

Polymerization of Monomers Initiated by Silyl Centers in SiO Deposits Prepared by Pulsed Laser Ablation

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ABSTRACT: Deposits from silicon monoxide prepared by pulsed laser ablation were allowed to react with acrylic and vinyl monomers—styrene, methyl methacrylate and 1,2 ethylene glycol dimethacrylate. It was revealed by means of FTIR, electron paramagnetic resonance (EPR), and NMR spectroscopies that silyl $\equiv\text{Si}\cdot$ reacts with monomer molecules and initiates the consecutive polymerization. Crosslinking is proved by the occurrence of bending $\delta(-\text{CH}_2)$ absorption peak at about 750 cm^{-1} in FTIR spectra. Because of very low concentration of the propagating radical for styrene we

used a radical scavenger *N*-phenyl-*t*-butylnitron for trapping. The measured EPR parameters were compared with the calculated ones. In case of styrene, NMR analysis manifested the presence of Si—C bonds in SiC_xO_y ($x + y = 2$) units, which can be taken as direct evidence of the reaction between silyl centers and monomer molecules. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4488–4492, 2006

Key words: pulsed laser ablation; surface defect; polymerization; silicon monoxide

INTRODUCTION

Significance of ultrafine particles has been booming for the last decade since the industrial technology needs new original shaped materials for the production of fillers, pigments, ceramics precursors, chemical catalysts, etc. The most used silicon-based material for preparation of ultrafine powders is silica (SiO_2), as it is commercially available and cheap. Silica is often chemically modified to achieve particular physical and chemical properties of the silica powder. In this way, physicochemical properties such as viscosity, colorfulness, corrosion resistance, catalysis efficiency, etc. have been significantly improved.¹

The chemical modification of silica is based on the reaction of hydroxyl groups SiOH on a surface.² The hydroxyl groups react with one or more chemical agents under specific process conditions (temperature, pressure, solvent, composition of the atmosphere, etc.) to yield new functional groups. A preheating often precedes this procedure (usually more than 400°C) to desorb water and other impurities off the surface.

Reactive silica³ containing defects has been prepared by thermochemical activation⁴ or mechanical treatment in an inert atmosphere⁵ so far. Chemical reactivity of the defects toward some chemical com-

pounds and generation of other radicals have been studied; for example reactions between silyl $\text{Si}\cdot$ and N_2O ,⁶ dioxysilirane group $\text{Si}(\text{O})_2$ and H_2 , CH_4 , C_2H_6 , C_2H_4 , and $\text{C}_2\text{H}_4\text{O}$,⁷ nonbridging oxygen hole center $\text{SiO}\cdot$ and NH_3 ,⁸ $\text{SiN}(\cdot)\text{H}$ and CO , H_2 , and C_2H_4 ⁸ or interaction of peroxy radicals $\text{SiOCH}_x\text{OO}\cdot$ with UV radiation.⁹ More detailed description and characterization of some defects are published in Ref. 10.

We prepared nanostructured reactive powder by infrared pulsed laser ablation (PLA) of silicon monoxide and dioxide. Several kinds of defects were detected: $\equiv\text{Si}\cdot$, silylen $=\text{Si}\cdot$, and to a lesser extent, peroxy radical $=\text{SiOO}\cdot$ and silanone $=\text{Si}=\text{O}$. Presence of peroxysilirane $\text{Si}=(\text{O})_2$ and peroxy binding $=\text{SiOOSi}=\text{O}$ were deduced from experimental data.¹¹ The concentration of silyl and silylen in the SiO_x ($x \sim 1$) deposits were up to $9 \cdot 10^{19}/\text{g}$ both. Exposure of this powdery matrix to NH_3 , MeNH_2 , and Me_2NH leads to the creation of $\text{SiNMe}_x\text{H}_{2-x}$ pending groups.¹²

We studied the reactions of SiO_x deposits with the acryl and vinyl monomers—styrene, methylmethacrylate (MMA), and ethylene glycol dimethacrylate (EGDM) at room temperature. We tried to prove that silyl and silylen can initiate polymerization of monomers.

EXPERIMENTAL

The experiments (ablation, polymerization) were carried out at room temperature in a glass cell evacuated by rotary pump with oil trap to prevent an oil vapor backstreaming. The ultimate vacuum was 5 Pa.

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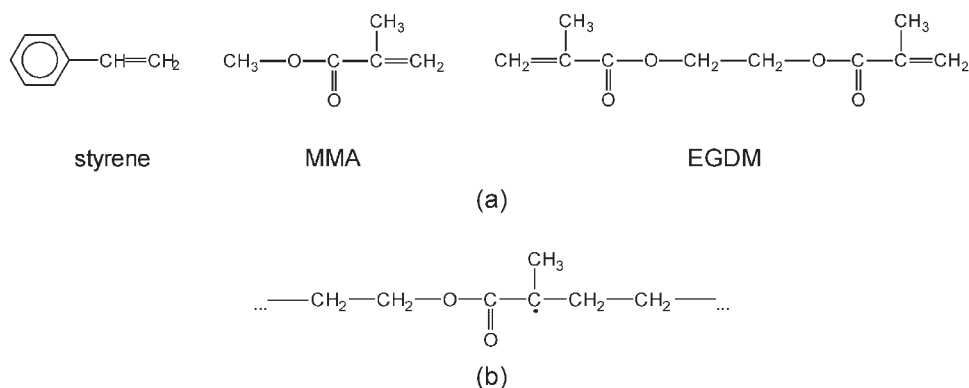


Figure 1 (a) Chemical formulae of styrene, MMA, and EGDM and (b) a radical produced in course of polymerization of EGDM.

The targets—lumps of silicon monoxide (Aldrich, USA)—were irradiated by TEA CO₂ pulsed laser (Plovdiv University, Bulgaria) operating with a frequency of 1 Hz on the *p*(20) line of 00 01 → 10 00 transition (994.19 cm⁻¹) with energy 0.80 J/pulse. The laser beam was focused onto the target by Ge lens with a 15-cm focus length. The gas Kr (0.99995, Linde, Germany) was used in experiments.

Deposits were collected on a small KBr window convenient for Fourier transformed infrared (FTIR) spectroscopy. Monomers—styrene, EGDM, and MMA [Fig. 1(a)]—were purified from stabilizers and degassed by several freeze–thaw cycles. After the laser ablation, the particular monomer was injected by a syringe into the cell under vacuum and the deposit on the window was exposed to the monomer vapors.

Another type of cell was used allowing a scratch in the deposit off the cell walls for electron paramagnetic resonance (EPR) detection. Deposit on the cell walls was scratched by a mechanical feed through and moved to the quartz side arm of the cell. For EPR measurements the arm was put into the resonator cavity. A liquid degassed monomer was introduced under vacuum in the side arm of the cell to get in touch with the collected material. EPR spectra were recorded at regular intervals to monitor the polymerization process.

The FTIR spectral analysis (FTIR Nicolet Impact 400, USA) was carried out on the films deposited on KBr sheets directly inside the glass cell at room temperature and the FTIR spectra were deconvoluted using the Microcal Origin 4.1 program.

EPR spectra were registered by the 9.4 GHz cw spectrometer (ERS 220, Germany) with 100-kHz magnetic field modulation at room temperature. 1 mW of microwave power and 0.115 mT modulation were used.

Solid-state NMR spectra were measured using a Bruker Avance 500 NMR spectrometer (Karlsruhe, Germany, 2003). Magic angle spinning (MAS) frequency was 8 kHz. Amplitude modulated cross-polarization (CP) with duration 1 ms was used to

obtain ²⁹Si and ¹³C CP/MAS NMR spectra. Intensity of B₁(¹H) field for TPPM decoupling (two-pulse phase-modulated) applied during signal detection corresponds to ω₁/2π = 89.3 kHz. ¹³C- and ²⁹Si NMR scale were calibrated by external standards glycine (176.03 ppm, carbonyl carbon) and M8Q8 (-109.8 ppm, the highest field signal).

Geometries optimization and calculation of resulting EPR parameters in the stationary points were made with the help of the Gaussian 98 W program.¹³ Restricted Hartree-Fock method with 3-21G* basis set was used for calculations of model molecules. Imploding 3-21G* basis set with polarization function seems to be optimal for the calculation of the molecules with the given number of atoms.

RESULTS

FTIR spectra

The native powdery deposit prepared by PLA of silicon monoxide on the KBr window was exposed to the saturated vapors of the monomer. After PLA of SiO, the monomer containing reservoir was evacuated and opened under vacuum to let stream the liquid monomer into the cell with the deposit. The next day after the experiment the cell was evacuated again and FTIR spectrum was measured so as to get the spectrum of the deposit with the polymerized film. The resulting films on the whole inner surface of the cell, in case of styrene and EGDM, were tough and very hard to remove from the walls regardless of the deposits being exposed to the monomer vapors or liquid. In the case of MMA the polymerized films were easily removable at places where only vapor monomer phase reacted.

The FTIR spectrum [Fig. 2(a)] of the native powdery deposit consists of a strong stretching ν(SiO) at about 1050 cm⁻¹ and a bending absorption band at 810 cm⁻¹. A rocking vibration is seen at 475 cm⁻¹.

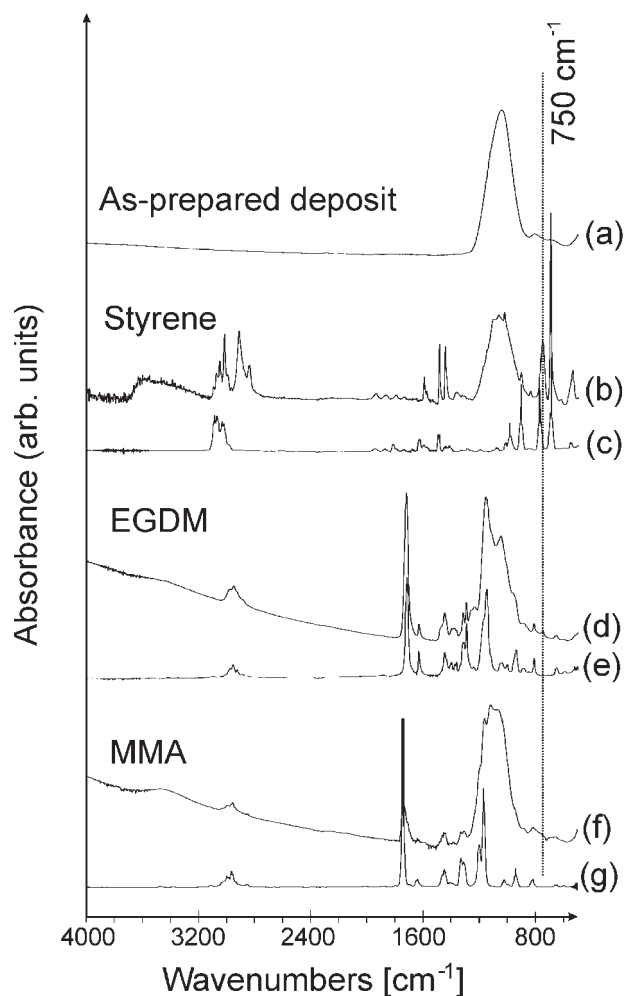


Figure 2 FTIR spectra of (a) a native deposit prepared in 500 Pa Kr and deposits exposed to (b) styrene, (d) EGDM, and (f) MMA vapors after about 24 h. FTIR spectra of monomers (c) styrene, (e) EGDM, and (g) MMA are shown as well.

FTIR spectra of the films that were formed in the reaction of the native deposit and monomer vapors reveal absorption lines of which most of them are identical with those found in the monomer spectrum [Fig. 2(b)–(g)]. The stretching $\nu(=CH)$ vibrations over 3000 cm^{-1} diminished and/or several ones disappeared. The quite new bands were detected at 2920 , 2847 , and 757 cm^{-1} for styrene, which can be ascribed to stretching $\nu(-CH)$ and bending $\delta(-CH_2)$ absorption bands. In case of MMA and EGDM, bending line $\delta(-CH_2)$ at 750 cm^{-1} was detected for the films formed in the liquid and vapor monomer phase. Obviously, other newly arising weaker bands are obscured by the original monomer bands.

EPR spectra

EPR spectra were taken only for EGDM and styrene. In case of MMA, EPR instrument was beyond its

tuning range because of the great microwave absorption at 9 GHz .

SiO deposit was exposed to both gaseous and liquid phase of EGDM. EPR signal of SiO with gas phase was weak, whereas the liquid phase provided sufficient high signal. EPR spectra (Fig. 3) showed new peaks with $g = 2.0034$ and $a = 2.24\text{ mT}$ related to the expected radical (Fig. 1).

Presence of this radical is evidence of the polymerization of EGDM.¹⁴ Concentration of the radical increased but after some time remained constant because of trapping of radical groups in the three-dimensional (3D) crosslinked polymer network.

The low concentration of the transient radicals did not allow the direct detection in the experiments with styrene. Styrene has only a single C=C double bond for polymerization, resulting in growing of a linear polymer network, whereas EGDM possesses two double bonds and so its polymer has 3D cross-linked structure in which the radicals are better trapped.

Application of radical scavengers of a special type usually denoted as “spin traps” allows to accumulate higher concentration of radical adducts. Typical spin trap is *N*-phenyl-*t*-butylnitrone (PBN). The presence of radical species after contact of styrene containing PBN with solid deposit is characterized by presence of three narrow lines in EPR spectrum marked with arrows in Figure 4(b). The two ways of interaction of the molecule of the spin trap PBN come into consideration: PBN binds to the silyl

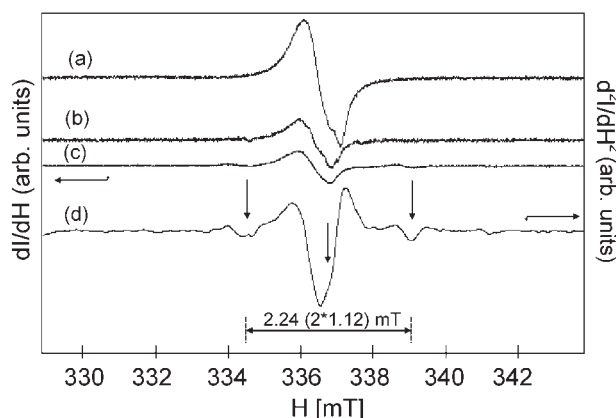


Figure 3 EPR spectra of (a) a fresh deposit (500 Pa Kr), (b) a deposit with a liquid EGDM at the start of the exposition (0 min), (c) after 2 days, and (d) the derivative of (c).

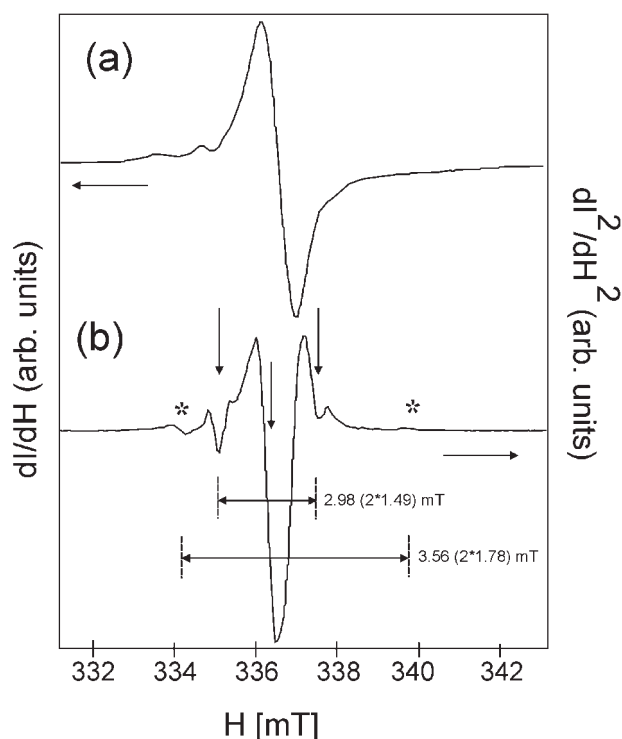
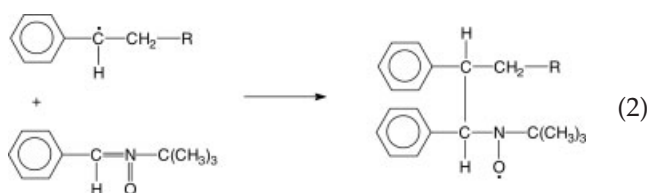


Figure 4 EPR spectra of (a) a deposit in contact with styrene after 3 days and (b) the derivative of (a). EPR spectrum of a fresh deposit was identical with the one as depicted in Figure 3(a).

or to the existing pending radical in the growing polystyrene network



NMR spectra

^{29}Si NMR spectrum provides very broad almost featureless signal that indicates large distribution and variation of Si structure units. Hence, it is reasonable to divide spectrum into main regions that can be clearly identified and assigned. The most intensive signals fall into the region from -90 to -130 ppm, which corresponds to siloxane structure units SiO_4 with various condensation rate. Usually these units are classified according to number of residual hydroxyl groups (Q^2 , Q^3 , and Q^4 correspond to structure unit containing two, one, and zero residual hydroxyls, respectively). From the literature¹⁵ and our previous studies on various siloxane networks and silicon-oxycarbide glasses^{16,17} it is clear that signals with resonant frequency between -50 and

-80 ppm reflect silicon atoms with one chemical bond to carbon and three chemical bonds to oxygen SiCO_3 (T^1 , T^2 , T^3 correspond to structure unit containing two, one, and zero residual hydroxyls, respectively). And finally signals ranging from 0 to -30 ppm usually reflect silicon species with two bonds to carbon and two chemical bonds to oxygen SiC_2O_2 (D^1 , D^2 correspond to structure unit containing one and zero residual hydroxyls, respectively). It is clear from the ^{29}Si CP/MAS NMR spectrum (Fig. 5) that all three main structure units are present in the studied system. Possibility to obtain ^{29}Si NMR signal through CP indicates that these structure units must be relatively close to hydrogen atoms. The average distance must not exceed 5 \AA .

^{13}C NMR spectrum is not shown here. It was typical for styrene and did not provide any evidence of Si—C bond between SiO matrix and styrene.

DISCUSSION

Comparing stretching $\nu(\text{C}=\text{C})$ peak at 1630 cm^{-1} for styrene and 1640 cm^{-1} for MMA and EGDM in FTIR spectra of SiO deposits with monomer precursors after a 2-day period showed decay of C=C bonds in the polymers. For EGDM, MMA, and styrene an integral absorbance of $\nu(\text{C}=\text{C})$ vibration was at 30, 20, and 0% in comparison with the initial value. At the same time a bending $\delta(-\text{CH}_2)$ peak manifests a creation of methylene bridges, e.g., the crosslinking process in the monomers. Unfortunately, a new peak of SiC anchoring bonding between SiO deposit and monomer was not detected because of the insufficient silyl concentration ($\sim 10^{19}/\text{cm}^3$) and/or the overlapping by other stronger peaks. The changes in FTIR spectra are accompanied with the decay of silyl centers in the deposit and a generation of the propagator radicals as indicated in EPR

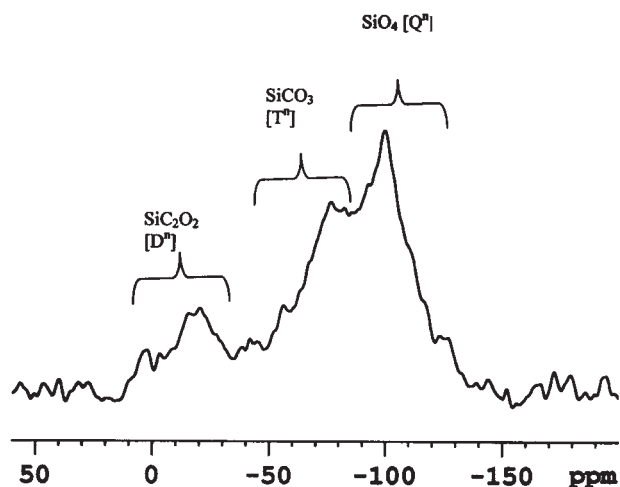


Figure 5 ^{29}Si NMR spectrum of the deposit exposed to the liquid styrene monomer 3 days after the experiment.

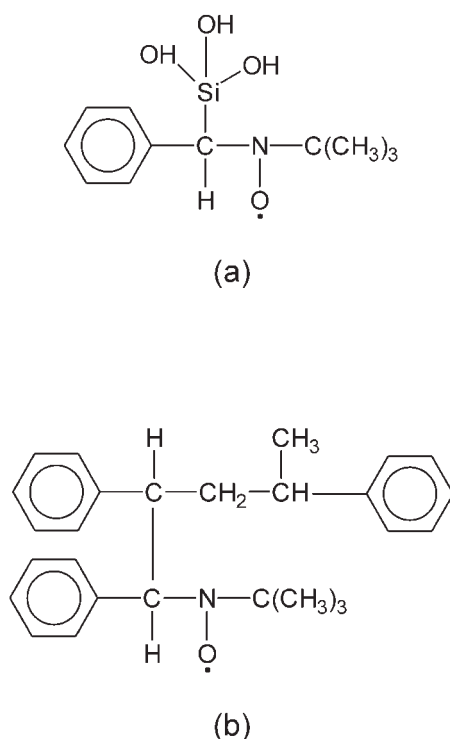


Figure 6 Model clusters used for calculations of (a) initiator radical in eq. (1) and (b) propagator radical in eq. (2).

spectra. Whereas the EPR parameters of the radical for EGDM are available,¹⁴ in case of styrene we calculated some EPR parameters of the initiator and propagator radicals for better identification and compared with the measured ones. As a model compound for the initiator radical in eq. (1) was used cluster structure depicted in Figure 6(a) and for propagator radical in eq. (2) the structure in Figure 6(b).

The central broad and intensive EPR line overlaps the middle line of PBN adduct. Nevertheless, the two outer lines situated on the shoulders allowed us to determine the hyperfine coupling from nitrogen as 1.49 mT. This value is in an acceptable agreement not very distant from calculated value for model compound of radical adduct of PBN equal to 1.52 mT.

The most outer lines denoted with asterisk in the Figure 4 are difficult to integrate. The high value of hyperfine coupling of 3.56 mT exceeds the calculated result for the adduct of silyl radical [Fig. 4(b)] equal to 1.78 mT. The elucidation of the outer lines manifest complexity of interactions of SiO matrix and the monomer with PBN. For example we focused at the only radical in the prepared deposit—silyl. However, another reactive center present in the prepared deposit is silylene =Si.¹¹ The magnitude of the concentration of this species is comparable with silyl ($\sim 10^{19}$ /g). Nonetheless, the concentration is rather low to be detected by FTIR

and also by EPR technique as =Si: is a diamagnetic defect.

CONCLUSIONS

We showed that silyl species in the prepared deposits from silicon monoxide by PLA can be utilized as the initiator centers for the consecutive polymerization process of the monomers EGDM, MMA and styrene. No extra experimental conditions or procedures (pressure, temperature, other chemicals, special atmosphere, etc.) are needed for the process. The direct proof was delivered by NMR spectrum (of styrene) that presented Si—C bonds we take as the products of initiation reaction between the SiO powdery matrix and the monomer (styrene).

The chemical behavior of the defects in the prepared silicon-based materials has not been consistently studied recently. They may promote efficiency of inorganic matrices in reactions with agents for chemical surface modification procedures in which solely —OH groups have been used so far.

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