Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2011, **21**, 157–159

Mendeleev Communications

Kinetics of decay of methyl radicals in irradiated dimethylsilanediol and polymethylsiloxanes

Lidiya N. Pankratova,*[a] Elizaveta V. Saenko,[a] Vladislav L. Bugaenko[b] and Valentin V. Makhlyarchuk[c]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 932 8846; e-mail: pankratova@rc.chem.msu.ru*

[b] *Institute for Theoretical and Experimental Physics, 117218 Moscow, Russian Federation*

[c] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2011.04.016

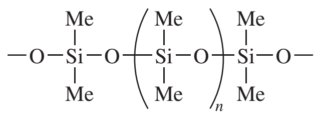
As found by EPR spectroscopy, the decay of methyl radicals in the test compounds upon X-ray irradiation at 77 K resulted from radical-center transfer rather than radical combination; the rate constants of decay of methyl radicals in polydimethylsiloxane and its structural analog dimethylsilanediol were almost the same.

The radiation chemistry of polyorganosiloxanes is of considerable current interest due to the widespread use of these materials in various branches of industry (including aerospace industry), medicine, *etc*.[1,2] The radiolysis of polyorganosiloxanes has been studied.[3] Methane, ethane and hydrogen have been identified in the gaseous radiolysis products of polydimethylsiloxane (PDMS).[4] The EPR spectra of PDMS irradiated at 77 K in a vacuum have been described.[5] The formation of stable $\equiv Si\dot{C}H_2$ radicals in PDMS has been detected.[6,7] A hypothesis has been proposed[5] that methyl radicals decayed in combination reactions by a diffusion mechanism and the kinetics of radical combination in PDMS was stepwise. More recently, it has been found[8] that methyl radicals decayed at 77 K as a result of radical-center transfer rather than combination. The decay of methyl radicals in siloxane block copolymers occurred in the same dimethylsiloxane microphase where they were formed. Therefore, the migration of methyl radicals from the parent microphase is unlikely, and the decay kinetics of methyl radicals in siloxane block copolymers is hindered because of the kinetic nonequivalence of chemically identical centers.

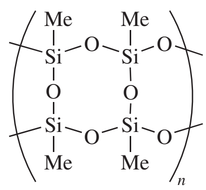
Pankratova and Bugaenko,[9] who studied the radiolysis of siloxane block copolymers using UV spectrometry, found that charge or excitation-energy transfer along a siloxane chain was strongly hindered. Lyashevich *et al*.[10] examined the irradiation of siloxane block copolymers containing PDMS and polyphenylsilsesquioxane (PPSQ) blocks and described a stabilizing effect of the rigid PPSQ block on the block copolymer as a whole. This effect was due to the presence of phenyl groups in a polymer or polymer blend regardless of the occurrence of siloxane cross-links. However, it remained unclear whether methyl radicals decayed within the same monomer unit.

The aim of this work was to study the decay kinetics of methyl radicals in X-ray irradiated PDMS, polymethylsilsesquioxane (PMSQ) and dimethylsilanediol (DMSD). To ascertain the effect of the structure and composition of polymethylsiloxanes on the rate of decay of methyl radicals, PMSQ with a ladder structure and the general formula $\{[Me_2SiO]_a[MeSiO_{1.5}(OH)]_b\}$, where $a{:}b = 2{:}1$, containing 2.2% OH groups was used for comparison.[†] At room temperature, the PDMS (SKTa grade) is a colorless viscous liquid and the PMSQ is a powder readily soluble in toluene.

[†] The test materials were synthesized at the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (Moscow).



PDMS



PMSQ

According to NMR spectroscopic data, the PMSQ is a non-cross-linked polymer.

Crystalline DMSD, a structural analog of the monomer unit of PDMS, was synthesized in accordance with a published procedure[13] immediately before measurements. Since the crystal lattice parameters of DMSD, which is highly hygroscopic, are unavailable, we calculated its structural characteristics. The molecular geometry of DMSD was determined using Gaussian 03 based on a full optimization by the MP2 method with the cc-pVTZ basis set (Figure 1). The molecular structure parameters of DMSD are very close to the characteristics of a monomer unit in PDMS (Table 1).

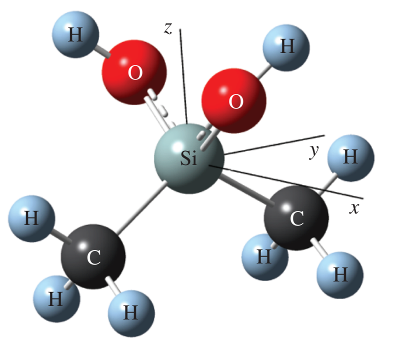


Figure 1 Molecular structure of DMSD calculated by the MP2 method.

Table 1 Selected bond lengths and bond angles in PDMS[14] and DMSD molecules.

Molecule	Bond lengths (Å)		Bond angles (°)		
	Si–O	Si–C	C–Si–C	O–Si–O	Si–O–Si
PDMS	1.63	1.9	109.5	110	145
DMSD	1.662	1.872	114.03	112.44	—

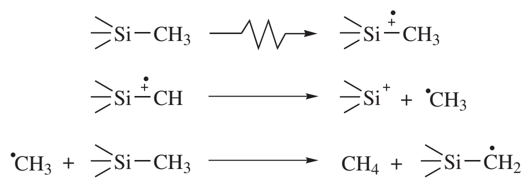
© 2011 Mendeleev Communications. All rights reserved.

Figure 2 EPR spectra of PDMS (*a*) immediately after irradiation and (*b*) 5 h after irradiation, PMSQ (*c*) immediately after irradiation and (*d*) 17 h after irradiation and DMSD (*e*) immediately after irradiation and (*f*) 5 h after irradiation.

The samples for EPR-spectroscopic measurements were evacuated in ampoules of SK-4B glass, which gave no EPR signal upon irradiation, to a residual pressure of 10 Pa and then irradiated with X-rays at 77 K using a 5BKhV6-W tube (30 keV) for 3 min at a dose rate of 10 kGy/h. Then, the EPR spectra were measured on an X-band EPR radiospectrometer with a high-frequency modulation of 0.15 mT at a microwave power of 0.2 mW. The test materials were solids under these experimental conditions. The EPR spectra of PDMS and DMSD were measured at regular intervals for 5 h after the termination of irradiation, and the spectra of PMSQ were measured for 7 h after the termination of irradiation. The EPR spectrum of PDMS recorded 17 h after the completion of irradiation did not contain lines attributed to methyl radicals, but lines due to $\equiv Si\dot{C}H_2$ and $\equiv Si^{\cdot}$ were observed. The experimental spectra were processed using the SpectraCalc software package.

The EPR spectra of irradiated DMSD, PDMS and PMSQ are the superposition of a narrow quadruplet with the splitting constant $a(3H) = 2.3$ mT due to $^{\cdot}CH_3$ radicals, an anisotropically broadened triplet with the average splitting of ~2.0 mT due to radicals of the $\equiv Si\dot{C}H_2$ type and a singlet due to paramagnetic centers like $\equiv Si^{\cdot}$ (Figure 2). The half-sum of the heights of the edge components of the EPR spectra corresponded to the relative concentration of methyl radicals. Based on the experimental data, we constructed the kinetic curves of decay for methyl radicals in the test materials; these curves were adequately described as exponential ones (the error in the EPR double-integration measurements of methyl radical concentrations was estimated at 5%). The kinetic curves were linearized in semilogarithmic coordinates (Figure 3). This fact suggests that the decay of methyl radicals in DMSD, PDMS and PMSQ occurred as a pseudo-first-order reaction, unlike siloxane block copolymers, in which the decay kinetics of methyl radicals was hindered.[8]

We propose the following reaction scheme for the decay of methyl radicals in irradiated PDMS and PMSQ:



We found that the total concentration of radicals remained unchanged in the course of the decay of methyl radicals in PDMS, PMSQ or DMSD; that is, the concentration of $\equiv Si\dot{C}H_2$ radicals increased simultaneously with a decrease in the concentration of methyl radicals (as estimated from the intensity of the central component of an anisotropic triplet). As an example, Figure 4 shows the corresponding kinetic curves for PDMS. Thus, the conceivable reaction of methyl radical combination was not observed and the above reaction scheme seems valid. The reaction rate constants of decay of methyl radicals in the samples upon irradiation determined from the linearized experimental curves are $k = 8.5\times10^{-5}$, 8×10^{-5} and 2×10^{-5} s^{-1} for DMSD, PDMS and PMSQ, respectively. Note that the irradiation times (3 min for PDMS or PMSQ and 4 min for DMSD) and times between the termination of irradiation and the first measurement of an EPR spectrum (5 min) were ignored in the determination of these rate constants. The decay reaction of methyl radicals occurred in a kinetic rather than diffusion region because the decay kinetics was qualitatively the same regardless of structure. The difference between the rate constants of decay in PDMS and PMSQ by a factor of 4 was due to different structures of these polymers and different concentrations of methyl groups in them. The radiation-chemical yields of methyl radicals per 100 eV $G(^{\cdot}CH_3)$ were 1.2, 1.0 and 0.7 at doses of 2.5, 1.5 and 1.7 kGy for DMSD, PDMS and PMSQ, respectively. The radiation-chemical yield of radicals in irradiated PDMS

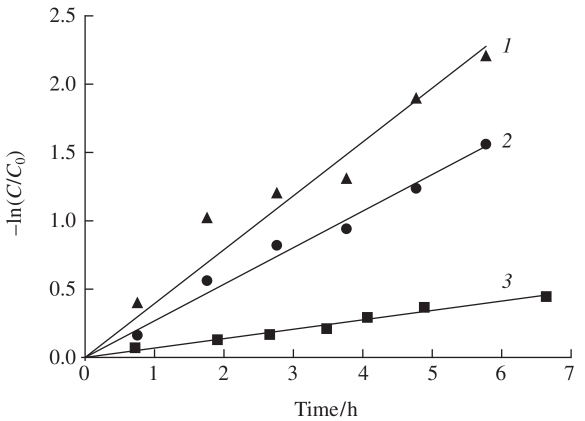


Figure 3 Kinetics of decay of methyl radicals in (*1*) DMSD, (*2*) PDMS and (*3*) PMSQ plotted on semilogarithmic coordinates.

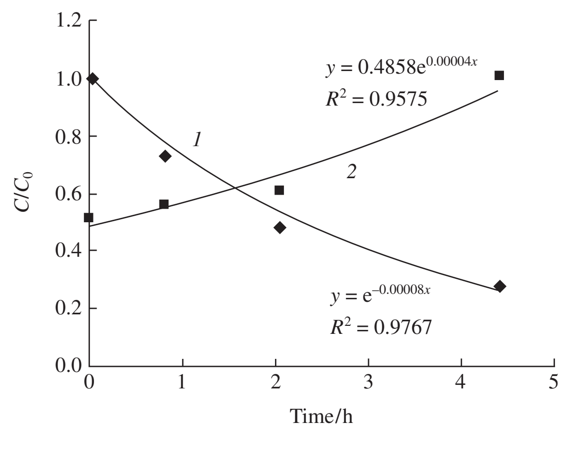


Figure 4 Kinetics of (*1*) $^{\cdot}CH_3$ decay and (*2*) $\equiv Si\dot{C}H_2$ buildup in PDMS.

is consistent with published data,[15] whereas those of radicals in PMSQ and DMSD were determined for the first time. The rate constants of decay and the radiation-chemical yields of methyl radicals in DMSD and PDMS are the same within the limits of experimental error. The radiation-chemical yield of methyl radicals in structurally different PMSQ is lower because of a smaller concentration of methyl groups in this polymer.

Thus, we demonstrated that the decay of methyl radicals in irradiated DMSD and PDMS occurs by the same mechanism, and these radicals in DMSD, PDMS and PMSQ at 77 K decay at the same monomer unit as a result of radical-center transfer rather than another reaction.

We are grateful to Professor V. I. Feldman (M. V. Lomonosov Moscow State University) for helpful discussions and encouragement.

References

1 M. H. Mazurek, in *Comprehensive Organometallic Chemistry III*, eds. R. H. Crabtree and D. M. P. Mingos, Elsevier, Amsterdam, 2007, vol. 3, p. 651.
2 B. G. Zavin, *Organosilikatnye materialy* (*Organosilicate Materials*), Znanie, Moscow, 1986 (in Russian).
3 L. N. Pankratova and A. V. Rudnev, *Khim. Vys. Energ.*, 2006, **40**, 191 [*High Energy Chem.* (*Engl. Transl.*), 2006, **40**, 154].
4 A. A. Miller, *J. Am. Chem. Soc.*, 1960, **82**, 3519.
5 T. S. Fedoseeva and A. S. Kuz'minskii, *Khim. Vys. Energ*., 1967, **1**, 248 (in Russian).
6 Yu. D. Tsvetkov, Yu. N. Molin and V. V. Voevodskii, *Vysokomol. Soedin*., 1959, **1**, 1805 (in Russian).
7 S. Pshezhetskii, A. Kotov, V. Milinchuk, V. Roginskii and V. Tupikov, *EPR of Free Radicals in Radiation Chemistry*, Wiley, New York, 1974.
8 O. Yu. Panov, L. N. Pankratova, V. I. Fel'dman and V. N. Belevskii, *Vysokomol. Soedin., Ser. A*, 1995, **37**, 600 (in Russian).
9 L. N. Pankratova and L. T. Bugaenko, *Khim. Vys. Energ*., 2005, **39**, 160 [*High Energy Chem*. (*Engl. Transl.*), 2005, **39**, 130].
10 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].
11 C. G. Delides, *Radiat. Phys. Chem.*, 1980, **16**, 345.
12 L. N. Pankratova, L. T. Bugaenko and A. A. Revina, *Khim. Vys. Energ.*, 2000, **34**, 19 [*High Energy Chem*. (*Engl. Transl.*), 2000, **34**, 16].
13 L. M. Khananashvili, *Khimiya i tekhnologiya elementoorganicheskikh monomerov i polimerov* (*Chemistry and Technology of Organoelement Monomers and Polymers*), Khimiya, Moscow, 1998 (in Russian).
14 M. G. Voronkov, V. P. Mileshkevich and Yu. A. Yuzhelevskii, *The Siloxane Bond: Physical Properties and Chemical Transformations*, Consultant Bureau, New York, 1978.
15 A. K. Pikaev, *Sovremennaya radiatsionnaya khimiya: tverdoe telo i polimery. Prikladnye aspekty* (*Modern Radiation Chemistry: Solids and Polymers. Applied Aspects*), Nauka, Moscow, 1987 (in Russian).

Received: 2nd November 2010; Com. 10/3623