Synthesis, Characterization, and Gamma Radiation Effects Over Well-Defined Poly(vinylsiloxanes) Copolymers

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ABSTRACT: Anionic ring-opening polymerization (AROP) was employed for the controlled synthesis of linear model block copolymers of 1,3,5,7-tetrametil-1,3,5,7-tetravinyl(cyclotetrasiloxane) (V_4) and 1,3,5-dimethyl(cyclotrisiloxane) (D_3) monomers by using *sec*-butyl lithium (*sec*-Bu^-Li^+) as initiator, and high-vacuum anionic polymerization techniques. V_4 copolymerization was promoted by employing D_3 and *sec*-Bu^-Li^+ producing living silanolates that open the stable V_4 ring. For this purpose, two strategies were applied: (a) sequential addition of monomers, and (b) one-step copolymerization at different reaction temperatures. According to the experimental results, higher levels of V_4 incorporation (~ 18.14 mol %) were obtained by mixing both co-monomers and performing the reaction at high temperature (80°C). This strategy allowed the control of the V_4 incorporation into the copolymer structure, giving the opportunity of synthesizing model vinyl-siloxane polymers. The gamma radiation of these materials showed that lower doses are needed to achieve the same gel content as in a *model* poly(dimethylsiloxane) (PDMS). In such a sense, these results constitute one of the first reports regarding the effect of gamma radiation on vinyl-containing silicon polymers, and may be of fundamental importance if a biomedical cross-linked rubber-type PDMS is needed at earlier doses of sterilization. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 832–839, 2012

Key words: anionic polymerization; copolymerization; cross-linking; vinyl-siloxane; gamma radiation

INTRODUCTION

Silicon-containing polymers are a particular class of materials that are well known in medical applications because of their biocompatibility and non-toxic nature.[1] In particular, siloxanes are silicon-based polymers that can be regarded as inorganic silicate derivatives partially substituted with organic groups. This fact provides a wide spectrum of properties that cannot be found in common organic polymers. They result from the combination of the polar Si—O backbone and the contribution of the organic groups.[2] For example, polymers based on poly(dimethylsiloxane) (PDMS) have been used in ophthalmologic surgery,[3] breast implants,[4] and for the fabrication of specific medical devices.[5,6]

To improve the applications of PDMS-based polymers, several modification methods are employed such as cross-linking by hydrosilylation[7] and physicochemical modification using high-energy radiation.[8–12] These methods are favored by the presence of carbon–carbon double bonds, and it would be desirable to obtain a PDMS-based polymer having a controlled amount of them in its structure. This could be obtained by different methods, but the most efficient is, undoubtedly, the copolymerization reaction of the suitable siloxane monomers.

The most effective method to synthesize homogeneous (model) siloxane-based copolymers is the anionic ring-opening polymerization (AROP) of hexamethyl(cyclotrisiloxane) monomer (D_3).[13] AROP is a process that transforms a particular cyclic siloxane monomer into a linear siloxane polymer as a result of the cleavage of the Si—O—Si bonds in the monomer ring and the subsequent reformation of this bond in the polymer chain. Therefore, to synthesize a siloxane-based copolymer containing pendant double bonds on the main chain, one should perform the AROP between D_3 and the corresponding cyclic siloxane monomer having double bonds.[14–16]

In this work, we report preliminary results regarding the controlled AROP copolymerization of D_3 and

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(1,3,5,7)-tetramethyl-(1,3,5,7)-tetravinyl(cyclotetrasiloxane) (V_4) to obtain *model* copolymers by using classical anionic polymerization techniques. This methodology was employed taking into account our own experience in the controlled synthesis of homo and copolymers based on siloxanes.[17,18] V_4 was chosen because of its lower cost and higher availability than the corresponding cyclic trimer. According to the literature, AROP of V_4 is complicated because of the high stability of the V_4 ring, which needs an optimum reaction promoter [cryptands, dimethylsulfoxide (DMSO), or tetrahydrofuran (THF)] and strong basic nucleophiles as initiators, such as (trimethylsilyl)methyllithium (TMSML).[19] Since TMSML is an expensive initiator, we tested the use of lithium silanolates as initiators in this work, generated by the reaction of *sec*-butyl lithium (*sec*-Bu^-Li^+) and a suitable siloxane monomer. *sec*-Bu^-Li^+ was chosen as initiator because it can be easily prepared in the laboratory.[20] Classical anionic polymerization techniques were employed to synthesize the corresponding block copolymers. The most favorable experimental conditions to obtain these copolymers were explored. In addition, the gamma radiation effects over the synthesized materials were studied. To do this, samples of the obtained copolymers were irradiated with gamma rays and compared with irradiated samples of *model* PDMS (PDMS 0).[12] We hope that the results reported in this work will contribute to the knowledge of the controlled V_4 polymerization reaction, as well as the understanding of the gamma radiation effects over V_4 containing polymers. Apart from the homopolymerization of V_4[21] and a work dealing with the synthesis of PDMS stamps through a kit containing vinylated silica compounds,[22] no reports were found in the specific literature regarding the effects of gamma radiation on vinyl-containing silicon polymers.

EXPERIMENTAL

Materials

All materials were purified by standard anionic polymerization procedures in whole-sealed apparatus specially designed for each reagent.[20,23] Concentrated *n*-butyl lithium solution in hexane (*n*–Bu^-Li^+ 2M, Aldrich, Argentinian Branch, Buenos Aires) was employed as purging agent. The initiator, *sec*−butyl lithium (*sec*−Bu^-Li^+), was prepared in vacuum from *sec*-butyl chloride (Fluka, Argentinian Branch, Buenos Aires) and lithium metal (Fluka). Details of the synthesis can be found elsewhere.[20] The exact concentration of the initiator was determined twice: first, by titration[24] using phenyl acetic acid (Aldrich), and then, performing the homopolymerization of a known quantity of styrene monomer (Aldrich) (purified according to standard anionic polymerization techniques) by using an exact volume of the initiator solution.[20] THF (Cicarelli, Santa Fé, Argentina) was used as promoter of the polymerization reaction, whereas benzene (Dorwill) and degassed methanol (Química Industrial Bahiense SA, Bahía Blanca, Argentina) were used as the solvent and terminating agent, respectively. Ampoules of pure D_3 and V_4 (Sigma-Aldrich, Argentinian Branch, Buenos Aires) monomer solutions were obtained following conventional routines described elsewhere.[13] The accurate monomer concentration was determined by ^1H NMR analyses. All materials were employed taking into account the safety procedures for classical anionic polymerization techniques according to the most recent available literature.[20,23]

Copolymer synthesis

All manipulations were performed under high vacuum in glass Pyrex® reactors equipped with breakseals for the addition of the reagents and constrictions for removal of products at different stages of the reaction. A scheme of the polymerization apparatus used for the synthesis is shown in Figure 1. The broken ampoules of reagents were used to collect samples at different stages of the polymerization reaction. When it was necessary, additional ampoules were attached to the main polymerization apparatus. Constrictions and heat-sealing procedures by using a flame torch were employed to obtain these samples. A description of the synthetic procedure employed is described as follows.

The apparatus was connected to the vacuum line, checked for pinholes, flame-dried, and pumped for 20–30 min to remove volatile species. Then, 5 mL of n–Bu^-Li^+ were injected through the purge constriction (PC) into the purge section flask (b). The whole apparatus was pumped for an additional 30 min to remove the hexane and air inserted during the injection. Then, an appropriate amount of pure solvent (40–50 mL of benzene) was distilled and degassed over 45 min. The apparatus was removed from the vacuum line constriction (VLC), and was then washed with the diluted n–Bu^-Li^+ solution inside by gentle manual movements. After this washing, the solvent was distilled to the reactor, and the purge section was removed by heat-sealing the middle constriction (MC) leaving the clean reactor (a) with an appropriate amount of pure solvent, and ready for the copolymerization experiences.

Copolymers of D_3 and V_4 were synthesized by using AROP (high-vacuum techniques) and *sec*-Bu^-Li^+ as initiator. The different experimental conditions tested are described as follows:

i. Block copolymers of D_3–V_4 at different reaction temperatures (labeled PDVb T#, where # stands for the final reaction temperature). A D_3

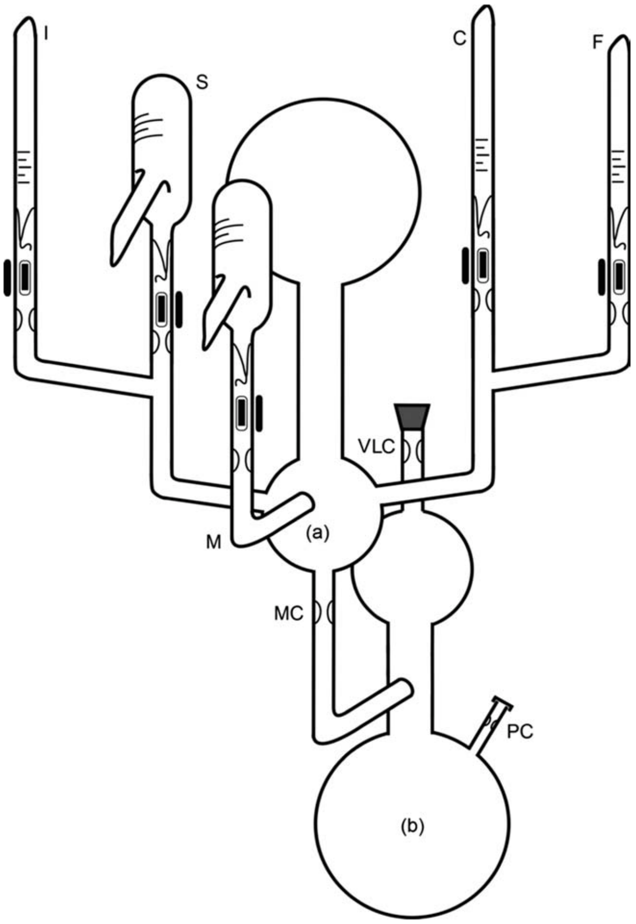


Figure 1 Polymerization apparatus for the synthesis of model V_4–D_3 copolymers. I: *sec*–Bu^-Li^+ ampoule; S: THF ampoule; M: D_3 monomer ampoule; C: V_4 monomer ampoule; F: Methanol ampoule; a: Reactor; b: Purge section; VLC: vacuum line constriction; MC: middle constriction; PC: purge constriction.

ampoule was first added into the reactor, and left to react with *sec*−Bu^-Li^+ during ≅ 20 h in hydrocarbon media (benzene) at room temperature (RT). Then, THF was added to promote D_3 polymerization. This step was done at RT for 21 h. After that, the reaction was continued for additional 3 h, at 50°C, to reach higher levels of conversion.[13] Subsequently, the V_4 monomer was added by breaking the break–seal of its ampoule. The crude reaction solution was divided in three fractions. One of these fractions was left to react at RT, the other at –15°C and the last one was placed on a water bath at 50°C. All experiences were finalized after 26 h of reaction. Up to our knowledge, the study of the copolymerization reaction of these monomers by sequential addition was never reported in the literature.

An experience was performed following a similar procedure but employing toluene instead of benzene as solvent to reach a higher temperature. The D_3 homopolymerization during 24 h at 50°C was followed by copolymerization with V_4 at 90°C during additional 26 h. An oil bath was used to reach the desired reaction temperature.

ii. Statistical copolymer of D_3–V_4 (PDVs T #). In this experience, D_3 together with V_4 were left to react with *sec*−Bu^-Li^+ in hydrocarbon media (benzene) at 50°C during 20 h. Then, THF was added to promote the copolymerization reaction at 50 or 80°C.

Samples of the resulting products were taken at different stages of the polymerization, and quenched with methanol. The sampling volume was around 1–2 mL of the reaction solution, and it was obtained by heat-sealing the constriction of the sampling ampoules. The final reaction product was precipitated in cold methanol and re-dissolved in pure THF. Finally, the remaining solvent was removed by using a rotatory evaporator. After this procedure, samples were dried at 40°C under vacuum until a constant weight.

Irradiation procedure

Samples of these copolymers were treated with gamma radiation at the Centro Atómico Ezeiza (CAE), Argentina, using a ^{60}Co source at RT. Samples were enclosed in sealed glass vials, which were evacuated under a conventional vacuum-line equipped with a mechanical oil pump, a mercury diffusion pump, liquid nitrogen traps, upper and lower glass tube rigs, and stopcocks during 4 h. The gamma radiation doses applied to the polymers were 3, 6, and 30 kGy, at a dose rate of 10 kGy/h. The applied doses were measured with a Red Perspex dosimeter.

To analyze the effect of vinyl double bonds on the irradiation procedure, the changes observed in the irradiated copolymers were compared with the results obtained for a *model* PDMS homopolymer (PDMS 0) with no vinyl content. This homopolymer was synthesized and irradiated in similar conditions to those reported for the copolymers synthesized in this article. For more details, see Ref. 12.

Physicochemical characterization

Size exclusion chromatography (SEC)

The different polymer samples were characterized by SEC on a system built with a Waters 515 HPLC pump and a Waters model 410 differential refractometer detector, equipped with four PLGel columns with 10-μm bead size and 500, 10^3, 10^4, and 10^6 Å porosity, respectively. The solvent employed was toluene at RT flowing at a rate of 1 mL/min. The injection volume was 200 μL, and polystyrene (PS) standards were used for calibration. The Mark-Houwink calibration constants used for each polymer were $K_{ps} = 3.45 \times 10^{-4}$, $\alpha_{ps} = 0.62$ for PS, and $K_{pdms} = 2.0 \times 10^{-4}$, $\alpha_{pdms} = 0.66$ for PDMS.[25]

Nuclear magnetic resonance (^{1}H and ^{29}Si−NMR)

The NMR spectra of the obtained copolymers were recorded on a Bruker ARX-300 instrument using deuterated chloroform (Aldrich) as solvent. The molar fraction of each monomer in the resulting copolymer was obtained through the ratio of the integrated areas of methyl to vinyl ^{1}H signals.

Fourier transform infrared (FTIR) spectroscopy

Chemical changes in the irradiated polymer were followed by FTIR, using a Micro-FTIR Thermo Nicolet equipment working on reflection mode. Spectra were obtained from a drop of the treated materials taken without further conditioning from the containers where they had been irradiated. The FTIR spectra were recorded at 4 cm^{-1} resolution over the 4000–400 cm^{-1} range using an accumulation of 20 scans and air as the background.

Gel extraction

Sol–gel analysis was performed to determine the gel fraction for the irradiated samples that received doses above the gel point. For this purpose, samples were weighed and extracted five times with toluene at RT for a week. These conditions assure complete extraction of the soluble fraction. The percentage mass of the gel fractions of the whole unextracted mass of the samples were calculated.

RESULTS AND DISCUSSION

Experimental conditions for the synthesis of D_3–V_4 copolymers

Before the copolymerization experiences, we tried to perform the AROP of V_4 monomer by using *sec*−Bu$^-$Li$^+$ as initiator following the experimental conditions used in our previous studies regarding the controlled AROP of D_3.[13] In our first attempt, we employed an equilibration reaction between V_4 and *sec*−Bu$^-$Li$^+$ without any promoter during 20 h followed by the addition of the promoter (THF) to achieve the monomer polymerization. Although we tested different temperatures (RT and 50°C) for both stages, no polymer formation was observed. The SEC chromatographs of the crude reaction product showed only a peak, which corresponds to the unreacted V_4 monomer. These results confirm that the stability of the V_4 ring toward *sec*−Bu$^-$Li$^+$ is strong, even at high temperature. In view of these results, we conclude that the main difference between *sec*−Bu$^-$Li$^+$ and others expensive or complex synthesized initiators, is the effect of the localized negative charge. In the particular case of TMSML, the negative charge is more stabilized on (trimethylsilyl)methyl anion because of the more positive inductive effect of the trimethylsilyl group over the methyl carbanion. Consequently, a strong nucleophile is generated, which would be able to attack the stable siloxane ring.[26]

Despite TMSML initiator, cyclic siloxanes with four repeated units can be homopolymerized by using strong bases or nucleophiles such as carbenes[27] or silazyl-lithium initators[28] and strong inorganic, organic, or organometallic bases.[29] Following this idea, we rationalized that the use of an "oxy" initiator would favor the stabilization of the negative charge over the base. Although the reactivity of the anionic active center is proportional to its basicity, the silanolate can be used to release the high ring strain of cyclic siloxanes.[30,31] Moreover, another advantage of these species is that they are not reactive enough to add to carbon–carbon double bonds[31] (present in the V_4 monomer), and a suitable nucleophile would be generated which might favor the ring-opening reaction of the higher cyclic monomer.[28] As it is reported in the literature,[32,33] "oxy" initiators can be easily prepared by reacting *sec*−Bu$^-$Li$^+$ and D_3 monomer. In the absence of any polymerization promoter, this reaction produces lithium silanolates ($R(CH_3)_2SiO^-\ Li^+$) that may be used as initiators for living anionic polymerizations.[34] The effect of these initiating species over the AROP of V_4 was explored for different experimental conditions. The results obtained in all the experiences performed are summarized in Table I.

The first four rows of Table I report the results obtained from the sequential polymerization of D_3 and V_4. According to these results, at low temperatures, there is no insertion of V_4 monomer. As temperature was raised, so did V_4 conversion. A similar behavior with respect to the temperature was observed by Zhang et al.[27] for the anionic homopolymerization of D_4. However, under these circumstances, the V_4 incorporation in the resulting block-copolymer is still low.

The best results from the point of view of V_4 incorporation were obtained when both monomers were mixed together, since higher levels of conversion were found (18.14 mol % at 80°C). These results suggest that the propagation step is kinetically favored in this situation. This could be explained taking into account that the initial living silanolates may have less steric hindrance, and also a better reactivity toward V_4 than the living lithium

TABLE I
Synthesis of D_3–V_4 Copolymers: Experimental Results

Polymer	M_n (Da)	PD	T^a (h)	T^a (°C)	V_4 ^{b} (mol %)
PDVbT-15	32,720	1.07	26	−15	–
PDVb T20	36,470	1.06	26	20	1.54
PDVb T50	37,500	1.14	26	50	3.7
PDVb T90	15,730	1.20	26	90	3.63
PDVs T50	79,400	1.29	48	50	16.34
PDVs T80	76,500	1.08	31	80	18.14^c

[a] Time and temperatures as taken from the moment of V_4 incorporation.
[b] Calculated by ^{1}H NMR.
[c] So as to compare, Yu et al.[17] found molar percentage incorporations from 10 to 26% of V_4, when using TMSML as initiator and DMSO as promoter of reaction.

macrosilanolate chains of the PDVb synthesis. Apparently, the mixing of both monomers improves the efficiency of the initiator, providing polymers with higher V_4 content. Such V_4 incorporation is similar to that of those previously reported in the literature by using TMSML[16] but in this case with a more common initiator. At this point, it is worth to mention that the polydispersity (PD) indexes obtained in almost all the experiences were low demonstrating that well-defined copolymers were obtained. The chromatograms shown on Figure 2 illustrate this fact. The molecular characterization results for the copolymers synthesized in this work can be favorably compared with those obtained by Yu et al.,[19] Chojnowski and coworkers,[14] and Bauer et al.,[16] that reported higher PD indexes.

On the other hand, it should be mentioned that the molar mass of the PDMS block obtained at 90°C by using sequential addition of monomers and toluene as solvent (solvent chosen to reach a higher reaction temperature) was three times shorter than the theoretical molar mass expected. This fact can be explained taking into account the occurrence of rearrangement reactions between sec−Bu^-Li^+ with toluene, as it is reported in the scientific literature.[26] These rearrangements reactions could have also affected the PD index of the resulting copolymers, since it was higher than those obtained at lower temperatures. It is worth to mention that the V_4 incorporation at this temperature is similar to that obtained at 50°C by using sequential addition and benzene instead of toluene as solvent, but in this last case, the resulting copolymer is close to be a model copolymer. Finally, we should also mention that the "higher" PD index obtained for the statistical copolymer at 50°C by using an initial mixture of monomers could be attributed to unforeseen experimental conditions, or to an inadequate purification of the monomers employed in this particular synthesis.

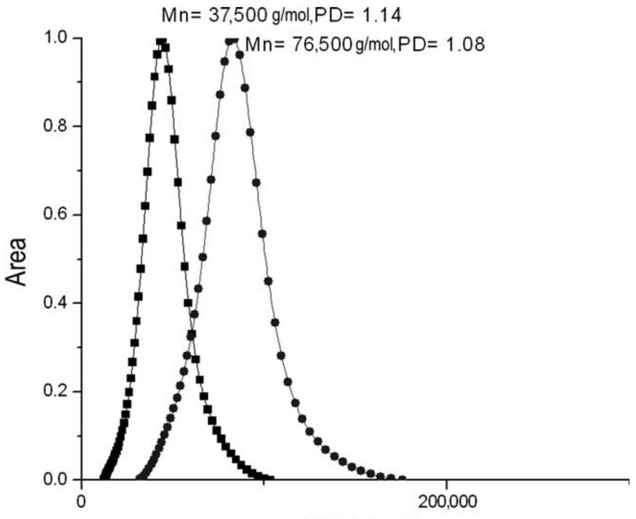


Figure 2 SEC chromatograms for D_3–V_4 copolymers: ● PDVs T80, ■ PDVb T50.

NMR analysis

The higher incorporation of V_4 obtained in statistical copolymers is clearly demonstrated by the comparison of the ^{1}H NMR and ^{29}Si NMR spectra of the two different types of copolymers synthesized in this work. Figure 3 displays the normalized ^{1}H NMR spectra in the vinyl region of the different copolymers at 5.85 ppm. For PDVs T80 [Fig. 3(a)], a higher incorporation of V_4 with respect to PDVb T50 [Fig. 3(b)] or PDVb T20 [Fig. 3(c)] is observed.

Moreover, the ^{29}Si NMR spectra in Figure 4 display the different structures arrangements of both copolymers. The statistical copolymer [Fig. 4(a)] shows two different groups of assignments at −21.5 and −35 ppm, due to the different functional groups attached to de Si nuclei. That is, the silicon NMR signal is shifted to −35 ppm when Si is bonded to a vinyl group and to −21.5 ppm when the Si nucleus is bonded to methyl groups. The statistical arrangement is confirmed through the peaks that arise at those chemical shifts, and are in agreement with the data reported by Yu et al.[19] These signals are related

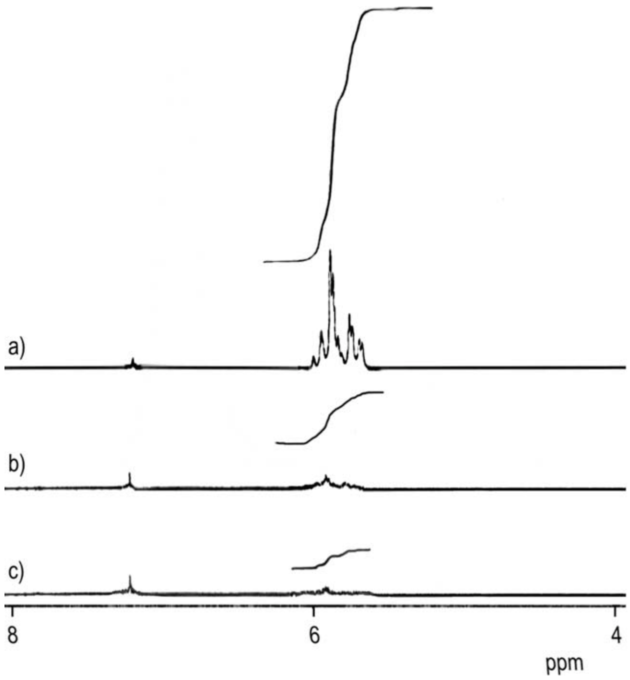


Figure 3 ^{1}H NMR spectra for D_3–V_4 copolymers: (a) PDVs T80, (b) PDVb T50, and (c) PDVb T20.

to the statistical sequences shown in Figure 4, where D is a dimethylsiloxane unit and V is a vinylmethylsiloxane one.

The spectrum shown on Figure 4(b) corresponds to the block copolymer. A well-established signal for a large sequence of dimethylsiloxane units (DDDDD) at −21.5 ppm of the predominant siloxane block can be observed. However, a minor peak corresponding to the sequence DVDDD is located near this peak. In addition, a couple of small peaks in the Si-vinyl bond area around −35 ppm are observed. This signal may be assigned to sequences of VVVVV and VVVDV. The appearance of this last sequence and DVDDD may be explained as follows. As it is reported in the literature,[13] the D_3 polymerization does not reach exactly the 100% of conversion, and some D_3 monomer is left in the reactor. This D_3 monomer could react with the entering V_4 monomer, which is in excess. If this reaction occurs, statistical VVVDV or DVDDD sequences may be observed. Summarizing, the block copolymer really behaves as a large PDMS block (nearly 95% of the copolymer), and then the rest of the chain may be half a V_4 block, and the other half a statistical section between D_3 and V_4 monomers.

Gamma radiation effects over D_3–V_4 copolymers

The V_4 containing copolymers were also exposed to gamma radiation in vacuum to compare the effects of cross-linking obtained in these copolymers with those achieved on a *model* PDMS homopolymer.[12]

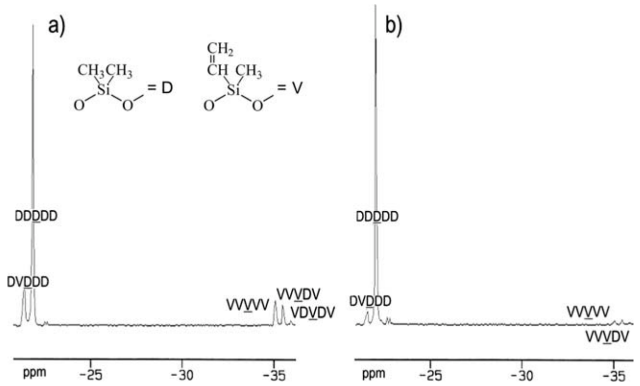


Figure 4 ^{29}Si NMR spectra for D_3–V_4 copolymers: (a) PDVs T80 and (b) PDVb T50.

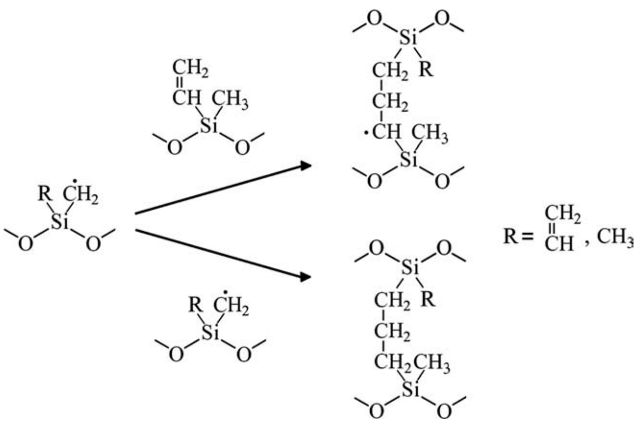
The data obtained with SEC and gel extraction are shown in Table II. In all cases, molar masses increase with dose as a consequence of cross-linking reactions due to gamma radiation. At the same time, these radioinduced reactions produce an enlargement in the PD indexes. These results are in accordance with those reported in the literature for irradiated PDMS polymers in vacuum.[11,12] At a certain dose within the range of doses explored in this work, the degree of cross-linking was high enough to reach the gel point generating a three-dimensional network. After this, the amount of gel raises by attaching more radioinduced macroradicals to its structure. Nevertheless, other macromolecules do not attach to the gel. These molecules constitute the soluble fraction of the sample, which was extracted and characterized by SEC. The results from the soluble fraction are typed in bold in Table II to distinguish them from the pre-gel data. As the soluble chains with higher molecular mass are more susceptible to form macroradicals that eventually will join the gel fraction, the average molecular weight of the soluble fraction decays with the magnitude of the radiation dose. This is the reason why the weight average molar mass (M_w) and the PD index of PDVs T80 with 6 kGy is lower than that of 3 kGy.

TABLE II
Increase of Weight Molar Mass and Gel Content in the Irradiated Copolymers Compared with a *Model* PDMS

Polymer	D (kGy)	M_w (Da)	PD	% Gel
PDMS 0	0	49,000	1.06	–
	10	61,400	1.34	–
	35	124,000	2.85	–
	60	285,200	4.66	–
	70	**399,900**	**3.31**	**8.1**
PDVb T50	0	42,750	1.14	–
	6	111,900	3.13	–
	30	**434,600**	**5.34**	**6.5**
PDVs T80	0	82,620	1.08	–
	3	**240,000**	**2.76**	**13.9**
	6	**113,760**	**1.2**	**25.5**

The effect of vinyl groups during the cross-linking mechanisms of the irradiation process was also followed by FTIR analysis. Figure 5 shows the FTIR spectra for the unirradiated (PDVs T80) and irradiated (PDVs T80 # kGy) statistical block copolymer in the stretching region between 2800 and 3100 cm^{-1}. There are two bands related to methyl ($-CH_3$) groups at 2900 and 2960 cm^{-1}, and also two bands related to the vinyl ($-CH=CH_2$) groups at 3017 and 3057 cm^{-1} on the original copolymers.[21] On irradiation, two other bands arise near 2850 and 2920 cm^{-1} that can be related to the formation of methylene ($-CH_2-$) groups. Scheme 1 shows two possible reactions that may explain the appearance of these methylene groups. The first implies the reaction between a macroradical and a vinyl group. The result is a greater macroradical containing a $-CH_2-CH_2-$ group that still can react with another radical site. The other reaction is a common H-type cross-linking between two lateral methylene functionalized macroradicals ($R-CH_2^{\cdot}$).[11,12] This reaction increases the original molar mass of each chain without leaving a reacting radical site.

The copolymers containing vinyl groups cross-link more efficiently under gamma radiation, as it was expected. For these copolymers, the increase in M_w with dose is faster, and the gel content due to cross-linking reactions is reached at lower doses than for PDMS 0. This can be deduced by comparing the gel content measurements achieved on pure PDMS 0 and on PDVb T50 reported on Table II. PDVb T50 irradiated with 30 kGy contains 6.5% gel while PDMS 0 needs almost the double dose to reach 8% gel. At this point, it is worth to mention that PDMS 0 and PDVb T50 have similar M_w values, and that cross-linking reactions are more noticeable in the statistical copolymer than on the block copolymer. There are two reasons that may explain this fact. One is that PDVs T80 has almost the double of M_w value. Consequently, this material needs half of the irradiation energy needed for PDVb T50 to reach the same level of cross-linking. But the statistical copolymer also has four times $-CH=CH_2$ than the block copolymer, and this variable is the main cause of the cross-linking differences between both copolymers. Less than 3 kGy are needed to reach almost 14% gel in PDVs T80, while less than half this value is reached with the irradiation at 30 kGy in the block copolymer. Moreover, if one compares gel amount obtained by irradiating the statistical copolymer with almost 20% of $-CH=CH_2$ with that of the PDMS 0 homopolymer, to attain a 10% gel >20 times dose is needed for the homopolymer. The above-discussed results clearly show that a PDMS-based material with enhanced mechanical properties may be obtained at lower radiation doses. In such a sense, the D_3–V_4 copolymers obtained in this work may provide suitable biomedical materials that require the minimum doses of radiation to reach gelation. These doses are in the order of those commonly used for sterilization purposes.



Scheme 1 Possible reactions that may explain the appearance of the methylene groups.

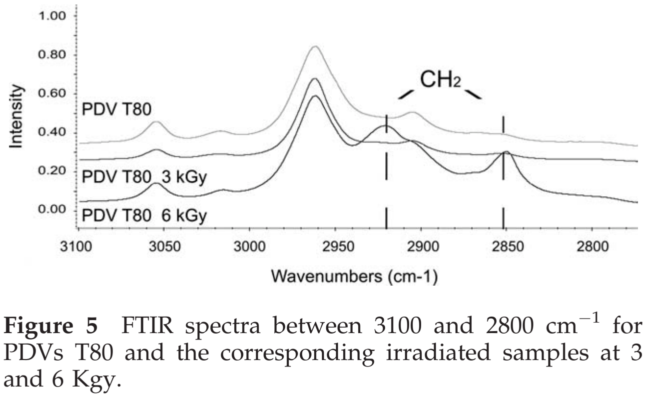


Figure 5 FTIR spectra between 3100 and 2800 cm^{-1} for PDVs T80 and the corresponding irradiated samples at 3 and 6 Kgy.

CONCLUSIONS

V_4 polymerization was promoted by using living silanolates to open the stable V_4 ring. By using this strategy, D_3–V_4 copolymers were obtained. These silanolates were obtained by the reaction of suitable siloxane monomers and *sec*$-Bu^-Li^+$. Higher V_4 incorporation was reached when D_3 and V_4 monomers were mixed together in the reaction media, and *sec*$-Bu^-Li^+$ was subsequently added. Apparently, the lithium silanolate generated when both monomers are mixed behaves as a strong base with less steric hindrance, which allows the AROP of V_4 promoted by THF. By using this strategy, a *model* statistical block copolymer with 18.14 mol % of V_4 was obtained (PD = 1.08). The higher V_4 incorporation in the synthesized copolymers was used to study the gamma radiation effects over these vinyl-functionalized polysiloxanes. Irradiation of the copolymers with higher V_4 content showed that higher molar masses and gel content were obtained at smaller doses compared with a *model* PDMS homopolymer with similar molar masses. This result may be of fundamental importance if a biomedical cross-linked rubber-type PDMS is needed at earlier doses of sterilization.

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