

Radiation-induced gel formation in a siloxane block copolymer in the presence of octamethylcyclotetrasiloxane

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The grafting of the open-chain radicals of octamethylcyclotetrasiloxane (D_4) to a block copolymer matrix is responsible for gelation in the test system under γ -irradiation at 10–40 kGy, as evidenced by viscometric, IR-spectroscopic and X-ray diffraction data.

Octamethylcyclotetrasiloxane (D_4) is one of the most extensively studied chemicals used primarily to make other silicone materials. During this manufacturing process, almost all of the substance is consumed, with only a minor amount of D_4 remaining. Moreover, an inevitable impurity of D_4 results from the synthesis of siloxane block copolymers (BCPs) with specified properties.^{1,2} However, this impurity in an unbound state may dramatically impair the performance characteristics of the resulting materials.

Previously, Pankratova with co-authors^{2–6} found that D_4 molecules were almost completely consumed under the action of ionizing radiation on the mixtures of BCPs with D_4 at absorbed doses of 40 kGy or lower. The irradiation of BCPs at these doses can be efficiently used for binding D_4 molecules in order to obtain optimum performance characteristics of the materials. Molecular hydrogen, methane, ethane and a gel formed by $\equiv\text{Si}-\text{CH}_2-\text{Si}\equiv$ and $\equiv\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ crosslinks in the polydimethylsiloxane (PDMS) blocks of BCPs were the main radiolysis products^{1–6} upon γ -irradiation to high doses of >100 kGy. The formation of these crosslinks considerably changed the physical properties of the BCPs, including thermal properties. According to X-ray diffraction data, the intensity of a reflection from the PDMS moiety of irradiated BCP macromolecules strongly decreased.⁵ Previous studies concerning gel formation in siloxane BCPs were performed at doses of 50–70 kGy or higher because polyorganosiloxanes are considered radiation-stable polymers.¹

As found by chromatography and NMR spectroscopy, the γ -radiolysis products of a mixture of cyclic D_x monomers, including D_4 , were higher molecular weight cyclic monomers and polymers.^{5–9} Three hypothetical mechanisms have been proposed to explain polymer formation based on the participation of silicenium ions,^{5,6,8,9} labile $\text{Me}_2\text{Si}=\text{O}$ species^{10,11} and D_4^+ radical cations.^{8,9} However, these hypotheses have not been tested experimentally.

Here, we report experimental results concerning radiation-chemical transformations in a siloxane BCP with the general formula $\{\text{Me}_2\text{SiO}\}_m\{\text{PhSiO}_{1.5}\}_a\{\text{PhSi(O)OH}\}_{1-a}\}_n$, where $m:n = 20:5$, containing ~7 mol% D_4 . The test samples as films 100–150 μm in thickness were prepared from a 30% solution of the 20:5 siloxane BCP containing 7 mol% D_4 in toluene

by casting onto a substrate. The films were dried in air at 25 °C and then heated at 120 °C for 3 h. The samples were irradiated on a K-120000 ^{60}Co γ -radiation source at a dose rate of 0.01 MGy h^{-1} in ampoules evacuated to a residual pressure of 10 Pa. In the course of irradiation, the sample temperature was no higher than 40 °C. The evaporation of D_4 from the samples was not detected in preliminary experiments performed under the specified conditions.

To determine the concentration of a gel fraction, the weighed portions of γ -irradiated samples were treated with toluene, and the gel was dried at 120 °C to constant weight. To measure the dynamic viscosity of both parent and irradiated siloxane BCPs containing D_4 , we prepared samples as cylinders 20 mm in diameter and ~1.5 mm in height. These samples were irradiated in specially designed ampoules, where the test samples did

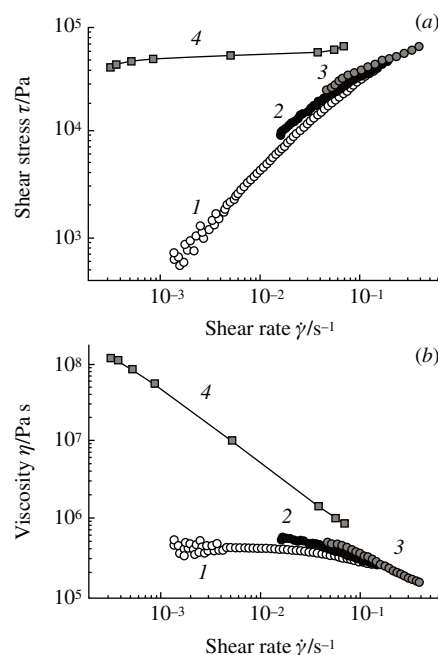


Figure 1 Characteristic viscosity of the 20:5 BCP containing 7 mol% D_4 after γ -irradiation at (1) 0, (2) 10, (3) 30 and (4) 70 kGy: (a) shear stress and (b) viscosity.

not undergo deformations. The characteristic viscosity of the materials was determined by rotational viscometry using a HAAKE RheoStress 1 instrument (Germany) in the controlled-rate mode with a parallel plate sensor system (20 mm diameter and 0.5 mm gap) at 90 ± 0.1 °C.

The X-ray diffraction studies were performed at room temperature on a Thermo ARL X'TRA diffractometer (United States–Switzerland) over the 2θ range of 3–40° at a step of 0.02° and an exposure of 1 s at each point (the interplanar spacings in the test samples were calculated using the Bragg equation). The IR spectra of BCP samples as pellets with KBr were recorded on a Bruker Tensor 27 FT-IR spectrometer over a range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} .

We found that the formation of a gel was almost complete at doses of ~10 kGy (the gel fraction content was about 20% upon the complete conversion of D_4). The dynamic viscosity of the BCP samples containing D_4 irradiated at 0, 10 and 30 kGy was almost the same, whereas a dramatic increase in the viscosity occurred as the absorbed dose was increased to 70 kGy (Figure 1). Thus, the irradiation of the BCP + D_4 system at low doses of 10–40 kGy resulted in the grafting of D_4 to BCP molecules with an insignificant change in the dynamic viscosity of the samples. Upon the γ -irradiation of the test system at high doses (70 kGy or higher), which occurred in the absence of D_4 (D_4 traces were completely consumed at 30–40 kGy), another gelation mechanism came into play to strongly affect the dynamic viscosity of the samples.

A comparison between the X-ray diffraction patterns of the unirradiated and γ -irradiated (30 kGy) BCP samples containing D_4 indicated that reflections due to PDMS and polyphenylsilsesquioxane (PPSSO) blocks ($2\theta = 7.2$ and 12.2° , respectively) remained almost unchanged upon γ -radiolysis (Figure 2). Thus, the initial ordering of siloxane chains in the blocks of the BCP remained intact at low γ -radiation doses. It is well known that PDMS chains form spatial coils.¹² At γ -radiation doses of 100 kGy or higher, the reflection from the PDMS blocks dramatically decreased with a simultaneous small decrease in the reflection from the PPSSO blocks. Evidently, gelation under the γ -irradiation of the BCP in the absence of D_4 resulted from the formation of crosslinks in the PDMS blocks of the copolymer.^{1–6} We believe that the γ -irradiation of BCP + D_4 samples at 50–100 kGy resulted in gel formation due to the crosslinking of PDMS blocks, including those modified with D_4 molecules, in the copolymer. This type of crosslinking can dramatically increase the dynamic viscosity of the samples upon γ -irradiation at doses higher than 50 kGy. It is likely that, under these conditions, γ -irradiation can activate

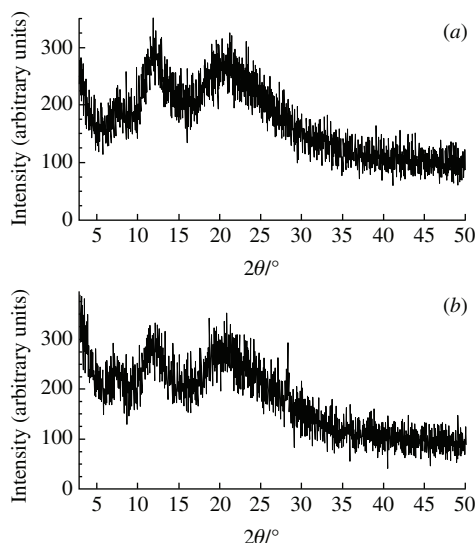


Figure 2 X-ray diffraction patterns of the 20:5 BCP containing 7 mol% D_4 : (a) unirradiated and (b) irradiated at 30 kGy.

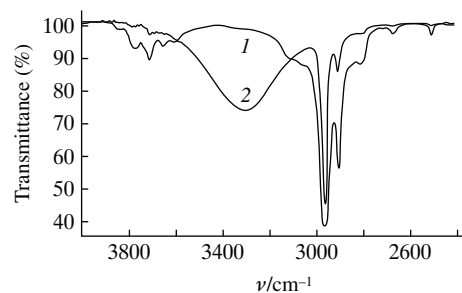


Figure 3 IR spectra of (1) the unirradiated 20:5 BCP containing 7 mol% D_4 and (2) the gel fraction separated from the 20:5 BCP containing 7 mol% D_4 after irradiation at 50 kGy.

both the PDMS blocks and the grafted molecules of D_4 for the formation of crosslinks. The radical products of the γ -radiolysis of PDMS and BCPs (at doses higher than 100 kGy) have been studied previously using EPR spectroscopy.^{13–16} Based on kinetic data, Panov *et al.*¹³ assumed that methyl radicals are the primary radical species in the BCPs. Then, these methyl radicals abstract hydrogen atoms from the methyl groups of the BCP to form $\equiv\text{Si}-\text{CH}_2$ radicals, which combine to form crosslinks.

Thus, we believe that D_4 molecules dissolved in the PDMS moiety of a BCP are activated by indirect ionization in a BCP matrix under γ -irradiation at 10–40 kGy and the radiolysis of D_4 results in ring opening with the formation of an open-chain radical. This is evident by the formation of OH groups, which were detected in the IR spectra of the irradiated BCP samples. An intense absorption band at ~ 3428 cm^{-1} (Figure 3) was attributed to $\nu_{\text{as}}(\text{OH})$. Gel formation at doses of 10–40 kGy is due to the grafting of the open-chain radicals of D_4 to the dimethylsiloxane units of PDMS blocks.

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