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Alloys

Synthesis of ABA Block Co-Oligomers of Polymethylmethacrylate and Poly (Dimethylsiloxane)

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ABSTRACT

A methoxysilyl macromonomer containing an acrylic chain is obtained by telomerization of methyl methacrylate with γ mercaptopropylmethyldimethoxysilane. This macromonomer is then reacted with a polydimethylsiloxane hydroxytelechelic leading to new block Co-Oligomers with acrylic and siloxane moieties.

INTRODUCTION

The aim of this work is to synthesize oligomers of the type PMMA-PDMS-PMMA containing one central silicone block and two peripheral polymethylmethacrylate blocks. Such compounds may have interesting uses, especially in the field of alloys of polymers. Several authors have worked on methyl methacrylate (MMA) copolymerization with organosilanes and have obtained graft or block structures. As regards graft polymers, the reaction proceeds according to Scheme 1. In this way chains (polyacrylic, for example) have been grafted on polyorganosiloxanes by initiating radical polymerization on methyl groups attached to the silicon atom. This has been done by ADAMAS [1], GETSON [2,3], NEUROTH [4], LINDSEY [5], SAAM [7], SWEET [7], RICHES [8], SCHONE [9] and KAWAKAMI [10], to name only the leading authors.

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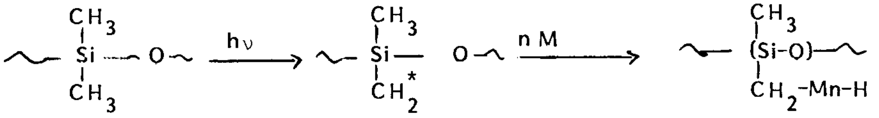
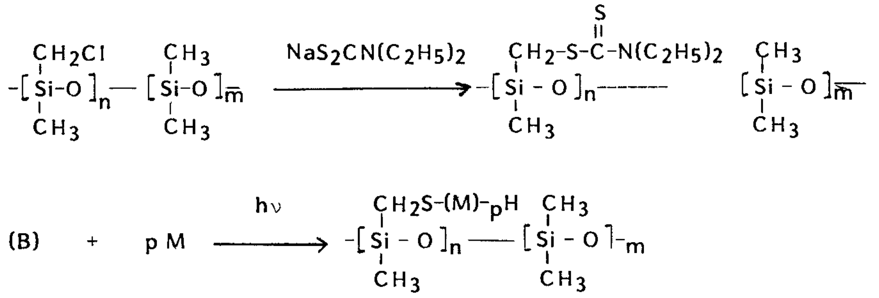


$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O\sim \xrightarrow{h\nu} \sim\underset{CH_2^*}{\overset{CH_3}{Si}}-\ O\sim \xrightarrow{n\,M} \sim(\underset{CH_2-Mn-H}{\overset{CH_3}{Si}}-O)\sim \qquad (A)$$

Scheme 1

Peroxides or azobis-isobutyronitryle [11] are used as initiators, but ultraviolets can also be used. For this method, the work of MERRYL [12], of HOFFMANN et al. [13, 14], MEABURN [11] and more recently WILSON [15] can be named. Graft copolymers can also be obtained either by chemical modification [16], or from copolymerization reactions using macromonomers [17, 18, 19]. In the chemical transformations, the reaction of sodium diethyldithiocarbamate on the $-CH_2Cl$ group of a polysiloxane results in a macromonomer suitable to initiate the polymerization of monomer M according to Scheme 2 :

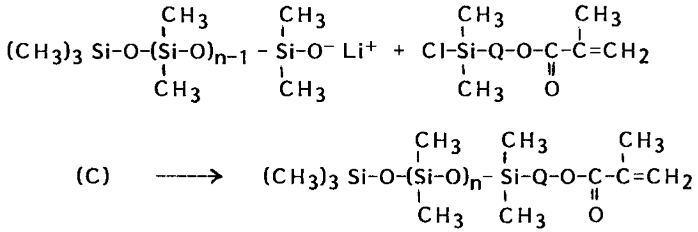


$$-[\underset{CH_3}{\overset{CH_2Cl}{Si}}-O]_n-[\underset{CH_3}{\overset{CH_3}{Si}}-O]_m \xrightarrow{NaS_2CN(C_2H_5)_2} -[\underset{CH_3}{\overset{CH_2-S-\overset{S}{\overset{\|}{C}}-N(C_2H_5)_2}{Si}}-O]_n-[\underset{CH_3}{\overset{CH_3}{Si}}-O]_m \qquad (B)$$

$$(B) + p\,M \xrightarrow{h\nu} -[\underset{CH_3}{\overset{CH_2S-(M)-_pH}{Si}}-O]_n-[\underset{CH_3}{\overset{CH_3}{Si}}-O]-_m$$

For the preparation of macromonomers, anionic polymerization is mostly used. By this method, KAWAKAMI et al. [17, 18] synthesized two types of macromonomer from a living prepolymer of PDMS [poly(dimethylsiloxane)] (C) with a selected degree of polymerization and prepared by anionic polymerization according to Scheme 3 :

$Q = -(CH_2)_2 - O\,(CH_2)-_3$ or $-(CH_2)_5-$



$$(CH_3)_3Si-O-(\underset{CH_3}{\overset{CH_3}{Si}}-O)_{n-1}-\underset{CH_3}{\overset{CH_3}{Si}}-O^-\,Li^+ + Cl-\underset{CH_3}{\overset{CH_3}{Si}}-Q-O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{C}=CH_2$$

$$(C) \longrightarrow (CH_3)_3Si-O-(\underset{CH_3}{\overset{CH_3}{Si}}-O)_n-\underset{CH_3}{\overset{CH_3}{Si}}-Q-O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{C}=CH_2$$

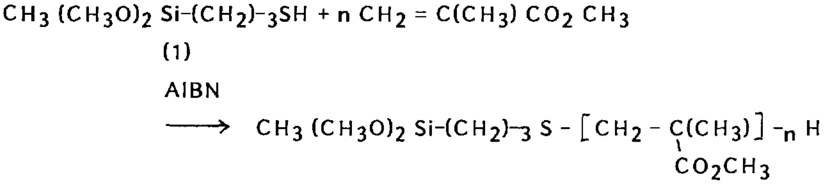
These macromonomers then react with MMA by radical copolymerization to yield graft copolymers.

Less work has been done on producing block copolymers from acrylic monomers, since ionic polymerization is mostly used. From the above living intermediate (C), a PDMS-PMMA block copolymer was prepared by JULIANO [20], and more recently by VARSHNEY [21].

Lastly we can name the work of SHIMADA [22] who prepared ABA block copolymers : (PMMA)s(PDMS)s(PMMA) by an original process which consists in coupling a difunctional PDMS with monofunctional acrylic telomers through the intermediary of a short relay molecule. In the present work we describe a synthesis similar to the latter but in which the reactants are entirely different as are the corresponding chemical reactions.

SYNTHESIS OF A MACROMONOMER CONTAINING A PMMA CHAIN

A telomerization of MMA with γ mercaptopropylmethyldimethoxysilane (1) and azobis-isobutyronitrile (AIBN) as initiator was carried out, resulting in telomer (2) :



$$CH_3\,(CH_3O)_2\,Si\text{-}(CH_2)\text{-}_3SH + n\,CH_2 = C(CH_3)\,CO_2\,CH_3$$

(1)

$$\xrightarrow{AIBN} CH_3\,(CH_3O)_2\,Si\text{-}(CH_2)\text{-}_3\,S - [CH_2 - \underset{CO_2CH_3}{C(CH_3)}]\text{-}_n\,H$$

(2)

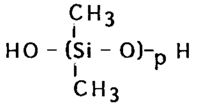
In order to control the PMMA chain length, we considered that $\frac{1}{\bar{n}}$ = Ro

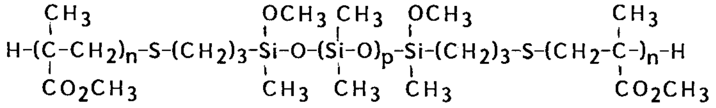
where Ro = $\frac{\text{thiol (1) concentration}}{\text{MMA concentration}}$ as is shown in the telomerization reactions [23].

As we wished short chains, we took Ro = 1. The resulting product contains predominantly telomers of degree of polymerization n = 1, but also telomers where n > 1. A fraction containing a mixture of telomers n = 1 and n = 2 was isolated by molecular distillation at 70° C at the pressure of 10^{-3} torrs and was identified by ^1H NMR (signal due to the protons of the $Si\text{-}CH_3$ group at 0×10^{-6} and signal due to the protons of the $C\,O_2\,CH_3$ at 3.6×10^{-6}). The $\bar{n}$ was calculated using the relative heights of the stepped integral of these signals. Moreover, ^{29}Si NMR spectra of thiol 1 as well as of telomer 2 showed a characteristic signal at -2×10^{-6} of the $-Si(OCH_3)_2$ group which proves that methoxyl functional groups are not altered during the telomerization.

SYNTHESIS OF BLOCK OLIGOMERS CONTAINING SILOXANE BLOCKS AND METHACRYLIC BLOCKS

The macromonomer 2 is able to react with dichlorosilanes or cyclosiloxanes, thereby permitting the incorporation of PMMA chains prepared previously [24]. Polycondensation from $Cl_2Si(CH_3)_2$ in the presence of water with or without KOH was unsuccessful. In fact, the reaction yielded some low molecular weight cyclosiloxanes with a predominance of tetrasiloxanes (D_4) mixed with PDMS. This is due to the weak reactivity of the reaction : cyclotetrasiloxane ----> linear polymer and to the difference of reactivity between the Si-Cl and Si-OCH_3 bonds of each reactant. When polymerization was attempted by opening the hexamethylcyclotrisiloxane (D_3) ring, in the presence of our macromonomer 2 and of KOH, the expected polymer was not observed.

In front of these difficulties, we finally developed a procedure using the previously prepared PDMS block in the form of a silanol 3, whose degree of polymerization 'p' is variable :  $HO-(Si(CH_3)_2-O)_p H$ 3 . The catalyst used is a salt obtained by the action of the 2-ethylhexanoic acid on tetramethylguanidine, known for preventing the equilibration process which occurs in reactions with polysiloxanes [25], [26]. First, compound 3, of degree of polymerization p = 50, was allowed to react with compound 2, composed of a mixture of telomers n = 1 and n = 2 (70 : 30). The reaction, performed in bulk with 2 moles of compound 2 for 1 mole of compound 3, at 100° C for 20 hours, yielded a block compound with the following predominant structure :

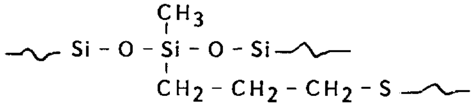


$$H-(C(CH_3)(CO_2CH_3)-CH_2)_n-S-(CH_2)_3-Si(OCH_3)(CH_3)-O-(Si(CH_3)_2-O)_p-Si(OCH_3)(CH_3)-(CH_2)_3-S-(CH_2-C(CH_3)(CO_2CH_3)-)_n-H$$

4 $1<n<2$ and $p \simeq 50$

This structure is clearly supported by three facts : first, the Si-OH vibration bands at 3690 cm^{-1} have disappeared on the infra-red spectrum ; next, on the gel-permeation chromatogram, the peaks at 21.02 ml and 22.02 ml, corresponding to alkoxysilane n = 2 and n = 1 respectively, have entirely disappeared, while the disilanol peak shifts from 15.62 ml to 15.42 ml. Lastly, the ^{29}Si NMR spectrum [27] shows the disappearance of signals of Si atoms bearing hydroxyl groups at -11.9×10^{-6}, the disappearance of signals of Si atoms bearing two methoxyl groups at -2.0×10^{-6}, while, on the other hand, signals of the Si atom appear bearing only a single methoxyl function at - 13 x 10^{-6}. The signal of Si atoms of the PDMS remains unchanged at - 22.1 x 10^{-6}.

The minor product observed results from the addition of two silanols to the two methoxyl groups of telomer 1. This is confirmed firstly on the G.P.C., where the mass increase is greater than that expected for structure 4, and secondly, on the ^{29}Si NMR spectrum by the presence of a signal at - 22.4 x 10^{-6}, corresponding to :



$$\sim Si-O-\underset{CH_2-CH_2-CH_2-S\sim}{\overset{CH_3}{Si}}-O-Si\sim$$

The research we have carried out to obtain ABA block oligomers could therefore be considered as a model for the synthesis of either ABA block copolymers (PMMA)s(PDMS)s(PMMA), or of graft copolymers (PDMS)g(PMMA).

Indeed, preparation of each type of copolymer can be optimized according to the number of Si-OCH_3 reactive functional groups of telogen 1 and according to the stoechiometry of the condensation reaction.

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