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Functional polysiloxanes

2. On the reaction of hydroxypropyl- and aminoalkyl-terminated polydimethylsiloxanes with cyclic anhydrides*

Mariana Pinteala[1], Valeria Harabagiu[1], Cornelia Cotzur[1], Marian N. Holerca[1], and Bogdan C. Simionescu[2,]**

[1]"P. Poni" Institute of Macromolecular Chemistry, [2]Department of Macromolecules, Polytechnic Institute of Jassy, RO-6600 Jassy, Romania

SUMMARY

Carboxyester- and carboxyamido-terminated polydimethylsiloxanes were obtained through the reaction of cyclic anhydrides (succinic, maleic and phthalic anhydride) with hydroxypropyl- and aminoalkyl-terminated polydimethylsiloxanes, respectively. The reactivity of the starting compounds and the influence of the reaction conditions on the characteristics of the final products are discussed.

INTRODUCTION

Organofunctional oligosiloxanes have received much attention due to their specific use as compatibilizing or modifying agents in polymer blends, surfactants, etc. At the same time, they are starting materials in the synthesis of block and graft copolymers.

The main synthetic routes leading to functional oligosiloxanes are the cationic or anionic equilibration of cyclic siloxanes in the presence of a functional disiloxane acting as an end-blocking agent [1] or the hydrosilation of unsaturated functional compounds with polysiloxanes containing Si-H active groups [1-4].

Carboxy-terminated polysiloxanes were recently obtained by hydrosilation reaction [5]. Other approaches consisted in the coupling of hydroxyhexyl- [6] or aminobutyl-terminated polysiloxanes [7] with succinic and maleic anhydrides, respectively. However, the last two proposed methods were not investigated in detail.

The present paper is concerned with the reaction of hydroxypropyl- and aminoalkyl-terminated polydimethylsiloxanes of different molecular weights with cyclic anhydrides, i.e., succinic (SA), maleic (MA) and phthalic anhydride (PhA).

EXPERIMENTAL

Hydroxypropyl-terminated polydimethylsiloxanes (HOPS) were synthesized by hydrosilation of allyl alcohol with hydride-terminated prepolymers, according to a procedure previously described [2].

Aminoalkyl-terminated polydimethylsiloxane (Tegomer^{R} A-Si 2320, Goldschmidt AG) (H_2NPS) was used as received.

Carboxyester-terminated polysiloxanes (CEPS) were obtained by reacting HOPS prepolymers with cyclic anhydrides, in toluene/dioxane solvent mixture containing 2 % water, in the presence of pyridine, at 100°C (Table 1). The volume ratio of the two solvents was toluene/dioxane 1:1 for $HOPS_1$, $HOPS_2$ and 5:1 for $HOPS_3$. The concentration of HO functional groups was 0.16

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**Corresponding author

mole/100 g solvent mixture in the case of HOPS$_1$, HOPS$_2$ and 0.05 mole/100 g for HOPS$_3$. A typical procedure is described as follows:

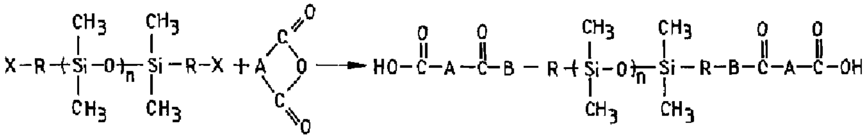
Into a 50 mL two-necked and round-bottomed flask fitted with a motor-driven stirrer and a reflux condensator, 0.72 g SA were introduced in 2.25 mL toluene and 2.25 mL dioxane. The solution was heated at 100° C under stirring and 0.04 mL pyridine, 0.08 mL water and 5 g HOPS$_2$ were added. The reaction mixture was kept at 100° C, under stirring, during 18 hours, then it was cooled at room temperature. The excess anhydride was precipitated with ethyl ether. After filtration and concentration of the filtrate, the remainder anhydride was precipitated with petroleum ether. The obtained solution was washed with diluted HCl and then repeatedly with water to remove pyridine, dried over Na_2SO_4, and the solvent distilled off under reduced pressure. Yield: 5.0 g CEPS (93.3 %).

Carboxyamido-terminated polysiloxanes (CAPS) were synthesized by the reaction of aminoalkyl-terminated prepolymer with cyclic anhydrides in $CHCl_3$ (total concentration, 25 %; anhydride/NH_2, 1:1 molar), at room temperature for SA, MA, and at 50° C for PhA. The reaction occured by contacting the reagents under stirring for 18 hours. The yields were higher than 98 %.

^{1}H-NMR spectra were recorded on a JEOL-C60 HL spectrometer. GPC data were obtained on a Waters Associated 440 instrument, in THF as eluent. Standard polystyrene was used for molecular weight calibration.

RESULTS AND DISCUSSION

Carboxyester- (CEPS) and carboxyamido-terminated polydimethylsiloxanes (CAPS) were obtained through the reaction of cyclic anhydrides (succinic, maleic and phthalic anhydride) with hydroxypropyl- and aminoalkyl-siloxane precursors, respectively (Table I), according to the following scheme:



HOPS : R=$(CH_2)_3$; X=OH　　A= $-(CH_2)_2-$,　　CEPS : B= –O–

H_2NPS : R=$(CH_2)_m$; X=NH_2　　–CH=CH–,　　CAPS : B= –NH–

o–C_6H_4–

The structures of the obtained carboxyfunctional polymers were proved by ^{1}H-NMR spectroscopy (Figs. 1, 2). Figure 1 presents the characteristic absorptions of the low molecular weight (M = 294) HOPS model compound and of its reaction products with the mentioned anhydrides. As one can see, the reaction is accompanied by secondary reactions, as revealed by the presence of the signals at 3.5 ppm, attributed to $-CH_2-O-CH_2-$ linkages resulted by condensation of hydroxypropyl end groups. The secondary reactions also explain the increase of the molecular weights of the final pro-

Table I. Synthesis and Characterization of Carboxyester- (CEPS) and Carboxyamido-terminated Polydimethylsiloxanes (CAPS)

Initial mixture								Carboxy-terminated polysiloxane				
Siloxane prepolymer					Anhydride			Sample	$\bar{M}_n$		$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Sample	$\bar{M}_n$		$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	SA/X	MA/X	PhA/X		(chem.an.)	(GPC)	(GPC)	(GPC)
	(chem.an.)	(GPC)	(CPC)	(GPC)	(molar)							
$HCPS_1$	1860	4230	6140	1.45	4	–	–	$CEPS_{1S}$	13200	16300	36400	2.23
"	"	"	"	"	–	4	–	$CEPS_{1M}$	6170	9530	26900	2.82
"	"	"	"	"	–	–	4	$CEPS_{1Ph}$	6650	4970	17000	3.43
$HCPS_2$	2800	6740	6920	1.03	2	–	–	$CEPS_{2S}$	19700	14400	25800	1.80
"	"	"	"	"	–	2	–	$CEPS_{2M}$	11200	17000	40000	2.36
"	"	"	"	"	–	–	2	$CEPS_{3Ph}$	7020	8850	26500	3.00
$HCPS_3$	–	18100	35900	1.98	2	–	–	$CEPS_{3S}$	33900	20300	37200	1.83
"	–	"	"	"	–	2	–	$CEPS_{3M}$	25800	30700	50100	1.66
"	–	"	"	"	–	–	2	$CEPS_{3Ph}$	13200	15900	46300	2.91
H_2NPS	2320	1440	3470	2.42	1	–	–	$CAPS_S$	2380	1280	3720	2.90
"	"	"	"	"	–	1	–	$CAPS_M$	2400	1140	3090	2.71
"	"	"	"	"	–	–	1	$CAPS_{Ph}$	3870	1310	4690	3.59

ducts as compared to the starting compound. The polymerization degrees of the siloxane units in the carboxyester-terminated siloxanes depicted in Figure 1 were determined from the ratios of the integrals corresponding to the $-CH_2-OCO-$ and $-Si-CH_3$ signals.

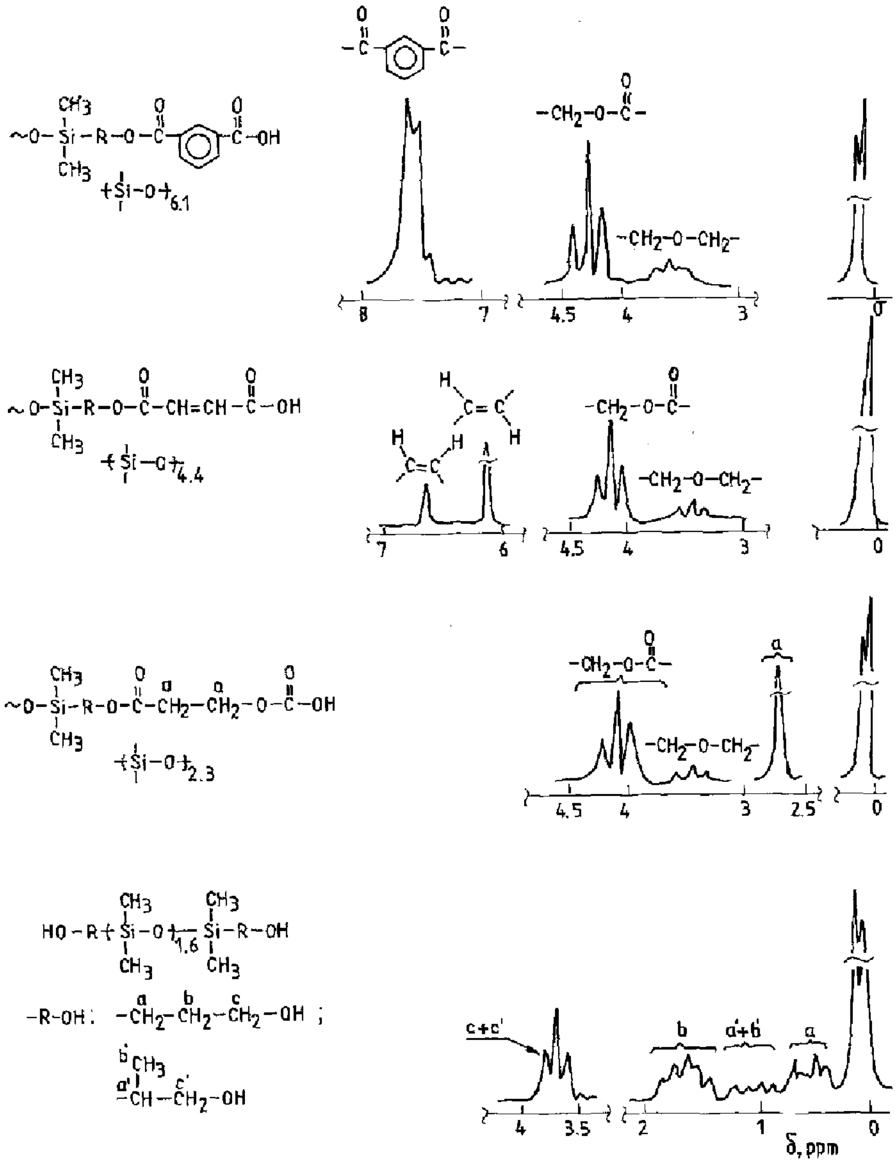


Figure 1. Characteristic ^{1}H-NMR absorptions of HOPS (M = 294) model compound and of its reaction products with cyclic anhydrides (CDCl$_3$, room temperature).

The ^{1}H-NMR spectra of the CAPS products and of their Tegomer^R precursor are presented in Figure 2.

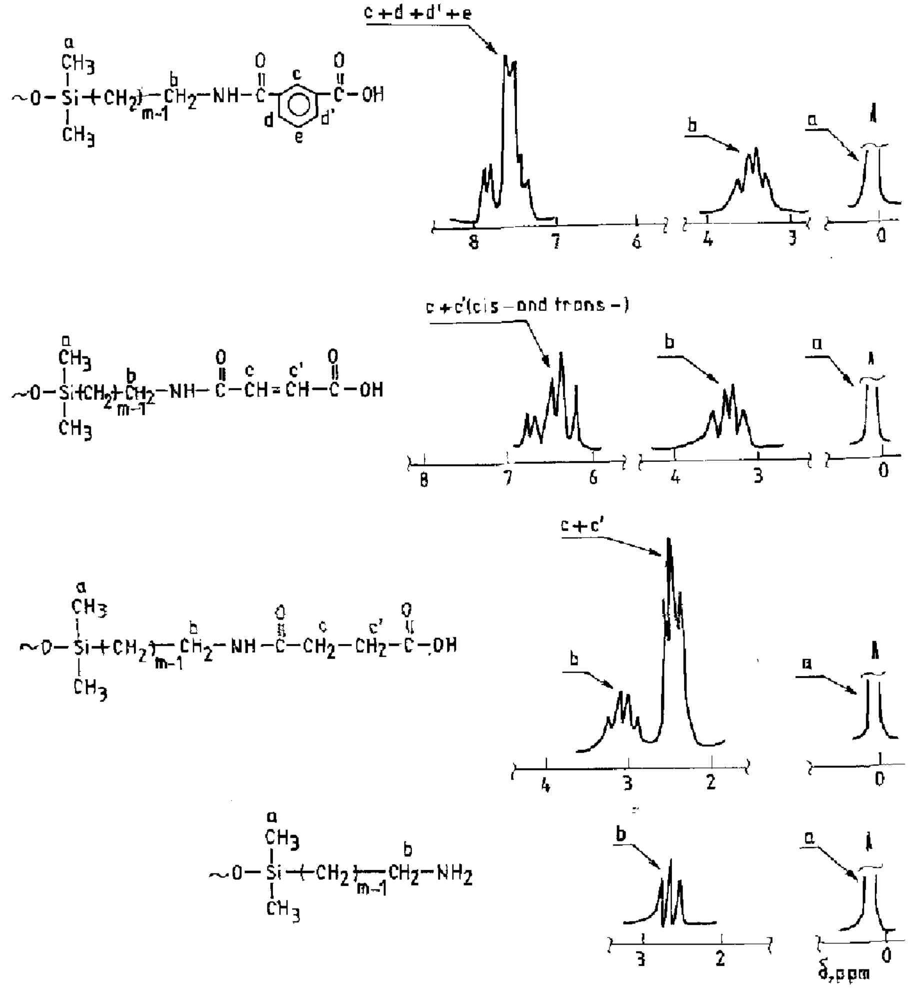


Figure 2. Characteristic ^{1}H-NMR absorptions of carboxyamido-terminated polysiloxanes and of their Tegomer^R precursor (C_6D_6 + DMSO-d_6, room temperature).

The reaction conditions depend on the nature of the starting compounds. The hydroxypropyl-terminated polysiloxanes undergo chemical transformation only at higher temperature (100° C), in the presence of a basic catalyst (pyridine), due to the lower reactivity of the aliphatic hydroxyl groups. The total consumption of -OH groups requires an excess of cyclic anhydride.

The increase of the molar masses (Table I and Figure 3) of the final products as compared to the starting compounds could be explained by the condensation of the hydroxyl groups as revealed by the ^{1}H-NMR spectra of the low molecular weight model compounds (Fig. 1; δ = 3.5 ppm). However, this secondary reaction occurs to a higher extent for the lower molecular weight samples (HOPS$_1$, HOPS$_2$). At the same time, a re-equilibration reaction of the siloxane chain must be considered as the polydispersities of the final compounds present noticeable higher values.

As expected, the reaction of cyclic anhydrides with the more reactive aminoalkyl compound requires mild conditions. According to the data in Table I (H$_2$NPS samples), aminoalkyl-terminated polysiloxane undergoes less evident secondary reactions as compared to hydroxypropyl-terminated homologues. The re-equilibration of the siloxane chain could be considered only for the PhA reaction product (CAPS$_{Ph}$).

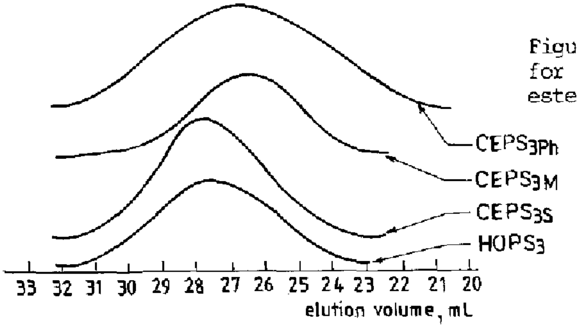


Figure 3. Typical GPC curves for hydroxypropyl- and carboxyester-terminated polysiloxanes.

CONCLUSIONS

Carboxyester- and carboxyamido-terminated polydimethylsiloxanes were synthesized through the reaction of cyclic anhydrides (succinic, maleic and phthalic anhydride) with hydroxypropyl- and aminoalkyl-terminated polydimethylsiloxanes, respectively. The amino-terminated precursor reacts in mild conditions and the final products preserve the molecular weight characteristics of the starting product in a higher extent.

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