

ESR Study of Radiation-Induced Polymerization of Styrene Adsorbed on Silica Gel

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Synopsis

The effect of the specific surface area of silica gels on the radiation-induced polymerization of styrene adsorbed on silica gel was studied by ESR. The same radicals were generated on the silica gels regardless of the specific surface area, but the stability of the radicals at room temperature depended on the specific surface area. This means that the decay of the radicals proceeded mainly on the surface of the silica gel. Almost all the radicals generated by irradiation were initially in the bulk of the silica gel and migrated from the interior to the surface of the gel. When styrene monomer was adsorbed on the surface of the silica gel, the silica gel radicals interacted with the monomer and initiated polymerization and then generated polymer. The rate of migration of the silica gel radical was rather fast in the case of silica gel with a large specific surface area. Thus, the polymerization behavior of styrene adsorbed on silica gel greatly depended on the specific surface area of the gel.

INTRODUCTION

Many studies have been reported on the radicals induced by radiation to silica gels by means of ESR.¹⁻⁴ The ESR spectra of silica gels varied according to the origin of the gels. Small impurities in the gels greatly changed the spectra, so that the differences in the reports can be considered due to the differences in the silica gels used. But common to all reports is that the ESR spectrum of irradiated silica gel is composed of several kinds of signals and one of them is the signal caused by trapped electrons in the oxygen vacancy in the lattice.

On the other hand, radiation-induced polymerization of styrene adsorbed on silica gel has been studied in detail by many workers.⁵⁻⁹ They reported that the polymerization behavior of adsorbed styrene is considerably different from that of free styrene. But the details are not yet worked out.

We have reported on the polymerization behavior of styrene adsorbed on silica gel by changing the dose rate¹⁰ and the amount of adsorbed styrene¹¹ and by polymer adsorption on silica gel.¹² It was found that radical and ionic polymerization proceeded simultaneously and that the rate of graft polymerization changed with the amount of monomer adsorbed on silica gel. Therefore, the effect of the specific surface area of the silica gel on the radiation-induced polymerization of styrene adsorbed on silica gel was studied to clarify the mechanism. This is the first part of our report; it describes the behavior of radicals by means of ESR in connection with the polymerization behavior.

EXPERIMENTAL

Materials

Three kinds of silica gels with different mean pore diameters and specific surface areas, manufactured by Fuji-Davison Chemical Co. Ltd., were used in this experiment. The properties of the silica gels are shown in Table I.

Styrene was purified in the conventional way and distilled under reduced pressure before use.

Other chemicals used were reagent grade and used without further purification.

Irradiation

Silica gels were dried at 400°C for 3 h and then evacuated at 10^{-4} torr for 20 h at room temperature. Subsequently, the samples were sealed in ESR tubes under vacuum. Some tubes contained break seals for subsequent addition of styrene to the silica gels to equilibrium at room temperature for a day. Then the samples were irradiated with Co-60 γ -rays at an exposure rate of 7×10^5 R/h at 20° and -196°C.

ESR Measurement

ESR spectra were measured with a JES ME ESR spectrometer with 100 kHz modulation. The microwave power used was 0.4 mW, and under these conditions no saturation effect was observed. Radical concentration was calculated by the double-integration method. Coal and Mn^{2+} were used as standard samples for radical concentration and position of spectra, respectively.

NMR Measurement

High-resolution NMR spectra were measured with a JNM-PFT-100 HR NMR spectrometer with a resolution time of 18 s at room temperature. Acetone- d_6 was used as NMR lock solvent. The diameter of the sample tube was 5 mm. Half-widths of the spectra were compared with each other.

RESULTS AND DISCUSSION

ESR spectra of silica gels with different specific surface areas and mean pore diameters measured at room temperature are shown in Figure 1. From the complicated shape of the spectra, it can be inferred that several kinds of radicals

TABLE I
Properties of Silica Gels

Average pore diameter, Å	40 ^a	70 ^b	165 ^b
Specific surface area, m ² /g	677	166	76
Equilibrium adsorption of styrene, g/g silica gel	0.6	1.0	0.6
Thickness of styrene adsorbed until equilibrium, no. of layers	2.1	13.9	18.3

^a Measured with Orr surface area pore volume analyzer.

^b Measured with mercury penetration porosimeter.

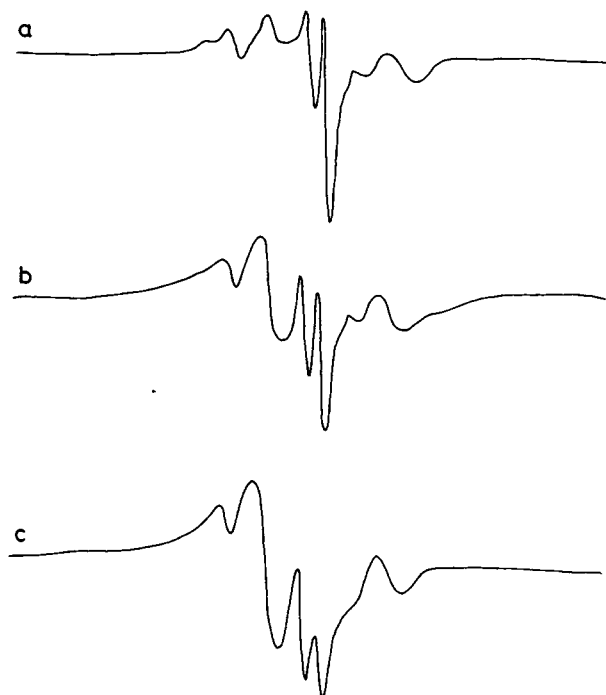


Fig. 1. ESR spectra of silica gels: (a) 40-Å silica gel; (b) 70-Å silica gel; (c) 165-Å silica gel.

are induced on the silica gels by irradiation. As the spectra are similar to each other regardless of specific surface area, the same kind of radical is considered to be formed on the silica gels by irradiation. But relative intensities of these radical species are different from the specific surface areas of the silica gels.

In Figure 2, the relative intensities of total radicals are plotted against the specific surface areas. Within these specific surface areas, the number of radicals induced on the silica gels decreases as the specific surface areas increase. But when silica gels were irradiated at -196°C and ESR spectra were measured at -196°C , the number of radicals was almost the same regardless of specific surface area. The shapes of the ESR spectra of the silica gels at -196°C also were similar regardless of the specific surface area. Therefore, the radical species induced at -196°C are considered to be the same in silica gels of different specific surface areas. Almost all radicals disappeared when the temperature was increased from

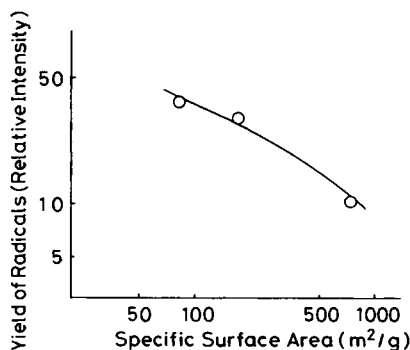


Fig. 2. Relation between specific surface area of silica gel and yield of radicals.

-196° to 20°C , in a 40-\AA silica gel with a large specific surface area. But about half the radicals decayed by increasing the temperature in 70-\AA and 165-\AA silica gels. The radical decay at 20°C on silica gel with large specific surface area is fast compared with that on silica gels with small specific surface areas. Probably decay of radicals at 20°C occurs readily on the surface of silica gels.

When styrene was introduced onto the irradiated silica gel under vacuum, the shape of the ESR spectrum did not change, but the spectral intensity decreased gradually. So, styrene was introduced onto the silica gel until equilibrium before irradiation. The amount of monomer introduced onto the gel until equilibrium adsorption at 20°C is shown in Table I. After irradiation at 20°C for 1 h, ESR spectra were measured at 20°C ; these are shown in Figure 3. For comparison, the ESR spectrum of polystyrene measured under the same condition is also shown in Figure 3(d). The ESR spectrum of 40-\AA silica gel adsorbing styrene is very similar to that of polystyrene. But those of 70- and 165-\AA silica gels as shown in Figures 3(b) and 3(c) are rather similar to those of silica gels.

The relative intensities of radicals induced by irradiation for 1 h on silica gels adsorbing styrene are plotted against the specific surface area as shown in Figure 4. The relative intensities of the radicals are contrary to those shown in Figure 2. The number of radicals induced on silica gels adsorbing styrene increases as the specific surface areas increase. Comparing Figure 4 with Figure 2, it is clear

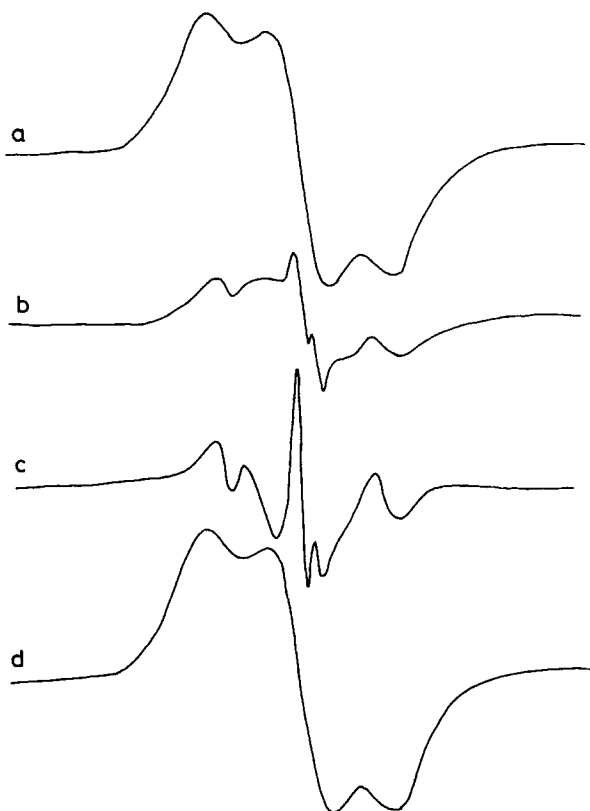


Fig. 3. ESR spectra of silica gels adsorbing styrene and polystyrene irradiated for 1 h: (a) 40-\AA silica gel; (b) 70-\AA silica gel; (c) 165-\AA silica gel; (d) polystyrene.

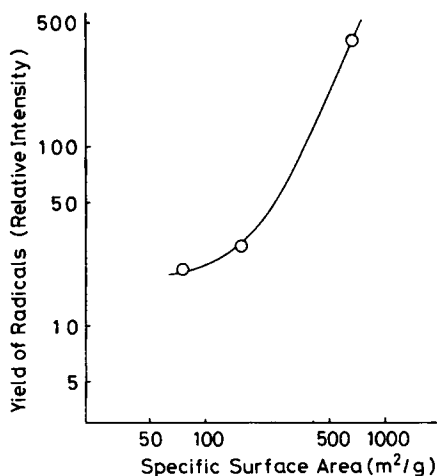


Fig. 4. Relation between specific surface area of silica gel and yield of radicals generated by irradiation for 1 h on silica gel adsorbing styrene.

that the yield of radicals induced on silica gel adsorbing styrene is more than that induced on silica gel alone in the 40-Å silica gel. But in the 165-Å silica gel, the relative intensity of radicals induced on silica gel adsorbing styrene is less than that induced on silica gel alone.

From the results, it is clear that styrene adsorbed on silica gel helps increase the radical concentration in the case of 40-Å silica gel. But in the case of 165-Å silica gel, styrene does not increase radical concentration. As the same amount of radicals are produced on silica gels by irradiation at -196°C regardless of specific surface area of silica gels, radical decay is fast on silica gels with large specific surface areas in the absence of styrene. In the presence of styrene, the decay of radicals is related to both silica gel and styrene. Also interaction between silica gel and styrene should be important. The thickness of the styrene layer adsorbed on silica gel until equilibrium at room temperature was calculated on the assumption that the cross-sectional area of styrene is 40 \AA^2 .¹³ As the thickness of styrene is thin in silica gel with a large specific surface area, the interaction between silica gel and styrene should be strong in silica gel with a large specific surface area.

In order to check the interaction between silica gel and styrene adsorbed on silica gel, high-resolution NMR spectra of adsorbed styrene were measured; these are shown in Figure 5. The half-widths of NMR spectra of styrene adsorbed on silica gels until equilibrium are 215, 106, and 74 Hz for 40-, 70-, and 165-Å silica gels, respectively. When 40-Å silica gel was immersed in styrene, the half-width of the NMR spectrum was 63 Hz, as shown in Figure 5(d). This means that mobility of styrene adsorbed on 165-Å silica gel until equilibrium adsorption is almost the same as that of liquid styrene. These results show that mobility of styrene adsorbed until equilibrium at room temperature is suppressed in 40-Å silica gel as compared with those in 70- and 165-Å silica gels. Most of the styrene adsorbed on 165-Å silica gel until equilibrium at room temperature is free and little of the monomer interacts with the gel.

Renie and Clifford¹⁴ reported on the relation between the lowering of the melting point of water in pores of silica gel and the pore size. They showed that

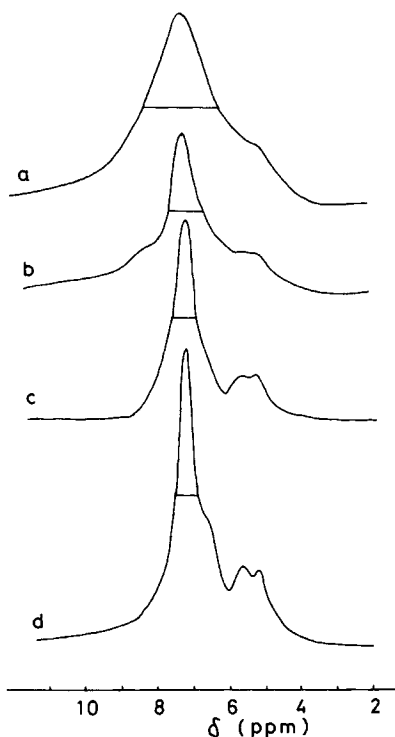


Fig. 5. NMR spectra of styrene adsorbed on silica gels: (a) styrene adsorbed on 40-Å silica gel until equilibrium; (b) styrene adsorbed on 70-Å silica gel until equilibrium; (c) styrene adsorbed on 165-Å silica gel until equilibrium; (d) styrene introduced in 40-Å silica gel in large excess.

the lowering of melting point of water adsorbed on silica gel was inversely proportional to the pore radius and that melting point of water adsorbed on a gel with a 75-Å mean pore diameter was not observed until the water became 2.5 layers thick. But when the water exceeded 2.5 layers, the melting point of water on the surface of the gel was the same as that of ordinary water, indicating that water which interacted with silica gel shows different physical properties than free water.

From these results, it appears that the interaction between silica gels and styrene adsorbed on the gels until equilibrium at room temperature is strongest in the 40-Å silica gel, and less so in the 70- and 165-Å silica gels. But the largest radical concentration in the 40-Å silica gel adsorbing styrene (compared with those of 70- and 165-Å silica gels) cannot be interpreted solely by the strength of interaction between silica gel and styrene.

Hydrogen was then introduced into the irradiated silica gels at room temperature by decomposition of lithium aluminum hydride. Almost the entire ESR signal disappeared within 1 min upon addition of hydrogen to the 40-Å silica gel at room temperature. On the other hand, the ESR signal remained about 31 and 23% of original concentration after addition of hydrogen to the 70- and 165-Å silica gels for 2 and 5 min, respectively. The average pore diameter of the silica gels was large enough to allow hydrogen to diffuse freely through the pore in both silica gels. The specific surface areas of the 40- and 165-Å silica gels were 677 and 76 m²/g, respectively. If all radicals are located on the surface of the

silica gels, the rate of radical decay should be the same in both gels. Therefore the ratio of radicals located on the surface to that in the interior, or the rate of transfer from the interior to the surface of the silica gels, should be different from that of other silica gels. Although probably almost all radicals are located on the surface of the 40-Å silica gel, a considerable amount of the radicals is located interior of the 165-Å silica gel and is transferred gradually from the interior to the surface of the gel.

When styrene monomer alone was irradiated for 1 h at room temperature, no radical was found by ESR measurement, and conversion of monomer to polymer was very low. But polymerization of styrene adsorbed on silica gel by irradiation for 1 h proceeded fast, and the conversion by radical polymerization was 9.1 and 3.7% for 40 and 165-Å silica gels, respectively.¹⁵ Radical polymerization of styrene adsorbed on silica gel proceeds fast compared with that of free styrene.

When silica gel and styrene were irradiated individually at -196°C , the relative yields of radicals were 4.2 and 121.0, respectively. The relative yield of radicals was 155.3 for silica gel adsorbing styrene under the same condition, indicating an energy transfer from silica gel to styrene. Probably, the energy transferred is more effective in silica gel with large specific surface area than in silica gel with a small specific surface area.

In Figures 6, 7, and 8, ESR spectra of silica gels adsorbing styrene irradiated at 20°C for 0.25–5 h are shown for 40-, 70-, and 165-Å silica gels, respectively. As mentioned above, the ESR spectrum of the 40-Å silica gel adsorbing styrene irradiated for 1 h is almost the same as that of polystyrene. But in silica gels with small specific surface areas, it takes more time to produce a similar spectrum to polystyrene. Such results are related to the strength of interaction of styrene with silica gel, that is to say, to the amount of energy transferred from the silica gel to styrene and the rate of radical migration to the surface of the gel.

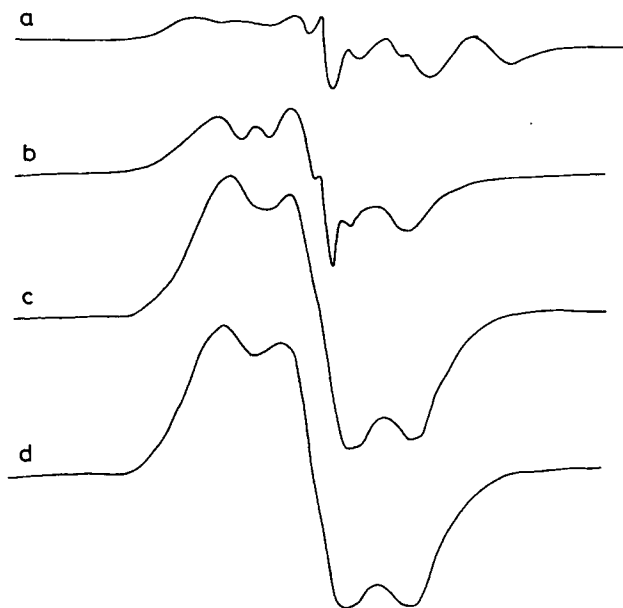


Fig. 6. Change in ESR spectra of 40-Å silica gel adsorbing styrene with irradiation time: (a) 0.25 h; (b) 0.5 h; (c) 1.0 h; (d) 3.0 h.

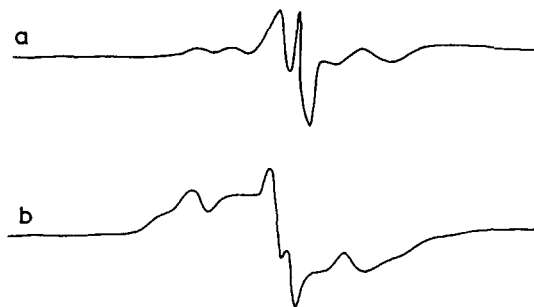


Fig. 7. Change in ESR spectra of 70-Å silica gel adsorbing styrene with irradiation time: (a) 0.25 h; (b) 1.0 h.

The relative intensities of radicals are plotted against irradiation time in Figure 9. The relative intensity of radicals induced on 40-Å silica gel adsorbing styrene is more than that generated on silica gels with small specific surface areas. It is reported that ESR signals of propagating styrene radicals could not be observed. But ESR signals of propagating radicals whose movement is limited by their surroundings could probably be observed. Probably the spectrum cannot be identified with that of polystyrene radical induced by irradiation. So both propagating radicals and polymer radicals contribute to the relative intensity of radicals in the present case.

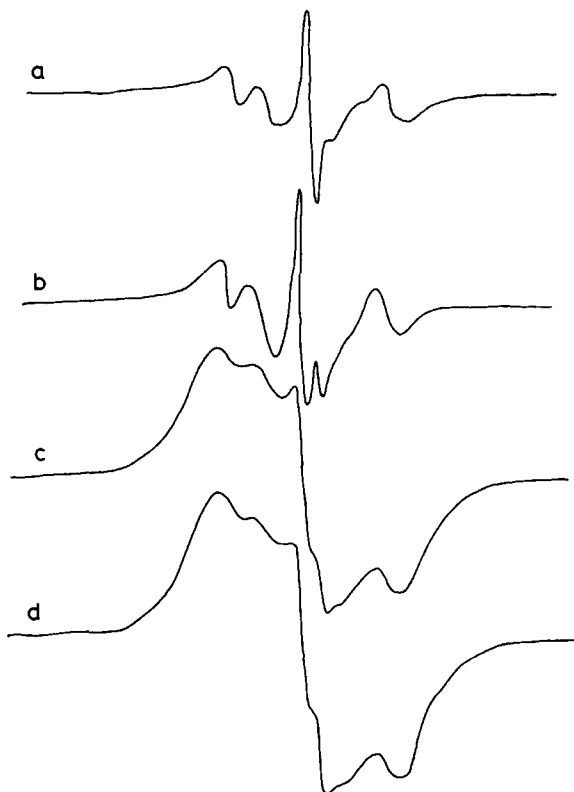


Fig. 8. Change in ESR spectra of 165-Å silica gel adsorbing styrene with irradiation time: (a) 0.5 h; (b) 1.0 h; (c) 3.0 h; (d) 5.0 h.

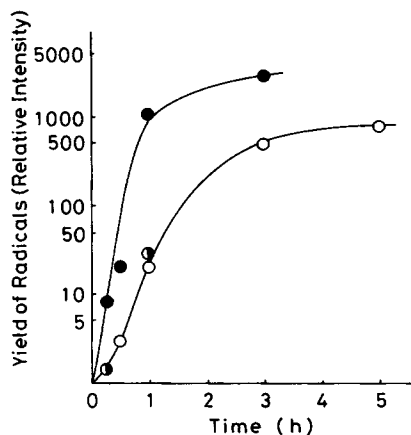


Fig. 9. Relation between irradiation time and yield of radicals: (●) 40-Å silica gel; (◐) 70-Å silica gel; (○) 165-Å silica gel.

From these results, it can be concluded that the decay of radicals mainly proceeds on the surface of the silica gel. For the gel with a large specific surface area, almost all the radicals generated by irradiation are initially in the bulk of the gel and easily migrate from the interior to the surface. When styrene monomer or styrene polymer is adsorbed on the surface of the gel, silica gel radicals immediately interact with these monomers or polymers and then generate polymer radicals. That the relative intensity of the 40-Å silica gel adsorbing styrene is more than that of the 40-Å silica gel alone may be attributed to the high probability of energy transfer due to the strongly bound interaction of the monomer with the surface of silica gel.

The ESR information can qualitatively explain most of the phenomena of radical polymerization of styrene adsorbed on silica gels with different specific surface areas. But it cannot explain the entire mechanism of the polymerization because ionic processes that cannot be detected by the ESR measurements proceed simultaneously with this polymerization. The details on the polymerization of styrene adsorbed on silica gels with different specific surface areas will be reported in our next article.¹⁵

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