vessel equipped with thermometer, mechanical stirrer and nitrogen inlet D₄ (4.5g) was introduced and the chain transfer agent (1.5g) was added. Then the cationite (0.15g, 2.5% wt.) was added. The stirring was maintained for 36 hours at 80°C. The reaction mixture was cooled at room temperature and the catalyst was filtered. The unreacted cyclic siloxanes were removed by distillation at 120°C/10 mmHg.

Synthesis of N-(4-carboxyphenyl)maleimide (4-CPM)

The product was obtained using the reported procedure [9]. In a three-neck flask equipped with a mechanical stirrer and thermometer, solution of 4-aminobenzoic acid (41.1g) in acetone (500 mL) was placed and maleic anhydride (29.4g) in acetone (100 mL) was added at 10°C over a period of 30 minutes. The reaction mixture was stirred for an additional 30 minutes at 10°C and yellowish-green precipitate (4-carboxyphenyl maleamic acid) was purified by recrystallization from DMF/ethanol (50/50 wt/wt) solution. Then a mixture of 4-carboxyphenyl maleamic acid (11.8g), acetic anhydride (20.4g) and sodium acetate (2g) was gradually heated to 85°C and reacted for 15 minutes. The final reaction mixture was cooled to ambient temperature and poured into ice water to obtain fine pale-yellow precipitate. This precipitate was recrystallized from ethylacetate/*n*-hexane (50/50 wt/wt) solution, filtered and vacuum dried. The melting point of the final product was 226-230°C.

Synthesis of N-[4-(chlorocarbonyl)phenyl]maleimide (p-CPMC)

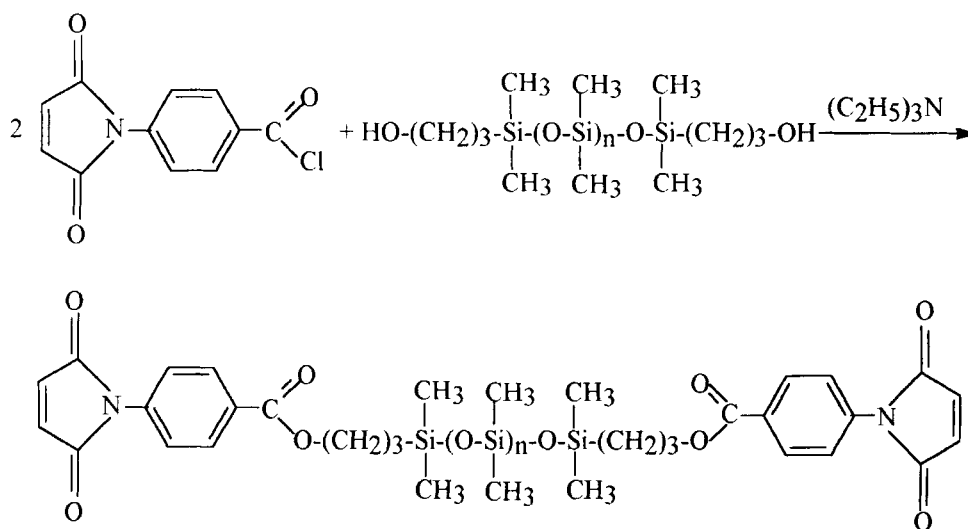
The product was obtained using the reported procedure [10]. A mixture of p-CPM (35.3g, 0.16 mol), thionyl chloride (400g, 4.02 mol) and tert-butylcatechol (0.01g) was refluxed for 2 hours. Unreacted thionyl chloride was evaporated out, and then the residual product was recrystallized from benzene to obtain pure p-CPMC (23.1g, yield 60.1%, mp 168-169°C).

Synthesis of 1,3-bis[4-(N-maleimido)propylenebenzoate]-1,1,3,3-tetra-methyl-disiloxane (I)

In a reaction vessel fitted with thermometer, magnetical stirrer and nitrogen inlet 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (1.86g, 0.007 mol) in 37 mL 1,4-dioxane was placed. Triethylamine (2.07 mL, 0.014 mol) was added and the mixture was stirred for 30 minutes at ambient temperature. Then p-CPMC (3.68g, 0.015 mol) was introduced and after 1 hour, the temperature was raised at 60°C. After 20 hours, the reaction mixture was cooled and the precipitate (mainly triethylamine chlorohydrate) was filtered. Then the solvent was distilled under low pressure. The resulting brown product was washed several times with petroleum ether, and dried in vacuum at 60°C overnight. Yield: 87%.

α,ω -Bis[4-(N-maleimido)propylenebenzoate]polydimethylsiloxane (II) by Equilibration (Redistribution) Reaction

A solution of D₄ (0.66g, 0.002 mol) and model compound I (1.44g, 0.002 mol) in 1,4-dioxane (10 mL) was placed in a flask equipped with magnetic stirrer,



SCHEME 1

thermometer and nitrogen inlet. After 30 minutes the cationite (VIONIT CS 34-C, 0.05g) was added. The reaction occurred for 30 hours at 60°C. After cooling the reaction mixture to ambient temperature, the catalyst was filtered, the cyclic unreacted siloxanes and the solvent were distilled. The obtained product was washed with petroleum ether and dried in vacuum for 10 hours. Yield: 93%.

Synthesis of α,ω -bis[4-(N-maleimido)propylenebenzoate]polydimethyl-siloxanes (III-V)

The synthesis procedure was similar to that described for the model compound I. The hydroxypropyl disiloxane was replaced by a series of α,ω -substituted oligomers having different molecular weights (e.g. 1000, 1300, 3000). The obtained oligomers were solids or waxes depending on the siloxane content. The yields were greater than 90%.

RESULTS AND DISCUSSION

The synthesis of the model compound is presented in Scheme 1. As can be

TABLE I. The Properties of the Oligomers (I-V)

Code	\bar{M}_n		Aspect /color	Softening points (°C)	Elemental analysis data			
	Prescribed	Found ^a			Si %		N %	
					calc.	found	calc.	found
I	648.5	620	solid/ brown	145-160	8.64	8.02	4.32	4.71
II	944.5	—	solid/ brown	170-180	17.78	16.85	2.92	3.25
III	1400	1300	solid/ yellow	160-165	22.32	21.84	2.00	1.88
IV	1900	1700	solid/ ochre	—	26.40	24.61	1.47	1.43
V	3400	3300	wax/ ochre	—	31.45	29.18	0.82	0.73

^a \bar{M}_n were estimated from ¹H-NMR spectra.

seen from Table 1, the elemental analysis data showed good agreement between calculated and found values. The IR spectrum (Figure 1) showed the displacement of the carbonyl bond absorbance from 1785 cm⁻¹ (-COCl) to about 1740 cm⁻¹ (-COO-) and the presence of such characteristic absorption bands as (1720 cm⁻¹, 1385 cm⁻¹, 1150 cm⁻¹, and 700 cm⁻¹, imide I-IV) as well as 1050 cm⁻¹ (Si-O-Si), 800 cm⁻¹, 1260 cm⁻¹ (Si-CH₃).

The ¹H-NMR spectrum of the product I (Figure 2) showed the characteristic signals in the region 8.05-6.775 ppm, assigned to maleimide-ester group, besides expected siloxane protons.

The hydroxypropyl- and maleimide-ester- siloxane oligomers were prepared by ring-opening polymerization of D₄ using the heterogeneous catalysis, hydroxypropyl- and 4-(N-maleimido)-propylenebenzoate disiloxane, respectively as chain-transfer agents (Scheme 2).

The preparation of maleimide-ester terminated polysiloxanes was similar to the model compound synthesis, using α,ω -hydroxypropyl polydi-methylsiloxanes of different molecular weights instead of the disiloxane (Scheme 1). The numerical molecular weights of the maleimide-ester terminated oligomers were estimated from the ratio of the integrated signals for the (CH₃)₂Si= protons (δ 0.15 ppm) versus aromatic and imide protons, and they were well correlated with the

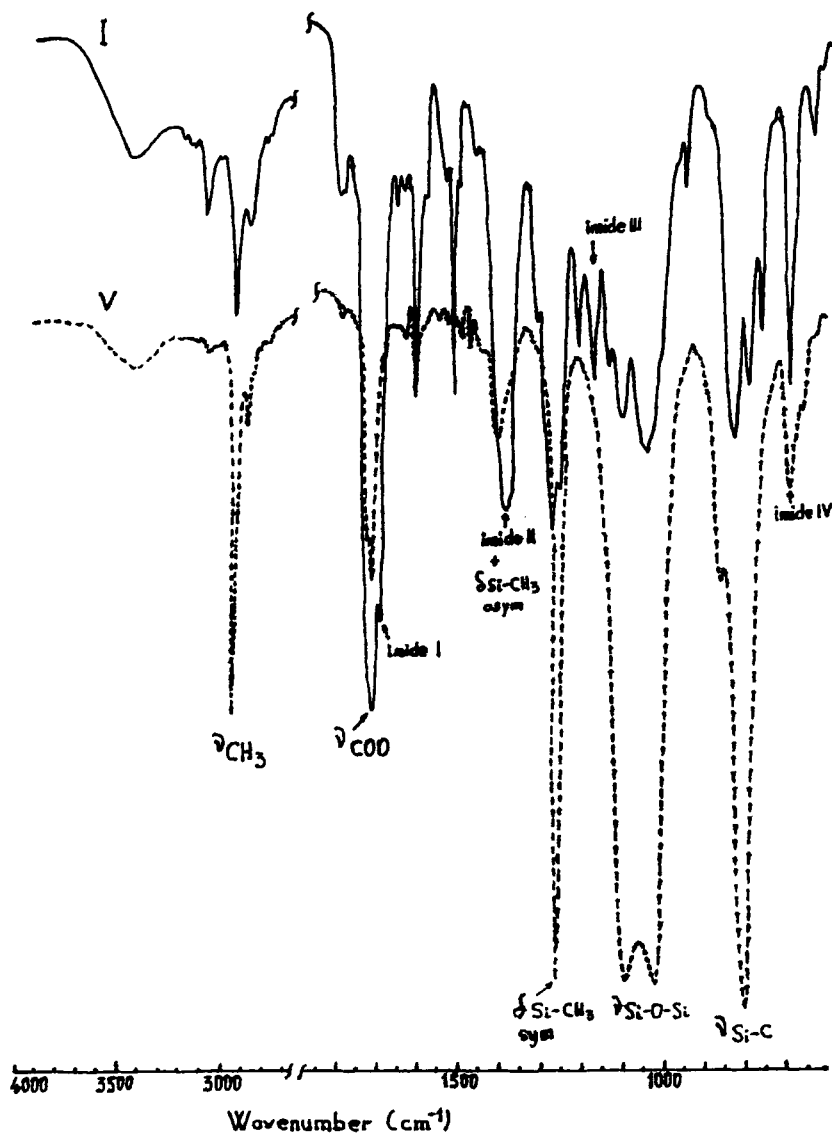


Figure 1. The IR spectra of the model compound (I) and the oligomer V.

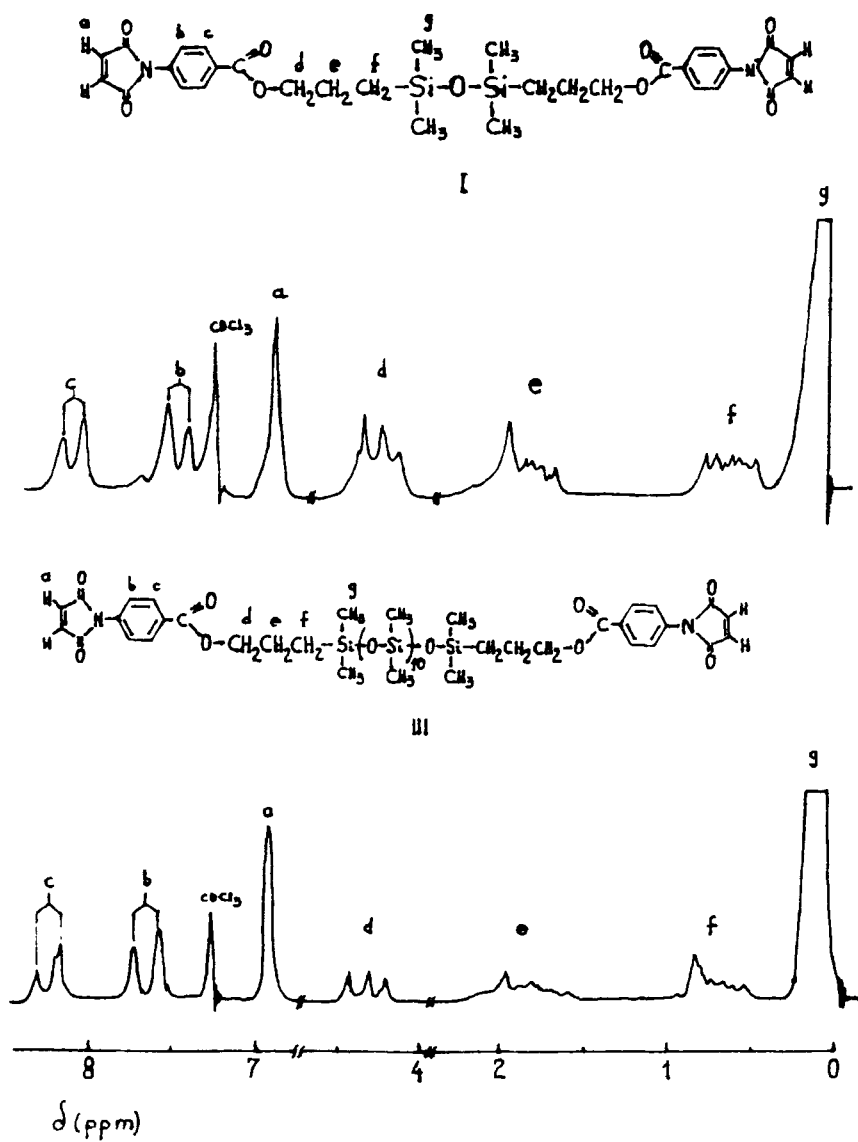
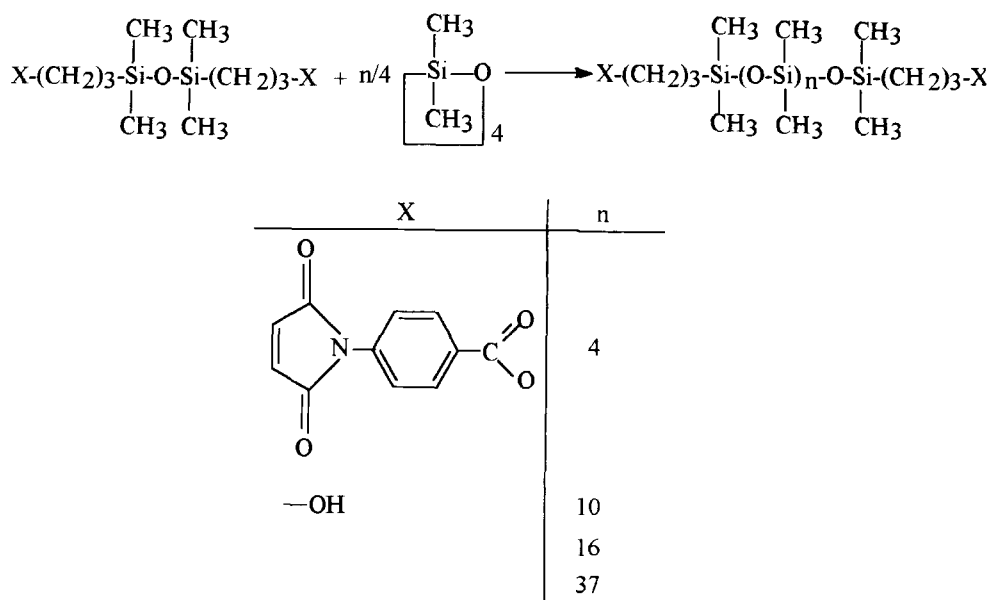


Figure 2. The $^1\text{H-NMR}$ spectra of the compound (I) and the oligomer V.



X	n
	4
-OH	10
	16
	37

SCHEME 2

TABLE 2. The Solubility of the Oligomers (I-V)

Solvent Code	Toluene 2.1 ^a	PhCl 4.9	Ethyl-ether 7.61	CCl ₄ 8.64	Benzene 9.02	CHCl ₃ 9.21	NMP 11.17
I	— b	—	—	—	—	+	+
II	—	—	—	+—	+—	+	+
III	+—	+—	+—	+—	+—	+	+—
IV	+—	+—	+	+	+	+—	+—
V	+	+	+	+	+	+	—

^aSolvent solubility parameter, δ (cal/cm³)^{1/2} [11]

prescribed values. Elemental analysis (Table 1), ¹H-NMR and IR spectra are in accordance with the proposed structures. Therefore, the IR spectra (Figure 1) showed the disappearance of the characteristic absorption band of the -COCl group at 1785 cm⁻¹, and the appearance of the -COO- absorption band at about 1740 cm⁻¹. All other bands mentioned above are also present.

TABLE 3. The Thermal Behavior of the Oligomers (I-V)

Code	TGA temperatures(°C) for various % decompositions					Curing exotherm			
	10	20	30	40	50	T _i (°C)	T _p (°C)	T _f (°C)	Δ (T _f -T _i)
I	340	380	405	463	530	130	275	320	130
II	265	310	370	410	490	252	335	—	—
III	290	345	370	400	455	170	238	320	150
IV	280	340	400	425	600	150	218	308	158
V	330	388	415	440	—	135	210	301	176

A typical example of the ¹H-NMR spectra of the oligomers is shown in Figure 2, with the corresponding assignment of peaks.

All the obtained maleimide-ester siloxanes were characterized by softening points, solubility determinations, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) measurements.

As can be seen in Table 2, the increasing of siloxane units amount enhances the oligomers solubility in nonpolar solvents. On the other hand, with the inclusion of maleimide-ester groups in polysiloxanes structure, the solubility in dipolar aprotic solvents was improved.

Crosslinking behaviors of the maleimide-ester siloxanes I-V, were studied by differential scanning calorimetry (DSC) in nitrogen, at a heating rate of 20°C/min, using the first heating cycle. Some of the DSC results are listed in Table 3 and Figure 3. As can be seen, the model compound I and the oligomers II, III exhibited melting endothermic peaks at 165°C, 208°C and 150°C, respectively. All the obtained products exhibited exothermic curing peaks (T_p) in the range of 210-338°C. The higher the siloxane content into the macromolecular chains, the greater the difference between the onset temperatures (T_i), and the final temperatures (T_f) for the exothermic peaks. This fact could be due to a longer time of the crosslinking reactions required by the oligomers with higher siloxane content, i.e. lower molecular mobility.

The thermal stability of the oligomers was evaluated by TGA in air at a heating rate of 9°C/min (Figure 4). Table 3 gives the temperatures for various percentage weight losses. All the oligomers showed similar decomposition patterns. The temperature for 10% weight loss (T₁₀) is considered to be the compound decomposition temperature and is used for comparing the thermal stabilities of

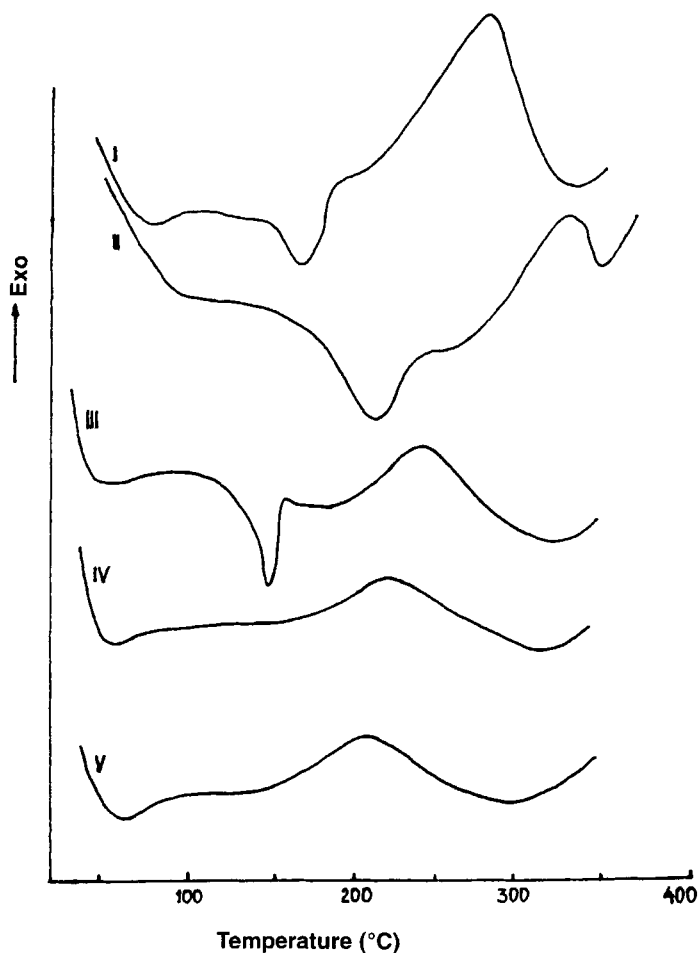


Figure 3. The DSC curves of the compounds I-V.

different oligomers. T_{10} values range between 240 and 335°C. The products can be arranged in the following order: II<IV<III<<V<I.

As can be seen, T_{10} values seem to increase with the increasing molecular weight of the oligomers, with the exception of the model compound I. It is known that a trend exists towards a higher thermal stability with increasing molecular weight, however the reasons for this are not clear [12].

A possible explanation for the higher T_{10} value of the model compound I could be the greater density of maleimide end groups which leads to a prolonged level of thermal stability by polymerization reactions.

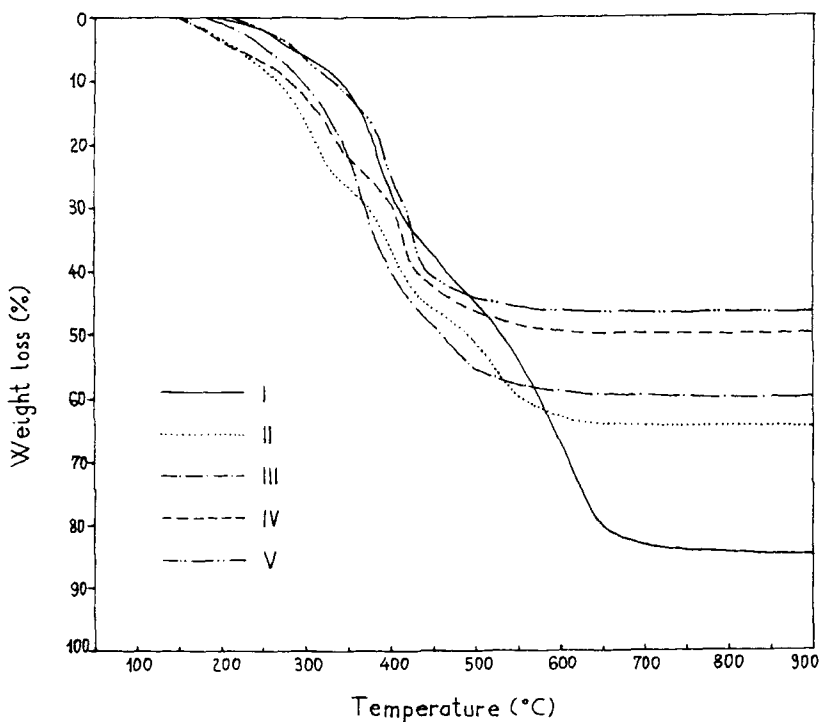


Figure 4. The TGA curves of the compounds I-V.

CONCLUSIONS

Bis-(maleimide-ester) organosiloxane oligomers were synthesized by two procedures: classical condensation reaction and heterogeneous catalyzed ring-opening cationic polymerization of cyclosiloxanes.

The obtained products were characterized by usual techniques. Cross-linking behavior was studied by DSC.

Modification of solubility with the increase of siloxane units content was noticed.

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Received December 20, 1996

Revision received March 30, 1997