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Synthesis and characterization of copolymers obtained from 1,3,5-trioxane and octamethylcyclotetrasiloxane by triflic acid initiator

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SUMMARY

A series of poly(oxymethylene-*co*-dimethylsiloxane) copolymers were synthesized in the molten state by cationic ring opening copolymerization of trioxane and octamethylcyclotetrasiloxane by using trifluoromethanesulfonic acid (triflic acid; CF_3SO_3H) as initiator. When the concentration of the oxymethylene comonomer units ($-OCH_2-$) in the copolymers are very high, crystalline copolymers are obtained. If the concentration of the dimethylsiloxane co-units ($-OSi(CH_3)_2-$) increases, rubberlike materials are obtained. Reaction mechanisms are proposed to explain the growth of the copolymer chains. FTIR and NMR studies suggest the existence of block copolymers and block copolymers with random segments. Thermomechanical characterization of the copolymers was also carried out. This new synthetic method allows us to obtain linear copolymers containing both oxymethylene and dimethylsiloxane comonomer units in the main chain. The copolymerization of these cyclic monomers was demonstrated.

INTRODUCTION

The aim of this work was to synthesize linear copolymers containing oxymethylene (OM) and dimethylsiloxane (DMS) comonomer units in the main chain with thermoplastic and/or elastomeric characteristics. Trioxane (TOX) polymerizes by cationic initiators (1-3), and octamethylcyclotetrasiloxane (D_4) by protonic acids (4-6). Therefore, the cationic copolymerization of these cyclic monomers as a new synthetic route to poly(oxyalkylene)-poly(siloxane) copolymers was examined. These are usually synthesized by polycondensation using prepolymers containing final functionalized groups (7), or by polymerization via hydrosilation, or by living anionic polymerization (8). TOX was chosen because the corresponding linear polymer, poly(oxymethylene) (POM) is crystalline and therefore builds up the hard segment in the copolymers. Also this polymer presents thermoplastic characteristics (9). The polymerization of D_4 gives poly(dimethylsiloxane) (PDMS) which provides the

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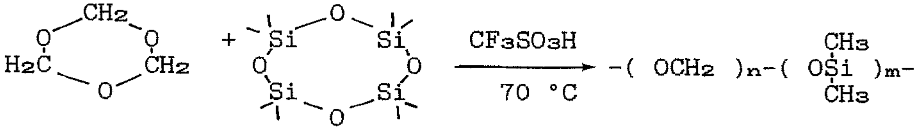
soft segments. FTIR and NMR spectroscopy suggest the existence of block copolymers and also block copolymers formed by segments of OM comonomers units which are chemically linked to segments of random copolymer chains and those bonded to segments formed by DMS comonomer units.

EXPERIMENTAL

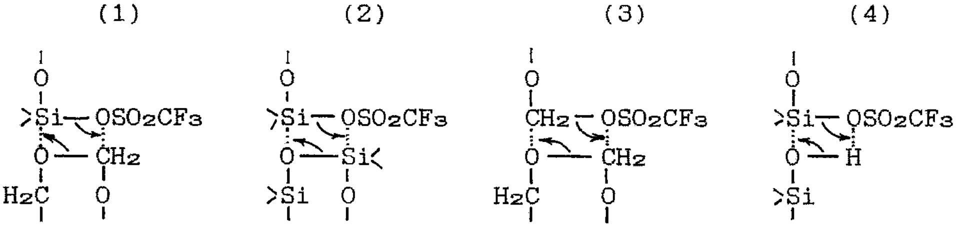
Trioxane and dichloromethane were purified as described previously (2). Octamethylcyclotetrasiloxane was dried by refluxing over molecular sieves for 24 h and then distilled under dry nitrogen before polymerization. Triflic acid was added in CH_2Cl_2 solution by means of a syringe through a rubber stopper. The reactions were carried out in the molten state at 70 °C (TOX : m.p. 64 °C, b.p.: 114.5 °C. D_4: m.p.: 17-18 °C, b.p. 175-176 °C). The initiator concentration in each copolymerization was $2.5x10^{-3}$ mol/l. The experimental work was carried out as described previously (2,3). The flasks were placed in a thermostat at 70 °C. Yields were determined gravimetrically, on the basis of the initial amount of both cyclic monomers. The composition was determined by elemental analysis expressed as the molar fraction of D_4 in the copolymers, X_{D4}. The spectroscopy studies were carried out by FTIR (Nicolet-5PC) in KBr pellets. ^1H and ^{13}C-NMR (Bruker AC-250-P) were measured on the soluble fraction of the samples in $CDCl_3$ with TMS as internal standard. Isothermal thermomechanical analysis (Mettler) was performed at 35 °C as function of time (during 20 min), by using a compression probe (hemispherical type probe), under nitrogen atmosphere and a load of 0.02 and 0.2 Newton.

RESULTS AND DISCUSSION

The poly(oxymethylene-*co*-dimethylsiloxane) copolymers were synthesized according to the reaction



The copolymer chains grow as a result of the combination of two mechanisms, i.e., the direct addition of TOX (10) or D_4 to the cationically active chain ends and a simultaneous polycondensation, which explains the formation of DMS chain segments (5,6,11). Silyl ester and silanol end groups are formed by cleavage of the siloxane bond -OSiOSi- (11), which through homo and heterocondensation reactions (12-14) lead to the formation of a new siloxane bond. Also, the reaction of CF_3SO_3H with D_4 would produce simultaneously a cationic center and a silanol end group (5). We propose other reactions that could also explain the growth of the copolymer chains. Scheme 1 shows the reaction of a final silylester chain with a OM folded chain segment, leading to the formation of siloxane-oxymethylene bond. Also, the scheme 2 shows the reaction of a silylester species with a DMS folded chain segment, and scheme 3 shows the reaction of a final oxymethylene ester chain with a OM folded chain segment; both cases explain the growth of DMS and OM chain segments, with formation of new active centers. The reaction of a silylester chain end with a silanol end group is shown in scheme 4. Here, free triflic acid is regenerated and a single polymer chain is created simultaneously.



Scheme 1-4. Growth sequence for the copolymer chains.

Table 1 shows the characteristics of the materials obtained upon variation of the initial stoichiometry. Depending on the concentration of oxymethylene and dimethylsiloxane comonomer units in the copolymers, three textures were obtained: white crystalline copolymers, white rubberlike copolymers and transparent rubbery copolymers. As described in Table 1, for values of X^{o}_{D4} up to 0.1, white crystalline powders are obtained, while values of $0.20 \leq X^{o}_{D4} \leq 0.50$ afford white rubberlike textures. Two different textures were found for values of $0.60 \leq X^{o}_{D4} \leq 0.87$ in each copolymerization reaction, except for the sample 9. These textures, white/rubber and transparent/rubber were mechanically separated. The copolymers displaying white/rubber texture show X_{D4} values ranging from 0.04 to 0.09. On the other hand, the copolymers assignated as transparent/rubber, have X_{D4} values ranging from 0.11 to 0.15, except for the sample 8. The appearance of two textures in the same copolymerization reactions (samples 7 to 10) would be consistent with a higher polymerization rate of trioxane, resulting first in white rubberlike materials, and then a transparent texture with lower concentration of OM comonomer units. Formation of only one phase would be prevented by incompatibility of both textures.

FTIR studies were carried out for poly(oxymethylene), for the copolymers and for poly(dimethylsiloxane) (Figure 1 a-c). The band at 1000-1130 cm^{-1} (Figure 1,b) corresponds to the vibration of the bonds Si-O-Si (15). As the siloxane chains become longer, the Si-O-Si absorption becomes broader and more complex, showing two or more overlapping bands. Also, long chains of dimethylsiloxane units show two very strong, diffe-

Table 1. Copolymerization of 1,3,5-trioxane (TOX) with octamethylcyclotetrasiloxane (D_4) in the molten state at 70 °C by using CF_3SO_3H as cationic initiator.

Sample	X^{o}_{D4}	X_{D4}	CONVERSION (%) White crystalline	 White rubber	 Transparent rubber
1	0.00	0.00	54.2		
2	0.10	0.04	55.4		
3	0.20	0.04		42.3	
4	0.30	0.06		79.6	
5	0.40	0.07		80.2	
6	0.50	0.09		88.8	
7	0.60	0.08		27.0	
		0.15			42.7
8	0.70	0.08		64.6	
		0.44			5.7
9	0.77	0.14			45.1
10	0.87	0.08		27.8	
		0.11			58.0
11	1.00	1.00			88.3

X^{o}_{D4} : Mole fraction of D_4 on the initial reaction mixture.
X_{D4} : Mole fraction of D_4 on the copolymers.

rent bands of about equal intensity at 1020 and 1088 cm^{-1} (15) (Figure 1,c). This suggests the existence of long siloxane chain segments in the copolymer. The bond C-O-C of POM presents a band at 1095.71 cm^{-1} (Figure 1, a) (16), which for longer oxymethylene chains shows an strong absorption; in the copolymer this band is overlapping with the bands corresponding to the absorption band of the Si-O-Si bonds and Si-CH$_3$ of the dimethylsiloxane groups. In any case, the broad band between 1000 and 1130 cm^{-1} in the copolymers, suggests that they are formed for long oxymethylene chain segments too. The other copolymers exhibit the same FTIR spectra. The results suggest that the copolymer has a blocky structure. We found similar results by TGA in copolymers obtained by copolymerization of TOX with hexamethylcyclotrisiloxane (17).

^{1}H-NMR spectra of sample 2 containing 4 mol % of D_4 in the copolymer (Figure 2) showed 3 types of protons; one at 0.06 ppm can be assigned to the 6 methyl protons bonded to silicon (inner (a) protons) neighboring DMS chain segments. The other peak at 0.09 ppm corresponds to 6 methyl protons bonded to silicon in different chemical environments (outer (b) protons) neighboring oxymethylene chain segments, showed a resonance at a lower field because they are more deshielded. The signal at 1.50 ppm was assigned to the protons of the OM chain

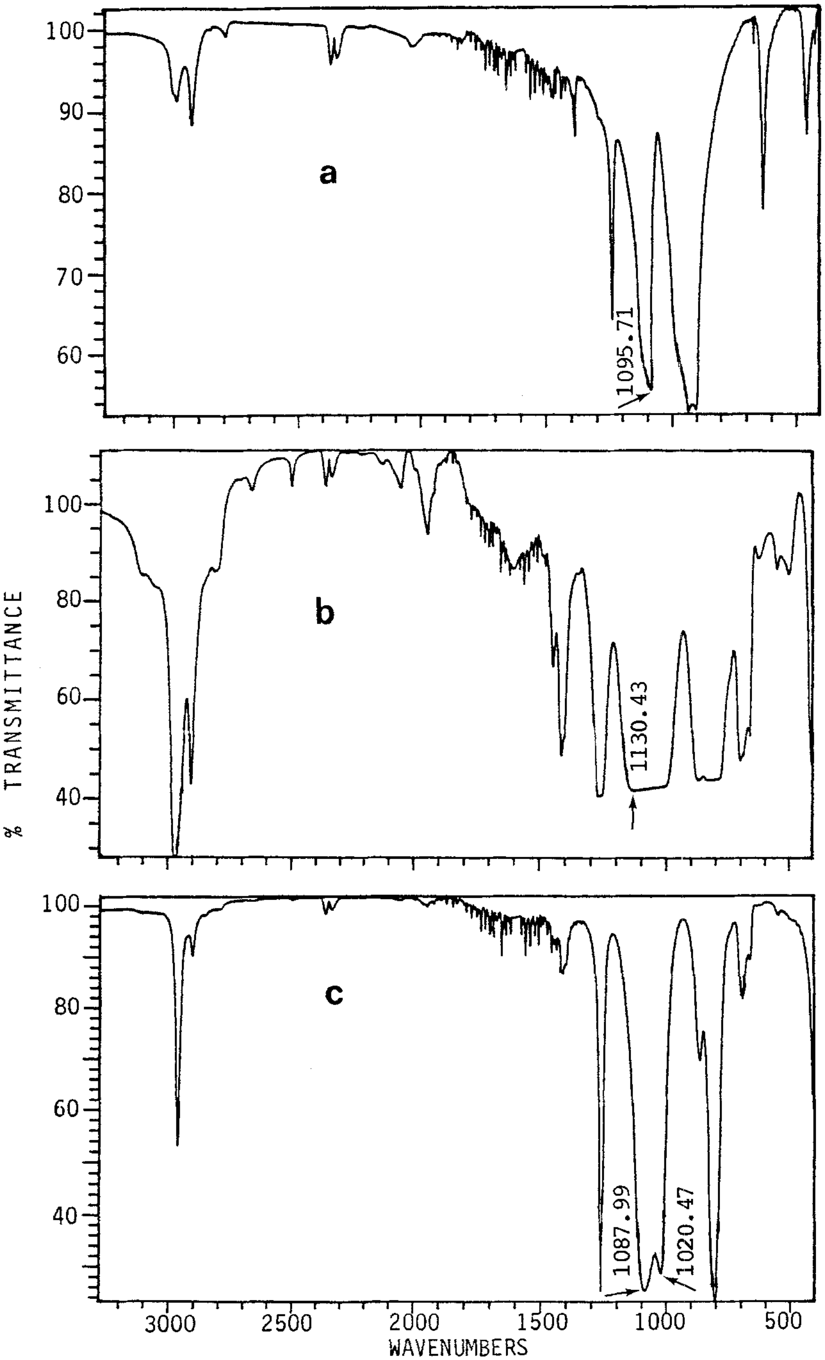


Figure 1. FTIR spectra of a) Poly(oxymethylene) b) Poly(oxymethylene-*co*-dimethylsiloxane) copolymer (sample 7, X_{D4}=0.15 and c) Poly(dimethylsiloxane).

segments ((c) protons). The signal at 5.06 ppm was assigned to residual trioxane protons. This sample suggest the existence of a copolymer formed by almost exclusively OM chain segments covalently bonded to segments of random copolymer chains, which in turn are bonded to segments formed by almost only DMS comonomer units. Figure 3 shows the ^{1}H-NMR spectrum of sample 5, that contains 7 mol % of D_4 in the copolymer, presenting a single peak at 0.06 ppm, corresponding to the methyl protons (6 (a) protons) bonded to silicon, and neighboring DMS segments. There is no evidence of the existence of outer (b)

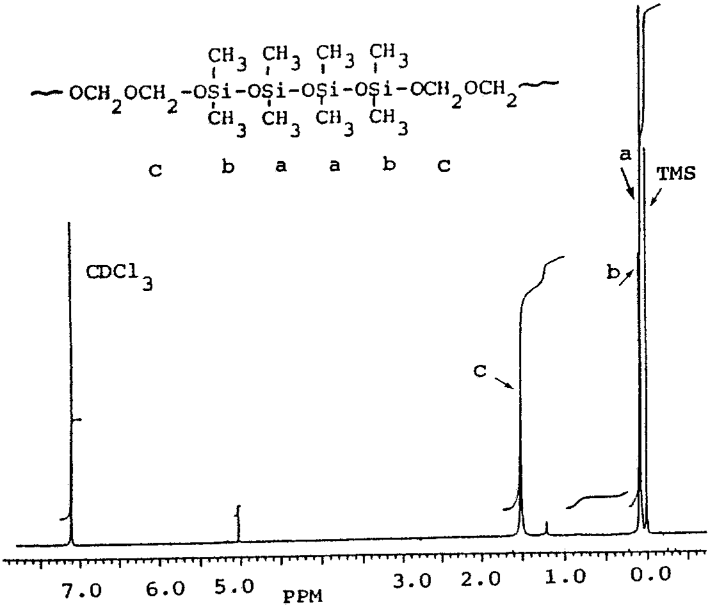


Figure 2. ^{1}H-NMR spectrum of sample 2 (X_{D4}=0.04) (250 MHz, $CDCl_3$, TMS, room temperature).

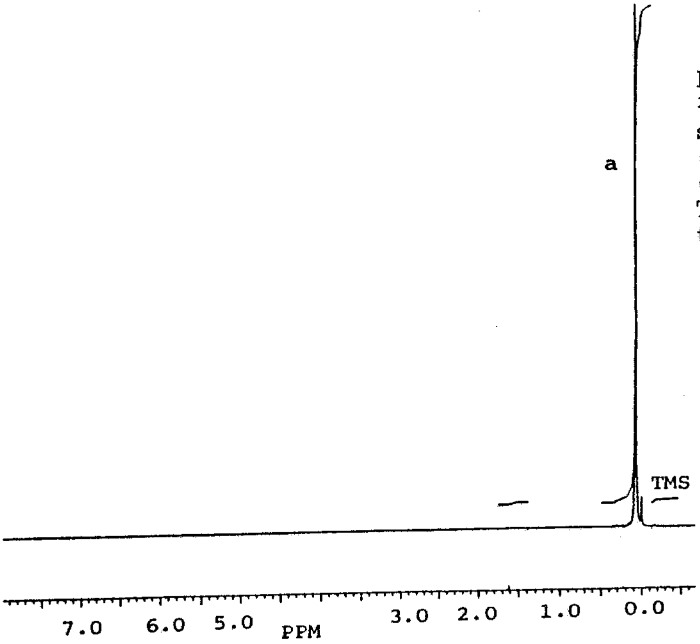


Figure 3. ^{1}H-NMR spectrum of sample 5 (X_{D4}=0.07) (250 MHz, $CDCl_3$, TMS, room temperature).

protons due probably to the very low concentration of the Si-OCH_2 bond. Also ^{13}C-NMR spectra of the same sample shows only one type of carbon at 0.86 ppm. This result suggests a block copolymer. In relation with the NMR analysis we must consider the very low solubility of the sample on $CDCl_3$.

According to the above discussion, the structures of the copolymers are given in Scheme 5.

Sample 2 ■■■■■■■■■■■■■-o■o■■ooo■o■■o■o■-ooooooooooooo

Sample 5 and 7 ■■■■■■■■■■■■■■■-ooooooooooooooo

Scheme 5. Structures of copolymers 2, 5 and 7.
■: $-(OCH_2)_3-$; o: $-(OSi(CH_3)_2)_4-$.

The compression-time curves obtained by TMA (Figure 4) for samples 2 and 7 showed that the deformation of the copolymers with high concentration of DMS increases.

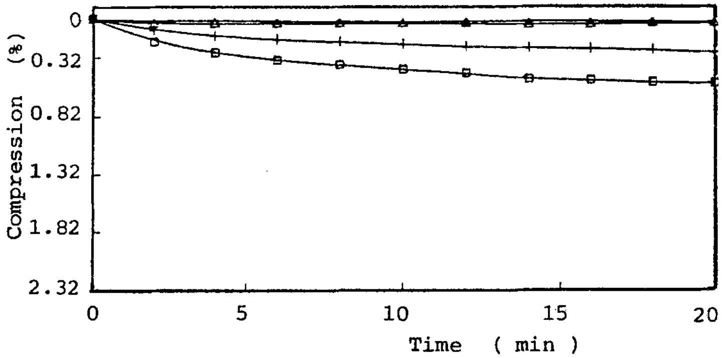


Figure 4. Compression-time curve. Sample 2 (X_{D4}=0.04). (•):0.02 and (+):0.2 Newton. Sample 7 (X_{D4}=0.08).(Δ): 0.02 and (□): 0.2 Newton.

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