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INCORPORATION OF THE SILOXANES IN HYDROLYTICALLY DEGRADABLE ORGANIC STRUCTURES. II. SEGMENTED SILOXANE-IMIDE POLY(ANHYDRIDE)S

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INCORPORATION OF THE SILOXANES IN HYDROLYTICALLY DEGRADABLE ORGANIC STRUCTURES. II. SEGMENTED SILOXANE- IMIDE POLY(ANHYDRIDE)S

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ABSTRACT

New segmented poly(anhydride)s containing pre-formed siloxane-imide sequences have been synthesized. The synthetic strategy involves the preparation of α,ω -bis(3-aminopropyl)oligodimethylsiloxane having certain molecular weight, their chemical modification by reaction with trimellitic anhydride, and subsequent polycondensation of the obtained diacid macromers in solution. The acetylation method was used for the *in situ* activation of the diacids. The structures of partial and final products and their degradability were confirmed by IR and ^1H NMR spectroscopy.

Key Words: Poly(anhydride)s; Poly(siloxane-imide)s; Hydrolytically degradability; Organo-siloxane copolymers; Segmented copolymers

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INTRODUCTION

In the past, a great deal of interest has been directed towards polymers with low stability. Such polymers can be used to reduce the pollution caused by plastic articles. As well, they have found them useful for other applications.^[1,2] The hydrolytic instability of the polymers may make them attractive in a number of applications, such as, for biomedical purposes, pharmaceuticals as controlled release of drugs, or as materials whose degradation will limit their long-term environmental impact (agriculture and packaging).^[1,3-5]

The degradation processes of polymers can occur either by absorption of energy (thermal, electromagnetic, mechanical or ultrasonic), which causes the propagation of molecular degradation through secondary reactions or by hydrolytic mechanisms that result in molecular fragmentation, usually for polymers with hetero-chains, where these processes appear to be the reverse of polycondensation.^[1,6] For the latter category of degradation processes, important efforts have been focused on the synthesis of new aliphatic polyesters,^[7] polyanhydrides,^[8] polysilyleters^[4] and polysilylesters^[9-11] due to their high susceptibility for biodegradation.

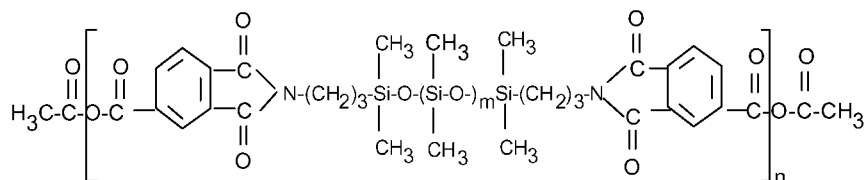
Polyanhydrides and their degradation products have been proven to be highly biocompatible.^[8,12] Unfortunately, the polyanhydrides have poor mechanic properties^[13] which present disadvantages to this class of polymers. By imidic bridges incorporation, an improvement can be obtained. However, due to their rigidity, the polyanhydrides containing imide in general, are brittle and therefore, difficult to process. The introduction of flexible segments with desired lengths (for example, sebacic acid) can allow the formation of high molecular weight polymers with low melting points, good solubility in common organic solvents and implicitly, and good processing.^[14]

Siloxanes, with their special properties like bio-compatibility, chemical and physiological inertness, hydrophobicity, low surface tension, high flexibility will be used as flexible segments in the present work.

In a previous paper,^[15] a series of poly(anhydride)s siloxane-imide have been synthesized by using α,ω -bis(carboxypropyl)oligo(dimethylsiloxane) and imidic diacids as precursors.

In this paper, oligosiloxanes having carboxy-imide groups on both ends, were synthesized and used as macromers in order to obtain new segmented siloxane-imide poly(anhydride)s by homopolycondensation. In order to increase the carboxyl reactivity, the anhydrization, with acetic anhydride, was made. The corresponding polymer was obtained by a transesterification reaction of the activated macromer. Poly(anhydride)s having perfectly alternating siloxanic and imidic sequences, respectively are expected to result.

Therefore, starting from trimellitic anhydride and oligosiloxane having aminopropyl ends, we synthesized new polymeric structures of the type:



Scheme 1.

with m having average values 0, 2.4, 9.4, 12.7 or 23.0.

By varying the siloxane units number in the macromer, the hydrolytic degradation rate can be tailored to specific requirements.^[16]

EXPERIMENTAL

Materials

Trimellitic anhydride (Aldrich Chemical), AT, was recrystallized from a mixture of hot toluene-acetic anhydride (m. p. 164–165°C).

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (Fluka AG), AP₀, was used as received.

Octamethylcyclotetrasiloxane, [(CH₃)₂SiO]₄, D₄, supplied by Fluka AG with the following characteristics : b.p. = 175°C; $n_D^{20} = 1.396$; $d_4^{20} = 0.955$, purity >99% (GC).

Tetramethylammonium hydroxide pentahydrate, (CH₃)₄NOH·5H₂O, (TMAH) solution 25% in methanol (Aldrich).

Acetic anhydride (Merck) was freshly distilled before use.

Solvents: chloroform, methylene chloride, petroleum ether, dimethylformamide were freshly dried and distilled before use.

Measurements

IR spectra were recorded on a Specord M80 spectrophotometer. Samples were pressed into KBr pellets.

¹H NMR spectra were taken on a JEOL C-60 HL spectrometer using CDCl₃ as solvent.

Differential scanning calorimetry (DSC) was performed by Mettler DSC12E instrument.

Procedure

Synthesis of the Siloxane Oligomer Telechelic Functionalized with Aminopropyl Groups

The determined quantity (0.1% wt) of TMAH as solution 25% in methanol is introduced in a three-neck flask having reflux condenser with CaCl₂

protection and inert gas inlet. Previously, all glassware was dried in flame. The solvent (methanol) was completely removed by vacuum distillation. Octamethylcyclotetrasiloxane and 1,3-bis(aminopropyl)tetramethyldisiloxane in pre-established molar ratio were added. The reaction mixture was stirred under a steady stream of nitrogen at 80°C for 10 h and then the temperature was increased to 150°C (1 h) in order to decompose the catalyst. The equilibrium cycles were removed by distillation in vacuum at 150°C.

Synthesis of α,ω -Carboxy-Functionalized Siloxane-Imidic Macromers

This was made by the chemical modification of the aminopropyl ending, which belongs to siloxane. In this procedure, a method reported in the literature by Staubli et al.^[13,14] was applied: condensation α,ω -bis(3-aminopropyl)oligodimethylsiloxane with trimellitic anhydride in excess (molar ratio AP:AT about 1:1.25) by refluxing in *N,N'*-dimethylformamide (sol. 5 molar) for 3 h. The solution was cooled, filtered, and concentrated in vacuum. Then, the solution was added to excess water to precipitate the formed diacid macromer. The product, a white solid, yellow paste or viscous oil, was then isolated and dried.

Polycondensation

For a typical procedure, diacid macromer was introduced in a three-necked flask equipped with a magnetic stirrer, a Dean-Stark trap with reflux condenser, gas inlet and outlet tube. Excess acetic anhydride (for a 0.02 molar solution) was added, and the reaction mixture was refluxed under a slow stream of nitrogen with stirring for 5 h. During the process, the formed acetic acid was removed as this was formed. Finally, introduction of nitrogen was stopped and a high vacuum was applied for removing the excess acetic anhydride from the reaction mixture. A yellow-brown solid or very viscous polymer in the shape of a transparent coating remained in the reaction vessel. After cooling, the resulting polymer was isolated mechanically as such. All these operations were performed in nitrogen atmosphere and all glassware was flame dried, then in vacuum to avoid the hydrolysis of the anhydride linkages under the influence of the environmental moisture.

The Degradation Tests

The polymers were placed in individual glass vials, which were open to the laboratory environment (about 20°C, 40% humidity). At the appropriate times (1, 2, 3 days to one week), the polymer samples were analyzed by IR and ¹H NMR spectrometry.

RESULTS AND DISCUSSION

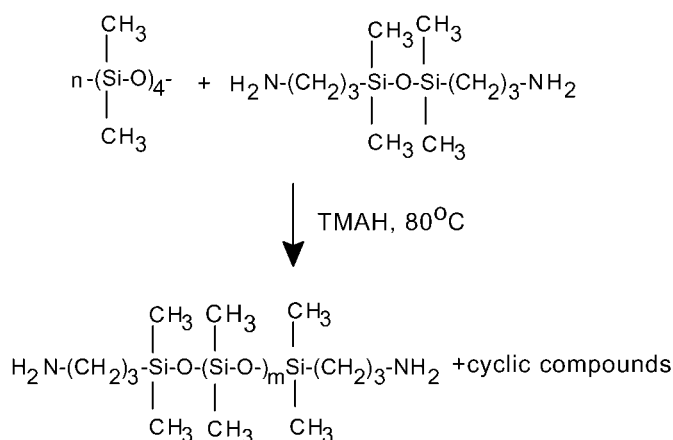
The most common method for the synthesis of polyanhydrides involves the copolymerization of activated diacids.^[8] Aromatic diacid contained in the chain inside a certain number of siloxane units was synthesized and used in this paper. By varying the siloxane units number, a certain ratio between hydrophilic/hydrophobic segments is created and polymeric materials with new properties can be obtained. These physical, chemical, or biological properties can be adapted for specific uses.

For obtaining the desired products, the following steps were followed.

The Preparation of the α,ω (3-Aminopropyl)Oligodimethylsiloxanes

The α,ω (3-aminopropyl)oligodimethylsiloxanes were prepared by bulk ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) in the presence of disiloxane containing the desired functions (amine groups) (Sch. 2), reaction which is usually called "equilibration" or "redistribution".^[17-19]

Even if the equilibration reaction can be catalyzed either by acid or base, a base was chosen as catalyst in this case because an acid can be blocked by reacting with the amine groups. Moreover, tetramethylammonium hydroxide was used because it can be easily removed in the end by increasing the temperature of the reaction mixture to 150°C when the catalyst is decomposed in volatile compounds (trimethylamine and methanol).^[20]



with: $m=0$ (AP_0), $m=4$ (AP_1) $m=9.7$ (AP_2) $m=12.7$ (AP_3) and $m=23$ (AP_4)

Scheme 2.

The average numerical molecular weights of the obtained oligomers were calculated on the basis of the ^1H -NMR spectra with the following relationship:

$$M_n = M_0 + 74(2h_1 - 6h_2)/3h_2$$

where: $M_0 = 248.3$ is the molecular weight of the 1,3-bis(3-aminopropyl)tetramethyldisiloxane (AP_0); h_1 , h_2 , are the heights of the integrals peak areas, corresponding to the protons in the methyl (0.0–0.2 ppm) and methylene, $\equiv\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$, (2.4–2.7 ppm) groups, respectively. The M_n obtained values are presented in Table 1.

The Preparation of the Siloxane-Imide Diacids

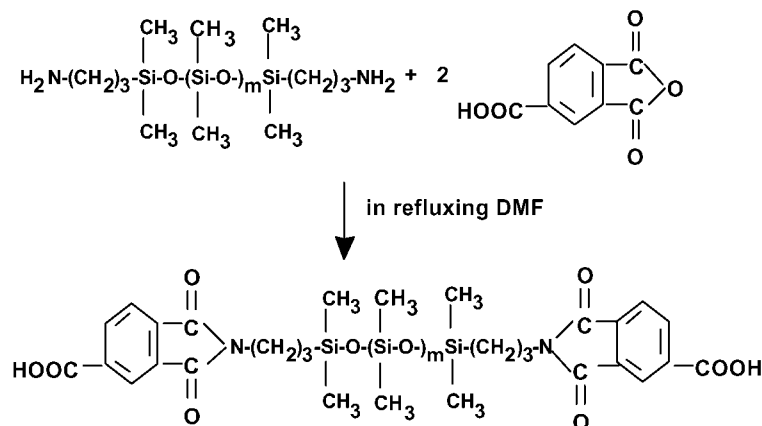
The preparation of the siloxane-imide diacids was achieved by reacting the trimellitic anhydride with the free ending amino groups of the siloxanes when the NH_2 group is trapped in cycloimidic structures^[13,21] (Sch. 3):

The reaction progress was followed by IR spectra in which the bands characteristic for cyclic anhydride at 1840–1870 cm^{-1} disappeared and a strong band at 1790–1720 cm^{-1} assigned to imide develops (Fig. 1b). Significant modifications also appear in the ^1H NMR spectra (Fig. 2b). So, the strong signal at 1.2–1.3 arises from the NH_2 protons of the amine groups of AP disappeared due to the inclusion of the amine groups in imidic cycles. The others specific signals suffer slight displacements as a result of the reaction: 1.4–2.0 instead of 1.3–1.7 ppm ($\equiv\text{Si}-\text{CH}_2-\text{CH}_2-$) and 3.5–3.9 instead of 2.4–2.7 ppm ($\equiv\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$). The new signals characteristic for aromatic protons (8.5–9.7 ppm) and carboxylic protons (10.0–10.3 ppm) appear.

The average numerical molecular weights of the modified siloxane oligomers were verified on the basis of ^1H NMR spectra taking into account the heights (h_1 and h_2) of the integrals peak areas, corresponding to the protons in the methyl (0.0–0.2 ppm), and at this time, aromatic (8.5–9.7 ppm) groups, respectively:

Table 1. The Synthesized Siloxane-Imide Diacids

Sample	m in Siloxane Oligomer	Yield, %	m in Siloxane-Imide Diacid	Aspect Product
$\text{AP}_0\text{-AT}$	0	95	0	White solid
$\text{AP}_1\text{-AT}$	4	45	2.4	Yellow paste
$\text{AP}_2\text{-AT}$	9.7	80	9.4	Yellow viscous oil
$\text{AP}_3\text{-AT}$	12.7	91	13	Yellow viscous oil
$\text{AP}_4\text{-AT}$	23	92	21	Yellow oil



Scheme 3.

$$M_n = 598.5 + 74(h_1 - 2h_2)/2$$

As can be seen in Table 1, the number of siloxane units of every imide diacid obtained, $m = (h_1 - 2h_2)/2$, is, in general, close to those of the starting oligomer. The little differences can be explained by inherent fractionation during the purification procedures. The preliminary test proved that depolymerization of the polysiloxanes by cyclization does not take place in the work conditions.

Polycondensation

The segmented copolymers were synthesized through the polycondensation of the bifunctional macromer, in solution.

According to the literature^[13] in these reaction types, for their activation the diacid must be converted first in a mixed anhydride (pre-polymer) by refluxing with acetic anhydride. Then, the purified pre-polymer (mixed anhydride) can be polycondensed in bulk or in solution. The separation and purification of the pre-polymers is quite difficult and laborious because the pre-polymers are moisture sensitive. Therefore, the alternative to performing the reaction in solution without isolation of the activated macromers was chosen in this work. Acetic anhydride was used as reaction environment starting directly from dicarboxylated monomers. The synthesis of the pre-polymers (mixed anhydrides) is made *in situ* during refluxing and polycondensation occurs as the formed acetic acid is removed from the system (Sch. 4).

The reaction occurs in homogeneous medium. In fact, in the present case, the polycondensation is a trans-anhydridization. The acetic anhydride used here in excess acts not only as solvent for the easy dissolving of macromers, but also as an activation agent. In this way, acetylation and poly-

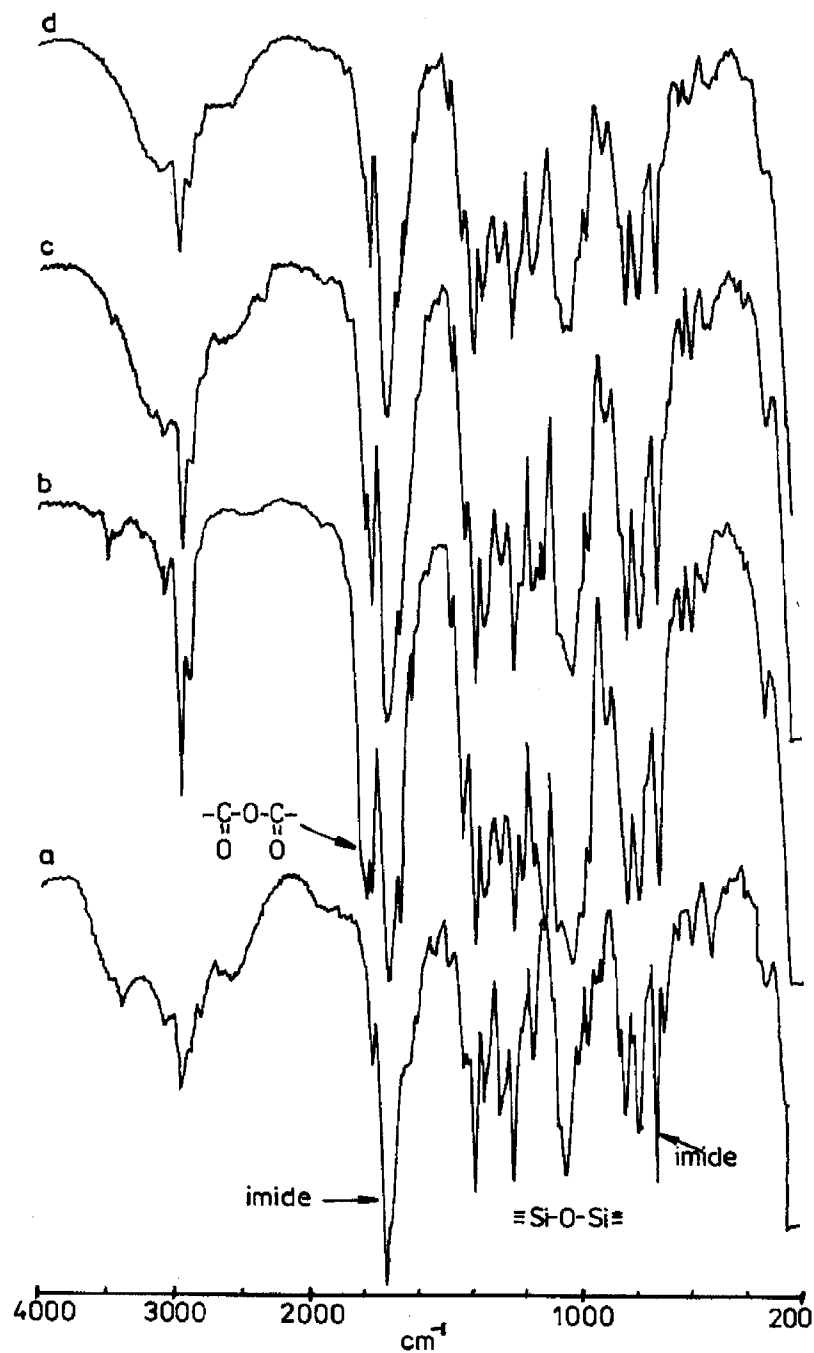


Figure 1. Modification of the IR spectrum during transformation from α,ω -Bis(3-amino-propyl)oligodimethylsiloxane (AP_1) (a); α,ω -bis(3-N-Trimellitylimido propyl)oligodimethylsiloxane (AP_1 -AT) (b); to the proper copolymer (AP_1 -AT) $_n$, freshly synthesized (c); and after 7 days exposed in atmosphere (d); respectively.

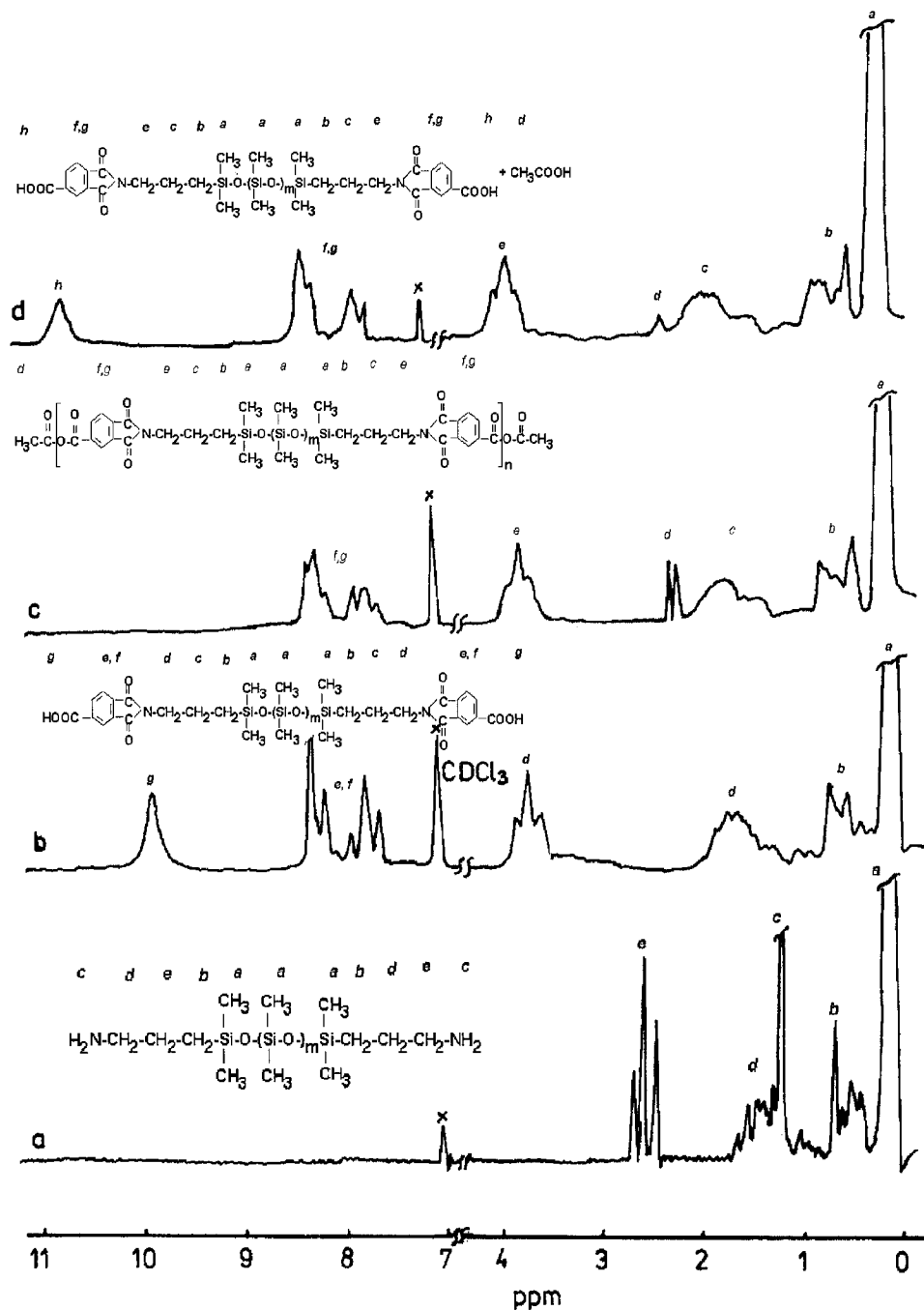
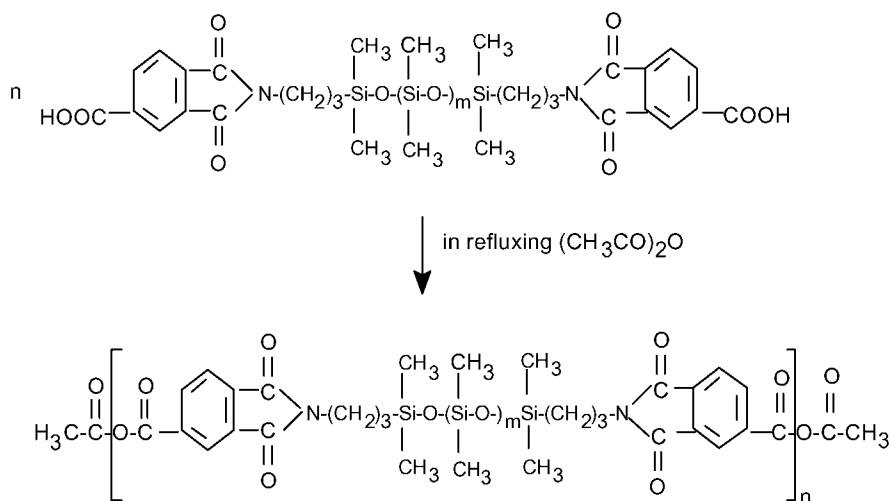


Figure 2. Illustrative ¹H NMR spectra for α,ω -bis(3-aminopropyl)oligodimethylsiloxane (AP₁) (a); α,ω -bis(3-N-Trimellitylimido propyl)oligodimethylsiloxane (AP₁-AT) (b); and the proper copolymer (AP₁-AT)_n freshly synthesised (c); and after 7 days exposed in atmosphere (d); respectively.



Scheme 4.

condensation were carried out in one step and, in the same reaction medium, thus considerably reducing the duration of the process. In all cases, the product remaining after removing the solvent was a clear yellow-brown transparent material.

The purification of the polymer by reprecipitation is difficult to achieve without degradation. Therefore, the purification was avoided, their use being possible, in our opinion, without purification.

Characterization of the Polymers

The polymers obtained are easily soluble at room temperature in polar organic solvents like, DMAA, NMP, DMF, $\text{C}_2\text{H}_5\text{OH}$, DMSO and even CH_3OH , as well as in less polar solvents (acetone, THF, CHCl_3 , CH_2Cl_2).

The IR spectra (KBr) for synthesized copolymers present all the characteristic absorption bands for the proposed structures (Fig. 1): 3100 cm^{-1} (OH carboxylic) $2900\text{--}3000\text{ cm}^{-1}$ (aromatic and aliphatic C-H), 1810 , 1780 cm^{-1} (anhydride), 1730 cm^{-1} (C=O imide), 1640 cm^{-1} (C=O carboxylic), 1360 cm^{-1} (imide C-N) 1250 cm^{-1} (Si-CH₃), $1000\text{--}1100\text{ cm}^{-1}$ (Si-O-Si), 800 cm^{-1} (Si-CH₃) and 730 cm^{-1} (imide ring deformation).

The ^1H NMR spectra also confirm the proposed structures. The positions of chemical shifts for each proton were readily assigned as shown in Fig. 2. Some modifications are produced in ^1H NMR spectra of the copolymers, compared to those of the starting monomers namely, in high frequency range. So, the signal at $10.0\text{--}10.3\text{ ppm}$ assigned to carboxylic diacid monomer disappeared as polycondensation occurs. The signals at 2.5 and 2.3 ppm are assigned to methyl groups on acetyl residues at the chain ends

and/or the methyl groups of acetic anhydride and acetic acid as potential impurities, respectively.^[22]

The average siloxane units number in every polymer sequence was determined by ¹H NMR spectrometry based on the ratio of the intensities of the signals corresponding to the protons from methylic groups attached to silicon atoms and the protons of the aliphatic or aromatic groups situated at the extremities of the siloxane segments. In all cases (Table 2), the average number of siloxane units from starting diamino siloxanes, diacid macromers, and the proper polymers are almost the same. Little differences which appear can be assigned to the losses by inherent fractionation during purification of the formed diacid monomers or by volatile fraction removing from the polycondensation reaction milieu. According to the literature^[23] and such as was demonstrated by preliminary tests^[15] it is thought that no depolymerization of the polysiloxanes by cyclization occurs during polycondensation.

There is no melting endotherm present in the DSC thermograms in the temperature range between 30 and 200°C, which is consistent with the amorphous nature of the obtained polymers.

All the polymers possess outstanding film-forming properties. So, after the solvent (acetic anhydride) was removed from the polycondensation mixture, the polymer as a transparent flexible film remains on the bottle.

IR spectra (Fig. 1), recorded at various time intervals, revealed the stepwise decrease in intensity until complete disappearance of the anhydride absorption band at 1810 cm⁻¹. Correspondingly, bands for the carboxylic groups formed in the hydrolysis process develop at 1720 cm⁻¹ (C=O), 3200–3400 and 950 cm⁻¹ (OH).

It seemed, on the basis of IR spectra, that the degradation rate increased with the increase in hydrophilicity content. So, (AP₀-AT)_n copolymer showed the fastest degradation among the others synthesized

Table 2. The Obtained Poly(Anhydride)s

Sample	Yield, %	m in Copolymer ^a	Aspect Product
(AP ₀ -AT) _n	98	0	hard yellow-brown transparent film
(AP ₁ -AT) _n	88	1.8	soft yellow-brown transparent film
(AP ₂ -AT) _n	98	8.7	yellow-brown viscous, transparent oil
(AP ₃ -AT) _n	97	13	yellow-brown viscous, transparent paste
(AP ₄ -AT) _n	95	20	yellow-brown transparent oil

^aDetermined on the basis of ¹H NMR spectra.

polyanhydrides while $(AP_4-AT)_n$ is the most stable because the longer siloxanic segments create a hydrophobic environment which better protects the hydrolyzable anhydride groups.

The recognized mechanism for the degradation in air is the hydrolysis of the anhydride bridge. When all anhydride bridges are broken, the copolymer is converted practically to the starting diacid macromer. This fact is sustained by the identity of an IR spectrum of the degraded copolymer and initial diacid (Fig. 1b and 1d, respectively).

In 1H NMR spectra of the degraded copolymer (Fig. 1d), it appears the proton signal of the carboxylic group formed as degradation occurs.

The singlet at 2.3 ppm assigned to methyl groups of the acetic acid formed as result of the acetic anhydride hydrolysis appeared instead of those of 2.5 ppm.

Studies on the advanced degradation and degradation in various environments are our further goal.

These copolymers are recyclable. After hydrolytic degradation, refluxing with acetic anhydride can regenerate them. Indeed, the IR spectra of the initial copolymer and of the regenerated copolymer are identical.

CONCLUSION

Oligosiloxanes having carboxy-imide ends, were synthesized and the new kinds of segmented poly(anhydride)s were obtained on their basis. The combination of the imidic cycle rigidity and the siloxane chain flexibility has resulted in the polymers with low softening points and good solubility in common organic solvents, which constitute a good premise for easy follow-up-processing. Preliminary tests proved the hydrolytic degradability of these synthesized polymers. The entire characterization of the synthesized copolymer type is now in progress.

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