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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 $\equiv$Si–CH$_2$–Si$\equiv$ and $\equiv$Si–CH$_2$–CH$_2$–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 $Me_2Si{=}O$ species[10,11] and $D_4^{+\cdot}$ 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 $\{Me_2SiO\}_m\{[PhSiO_{1.5}]_a[PhSi(O)OH]_{1-a}\}_n$, 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

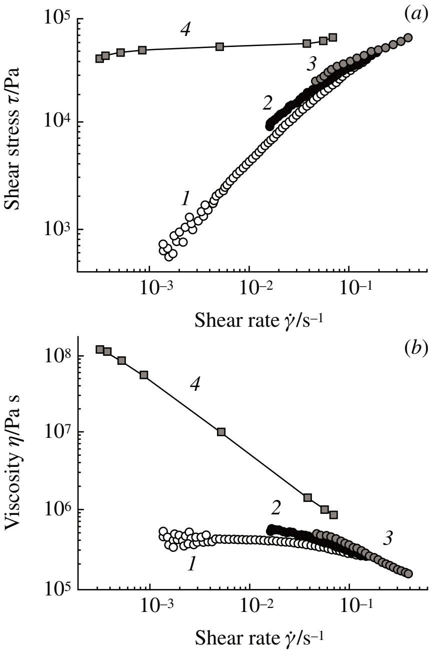

Figure 1 Characteristic viscosity of the 20:5 BCP containing 7 mol% D_4 after γ-irradiation at (*1*) 0, (*2*) 10, (*3*) 30 and (*4*) 70 kGy: (*a*) shear stress and (*b*) viscosity.

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 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 $\equiv$Si–CH$_2^{\bullet}$ radicals, which combine to form crosslinks.

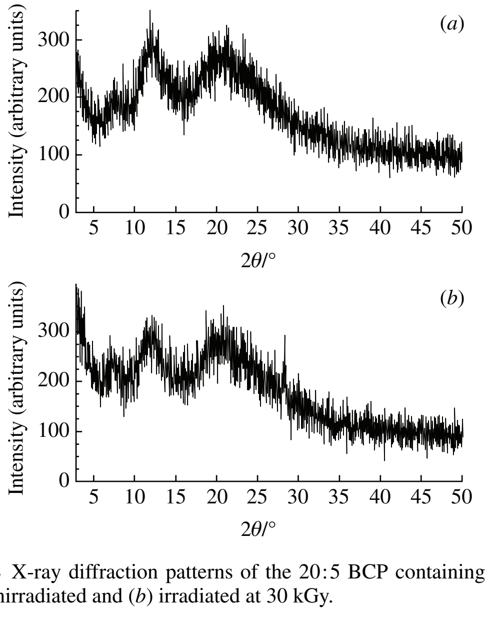

Figure 2 X-ray diffraction patterns of the 20:5 BCP containing 7 mol% D_4: (*a*) unirradiated and (*b*) irradiated at 30 kGy.

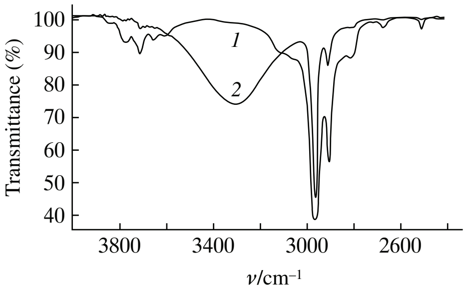

Figure 3 IR spectra of (*1*) the unirradiated 20:5 BCP containing 7 mol% D_4 and (*2*) the gel fraction separated from the 20:5 BCP containing 7 mol% D_4 after irradiation at 50 kGy.

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 ν_{as}(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.

References

1 V. V. Lyashevich, L. N. Pankratova, O. Yu. Panov, E. R. Klinshpont, B. G. Zavin and A. Yu. Rabkina, *Khim. Vys. Energ.*, 1991, **25**, 238 [*High Energy Chem.* (*Engl. Transl.*), 1991, **25**, 199].

2 L. N. Pankratova, M. G. Zhizhin and L. T. Bugaenko, *Khim. Vys. Energ.*, 2005, **39**, 438 [*High Energy Chem.* (*Engl. Transl.*), 2005, **39**, 382].

3 L. N. Pankratova, I. I. Dubovik, A. Yu. Rabkina and L. T. Bugaenko, *Khim. Vys. Energ.*, 2003, **37**, 470 [*High Energy Chem.* (*Engl. Transl.*), 2003, **37**, 400].

4 L. N. Pankratova, N. V. Mazurina, A. Yu. Rabkina, L. I. Kuteinikova and L. T. Bugaenko, *Khim. Vys. Energ.*, 1998, **32**, 338 [*High Energy Chem.* (*Engl. Transl.*), 1998, **32**, 301].

5 L. N. Pankratova, V. S. Tikhomirov, E. S. Obolonkova and L. T. Bugaenko, *Khim. Vys. Energ.*, 2002, **36**, 13 [*High Energy Chem.* (*Engl. Transl.*), 2002, **36**, 10].

6 L. N. Pankratova, M. G. Zhizhin and N. V. Novoselova, *Khim. Vys. Energ.*, 2007, **41**, 438 [*High Energy Chem.* (*Engl. Transl.*), 2007, **41**, 339].

7 A. N. Lazarev, I. S. Ignat'ev and T. F. Tenisheva, *Kolebaniya prostykh molekul so svyazyami Si–O* (*Vibrations of Simple Molecules with Si–O Bonds*), Nauka, Leningrad, 1989 (in Russian).

8 D. M. Naylor, V. T. Stannet and A. Deffieux, *Polymer*, 1991, **32**, 1084.

9 D. M. Naylor, V. T. Stannet, A. Deffieux and P. Sigwalt, *Polymer*, 1994, **35**, 1764.

10 R. Withnal and L. Andrews, *J. Am. Chem. Soc.*, 1986, **108**, 8118.

11 N. N. Makarova, L. M. Volkova, E. V. Matukhina, A. V. Kaznacheev and P. V. Petrovskii, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1526 (*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1610).

12 M. G. Voronkov, V. P. Mileshkevich and Yu. A. Yuzhelevskii, *Siloksanovaya svyaz'* (*Siloxane Bond*), Nauka, Novosibirsk, 1976 (in Russian).

13 O. Yu. Panov, L. N. Pankratova, V. I. Fel'dman and V. N. Belevskii, *Vysokomol. Soedin., Ser. A*, 1995, **37**, 600 (in Russian).

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