Macromolecules **1984**, *17*, 1655–1659 **1655**

(3) McCall, D. W.; Anderson, E. W.; Bair, H. E.; Blyler, L. L.; Gilroy, H. M.; Johnson, G. E. *Polyethylenes 1933-1983*, June 1983, London.

(4) McCall, D. W.; Douglass, D. C.; Blyler, L. L., Jr.; Johnson, G. E.; Jelinski, L. W.; Bair, H. E. *Macromolecules*, preceding paper in this issue.

(5) Cheng, H. N.; Schilling, F. C.; Bovey, F. A. *Macromolecules* **1976**, *9*, 363.

(6) Dorman, D. E.; Otocka, E. P.; Bovey, F. A. *Macromolecules* **1972**, *5*, 574.

(7) Bovey, F. A.; Schilling, F. C.; McCrackin, F. L.; Wagner, H. L. *Macromolecules* **1976**, *9*, 76.

(8) Young, J. F. *J. Appl. Chem.* **1967**, *17*, 241.

(9) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 492.

(10) Jeffrey, K. R.; Bloom, M.; Valic, M. I.; Higgs, T. P. *Chem. Phys. Lett.* **1976**, *42*, 390.

(11) Blinc, R.; Rutar, V.; Seliger, J.; Slak, J.; Smolij, V. *Chem. Phys. Lett.* **1977**, *48*, 576.

(12) Luongo, J. P. *J. Polym. Sci.* **1960**, *42*, 1.

(13) Chan, M. G.; Hawkins, W. L. *Polym. Eng. Sci.* **1967**, *7*, 264.

(14) Chapiro, A. "Radiation Chemistry of Polymeric Systems"; Interscience: New York, 1962; p 410.

(15) Luongo, J. P. *Appl. Spectrosc.* **1965**, *19*, 117.

(16) Collignon, J.; Sillescu, H.; Spiess, H. W. *Colloid Polym. Sci.* **1981**, *295*, 220.

Radiation-Induced Degradation of Poly(α-methylstyrene) in Solution[1]

Tomiki Ikeda,[2] Hans S. von Euler-Chelpin,[3] and Seizo Okamura

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan

Hitoshi Yamaoka*

Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-04, Japan.

Received June 21, 1983

ABSTRACT: Radiation-induced degradation of poly(α-methylstyrene) was studied in benzene solution. Random scission of the polymer chain was confirmed by GPC measurements. The G value for chain scission was found to be independent of dose rate and was estimated to be 0.78. The degradation was accelerated by the addition of chlorine-containing compounds with high G values for radical production. The ESR spectroscopy spin trapping technique revealed that phenyl and trichloromethyl radicals were derived during γ-irradiation from chlorobenzene and carbon tetrachloride, respectively. The trapped polymer radical was identified as the species formed through hydrogen abstraction from methylene groups of the polymer chain. These results indicate that the attack of a reactive radical on the polymer chain, followed by hydrogen abstraction, plays an important role in radiation-induced degradation of poly(α-methylstyrene) in dilute solution.

Introduction

A number of investigations have been performed on the radiation chemistry of polymers, being devoted to chemical changes of polymers such as degradation and cross-linking.[4] As proposed by Miller,[5] polymers can be generally classified into two groups, degradation-type polymers and cross-linking-type polymers, with exposure to γ-rays or electron beams. Poly(methyl methacrylate) (PMMA) is well-known as a typical degradation-type polymer, and experiments on this polymer have been extensively carried out. However, little attention has been paid to the radiation-induced degradation of poly(α-methylstyrene) (PMSt), which is also a degradation-type polymer.

The radiolysis of PMSt in bulk was first reported by Kotliar.[6] He interpreted the observed degradation in terms of a simple scission of a carbon–carbon bond in the main chain of the polymer. Recent experiments performed by Yamamoto et al.[7] revealed that various kinds of dimer are formed in the radiolysis of PMSt at high temperatures by an ionic chain reaction.

The radiation-induced degradation of polymers in bulk has been well understood by the mechanism of the above-mentioned chain scission.[4d] On the other hand, the radiolysis of polymers in solution has been found to be very complicated, depending on several factors such as the nature of solvent, the concentration of polymer, and the atmosphere.[4c] The present paper is concerned with the radiation-induced degradation of PMSt in benzene. The effect of added chlorine-containing compounds on the chain scission has been studied and interpreted on the basis of ESR measurements by means of the spin trapping technique.

Experimental Section

PMSt was prepared by cationic polymerization and then purified by conventional methods. 2-Methyl-2-nitrosopropane (t-BuNO) was carefully purified as reported in the previous paper.[8] Similar precautions were taken to exclude light because t-BuNO is easily photolyzed by long-wave visible light to form di-*tert*-butyl nitroxide.[9] Additives were the best grades commercially available and were once distilled prior to use, the middle cuts being employed. Ethanol contained in chloroform was removed by Vogel's method.[10] Spectroscopic grade benzene was distilled over sodium metal just before use.

γ-Irradiations were performed with a 12 000-Ci ^{60}Co source at the Research Reactor Institute, Kyoto University. The apparatus used for evaluation of the extent of chain scission was composed of a cylindrical quartz tube with an attached capillary viscometer. All samples were degassed by several freeze–thaw cycles under high vacuum and then sealed off.

In the present study, the polymer concentrations are expressed as moles per liter based on the monomer unit, and all experiments on degradation were carried out at the constant polymer concentration of 4.2×10^{-2} M (0.5 g/dL).

Molecular weight distributions of the polymer were measured with a Toyo Soda Model 801A gel permeation chromatograph calibrated to a standard PMSt sample for GPC measurements. From analogous considerations on the molecular weight distribution of the polymer as in the case of photosensitized degradation of PMSt,[11] the molecular weight of the polymer and the extent of chain scission were determined by viscometry. All G values for chain scission were calculated on the basis of the radiation energy that was absorbed by the polymer itself.

0024-9297/84/2217-1655$01.50/0

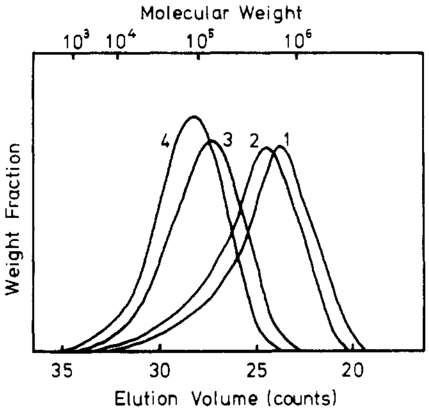


Figure 1. Gel permeation chromatograms of original PMSt and degraded polymers for irradiation doses of (1) 0, (2) 2.0, (3) 15.0, and (4) 27.0 Mrd; dose rate = 1.5 × 10^6 rd/h.

Table I
Molecular Weight and Polydispersity Index of PMSt before and after Irradiation[a]

total dose, Mrd	M_n	M_w/M_n
0	3.14×10^5	2.4
2.0	1.93×10^5	2.4
15.0	6.70×10^4	2.3
27.0	4.87×10^4	2.3

[a] Determined by GPC.

Table II
***G* Values for Chain Scission of PMSt at Different Dose Rates**

dose rate, rd/h	G_s
1.5×10^6	0.74
6.6×10^5	0.80
1.6×10^5	0.81
7.1×10^4	0.77
4.2×10^4	0.78

ESR spectra were measured in the dark at room temperature immediately after irradiation with a Varian E-3 X-band spectrometer employing 100-kHz modulation. Hyperfine splitting constants of the spectra observed were determined by comparison with that of di-*tert*-butyl nitroxide radical (a_N = 15.2 G).[12]

Results

GPC Measurements of Irradiated Polymers. Gel permeation chromatograms of the unirradiated and the irradiated polymers are shown in Figure 1. The peak was successively shifted to the lower molecular weight region with increasing irradiation dose. No gelation of the polymer was found for doses up to 27 Mrd. The molecular weight and the polydispersity index of the polymer at each absorbed dose are given in Table I. The molecular weight of the polymer decreases with increasing doses whereas the polydispersity of the polymer is kept constant throughout the course of degradation. This means that the mode of degradation on γ-irradiation is random scission of the polymer chain. The random chain scission was also confirmed in the presence of additives.

Effects of Dose Rate and Temperature. The changes in the ratio of molecular weights of the polymer before and after irradiation at different dose rates are shown as a function of irradiation time in Figure 2. *G* values for chain scission of the polymer (G_s) were calculated from the slopes of the plots and are listed in Table II, indicating that G_s is independent of the dose rate over the whole experimental range of dose rates.

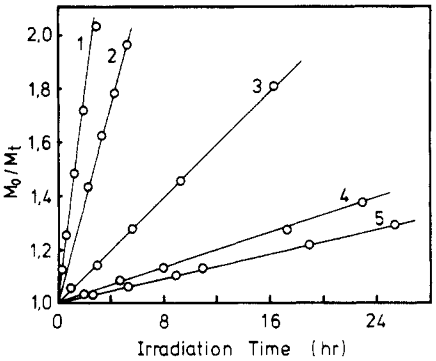


Figure 2. Radiation-induced degradation of PMSt in benzene at 30 °C for different dose rates: (1) 1.5 × 10^6, (2) 6.6 × 10^5, (3) 1.6 × 10^5, (4) 7.1 × 10^4, and (5) 4.2 × 10^4 rad/h.

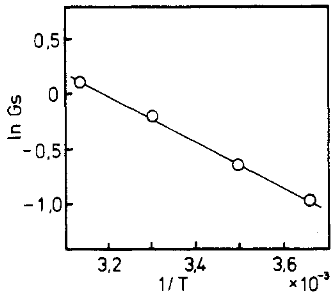


Figure 3. Effect of temperature on *G* value for chain scission of PMSt; dose rate = 6.6 × 10^5 rd/h.

Table III
Accelerating Effect of Additives on Chain Scission of PMSt in Benzene[a]

additive	G_s	G_s/G_s^0	G_r[b]
chlorobenzene	26	33	8.3
carbon tetrachloride	23	30	9.5
chloroform	19	24	10
acetone	1.0	1.3	2.4[c]
none	0.78	1.0	0.6

[a] All G_s values were calculated on the basis of the radiation energy that was absorbed by the polymer. [b] *G* value for radical production in 10% additive solution in benzene. [c] *G* value for radical production in neat solution.

G_s values were also determined over the temperature range 273–319 K. In Figure 3 are presented plots of logarithm of G_s vs. reciprocal of irradiation temperature. The slopes of the plots give a value of 17.2 kJ mol^{-1} as an overall activation energy of the degradation.

Effect of Additives. From the viewpoint of the degradation caused by an attack of reactive species on the polymer chain, additives with a large *G* value for radical production (G_r) are expected to accelerate the degradation, depending on the reactivity of radicals derived from additives. The results of additive experiments on the degradation are given in Table III. In the table are listed G_s values in the presence of 0.1 M additives and the ratios of G_s value to that in the absence of additives, G_s/G_s^0, along with G_r values for 10% additive solutions in benzene reported by Chapiro.[13] The results obtained clearly demonstrate that chlorine-containing compounds with a high G_r value exert a marked accelerating effect on the chain scission of PMSt.

Identification of Reaction Intermediates by ESR Measurements. In order to detect short-lived radical intermediates formed during γ-irradiation, a spin trapping technique was applied to the present system by means of ESR spectroscopy. When a PMSt solution in benzene was irradiated in the presence of *t*-BuNO as a spin trapping agent, only a triplet spectrum with the hyperfine splitting due to a nitrogen nucleus (a_N = 15.2 G) was observed as

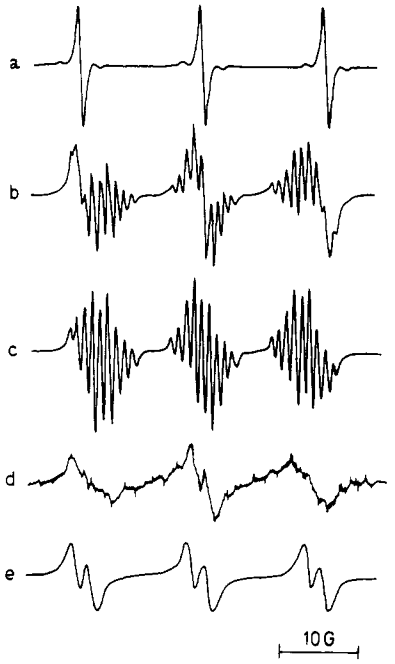
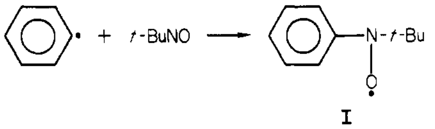


Figure 4. ESR spectra of nitroxide radicals formed during γ-irradiation of PMSt solution in benzene in the presence of chlorobenzene and *t*-BuNO: (a) [*t*-BuNO] = 7 × 10^{-3} M; (b) [PMSt] = 6 × 10^{-1} M, [chlorobenzene] = 1 M, [*t*-BuNO] = 7 × 10^{-3} M; (c) [chlorobenzene] = 1 M, [*t*-BuNO] = 7 × 10^{-3} M; (d) measured after precipitation, [PMSt] = 3 × 10^{-1} M in benzene; (e) computer-simulated spectrum of the polymer nitroxide radical III.

shown in Figure 4a. The spectrum is attributed to a di-*tert*-butyl nitroxide radical, which is produced by a reaction of the spin trapping agent itself.[12] When a small amount of chlorobenzene was added to the above-mentioned solution, the spectrum depicted in Figure 4b was obtained. Figure 4c shows a spectrum under γ-irradiation of a benzene solution of chlorobenzene in the presence of *t*-BuNO. The spectrum consists of a clear triplet due to a nitrogen nucleus (a_N = 12.4 G) with further splitting of each line into nine lines. This spectrum agrees well with that of *tert*-butyl phenyl nitroxide radical observed by Mackor et al.[14] Each nine-line structure is reasonably interpreted as arising from the coupling of three equivalent protons at para and ortho positions of the phenyl ring ($a_H^{p,o}$ = 1.9 G) plus two equivalent ones at meta positions (a_H^m = 0.9 G). The values of splitting constants are in fair agreement with those reported (a_N = 12.4 G, $a_H^{p,o}$ = 2.0 G, and a_H^m = 0.9 G).[14] This indicates the presence of phenyl radical produced by γ-irradiation of chlorobenzene, resulting in the formation of *tert*-butyl phenyl nitroxide radical I:



(1)

I

Figure 4d shows a spectrum of a trapped polymer radical which was isolated after irradiation by precipitation in methanol. This spectrum is very similar to that of the polymer nitroxide radical formed by trapping of the polymer radical II in the course of the photodegradation of PMSt by benzophenone.[8] Figure 4e is a computer-simulated spectrum of the polymer nitroxide radical III where the hyperfine splitting constants of a_N = 14.8 G and a_H = 1.8 G were assumed. A comparison between spectra 4d and 4e will be discussed later. The spectrum shown in Figure 4b was well reproduced by the best fitting method using a computer with relative intensity ratios of spectra 4a:4c:4e = 0.1:0.4:1.0. This means that both the phenyl radical and the polymer radical II coexist in the system of chlorobenzene-added polymer solution under γ-irradiation.

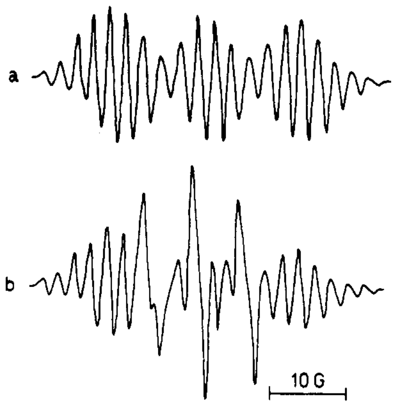
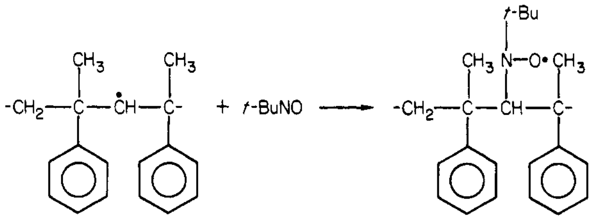


Figure 5. ESR spectra of nitroxide radicals formed during γ-irradiation of PMSt solution in benzene in the presence of carbon tetrachloride and *t*-BuNO: (a) [carbon tetrachloride] = 1 M, [*t*-BuNO] = 7 × 10^{-3} M; (b) [PMSt] = 6 × 10^{-1} M, [carbon tetrachloride] = 1 M, [*t*-BuNO] = 7 × 10^{-3} M.



(2)

II III

On addition of carbon tetrachloride, the ESR spectra shown in Figure 5 were obtained. In the presence of both the polymer and the additive, two kinds of spin adducts were observed as illustrated in Figure 5b. By analogy with the chlorobenzene-added solution, it appears that one is derived from the polymer and the other is from the additive. Figure 5a demonstrates a spectrum obtained in the absence of the polymer, which is in good agreement with that of *tert*-butyl trichloromethyl nitroxide radical reported by Perkins et al.[12] Splitting constants of the observed spectrum were a_N = 12.5 G and a_{Cl} = 2.4 G, coinciding with the authentic values of a_N = 12.5 G and a_{Cl} = 2.2 G.[12] This fact indicates that the trichloromethyl radical is produced from carbon tetrachloride by γ-irradiation. The nitroxide radicals formed in the presence of carbon tetrachloride were so unstable that the spectra decayed out in 10 min after irradiation. The separated polymer gave no signal when the polymer was isolated after irradiation.

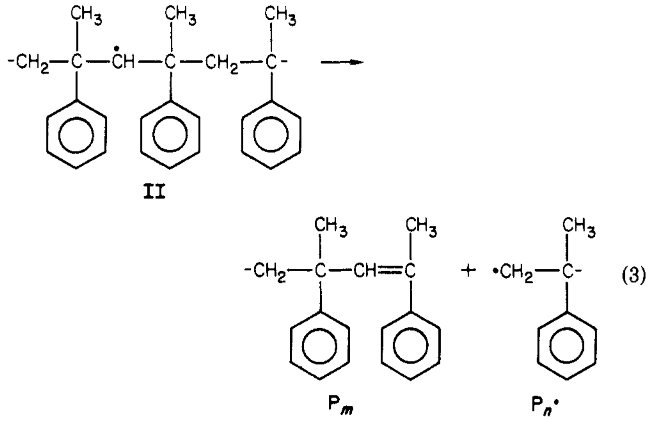
Discussion

The G_s value for PMSt in benzene was determined to be 0.78 ± 0.04 over the wide range of the dose rates shown in Table II. This value is nearly equal to the G_s value in bulk (0.25^6 and 1.4^7). In the presence of additives with high G_r values, however, the G_s values increased as seen in Table III. These findings clearly indicate that the radicals derived from the additives play an important role in the chain scission of the polymer occurring in dilute solution.

The spin trapping experiments have proved the formations of the phenyl radical from chlorobenzene and of the trichloromethyl radical from carbon tetrachloride. The phenyl radical is highly reactive in hydrogen abstraction.

The rate constant for hydrogen abstraction by the phenyl radical from toluene has been estimated to be 1.0×10^6 M^{-1} s^{-1} and that from methanol has been determined to be at least 1.4×10^5 M^{-1} s^{-1} at room temperature.[15,16] In comparison with the phenyl radical, the reactivity of the trichloromethyl radical seems to be rather low. The rate constant for hydrogen abstraction by the trichloromethyl radical from cyclohexane has been reported to be 23 M^{-1} s^{-1} at 313 K in the gas phase.[17,18] The values listed in Table III demonstrate that the radical production is favored in carbon tetrachloride solution over that in chlorobenzene solution, whereas the rate of chain scission of PMSt is higher in the latter. The lower reactivity of the trichloromethyl radical on hydrogen abstraction from the polymer chain appears to explain the lower G_s value in carbon tetrachloride solution.

The ESR spectrum shown in Figure 4d is a little complicated, compared with the simulated spectrum of the trapped nitroxide of the polymer radical (Figure 4e). The observed spectrum is composed of a main triplet with further splitting of each line. The central peak consists of a clear doublet, while both the right and the left sides of the peaks are made up by the superposition of a doublet and other split lines. This suggests that two or more kinds of polymer radicals are trapped by *t*-BuNO. One of them is evidently the above-mentioned polymer radical II, which is formed through hydrogen abstraction from the main-chain methylene group of the polymer. Chain scission of the polymer presumably takes place according to the same unimolecular process as in the case of the benzophenone-sensitized degradation of PMSt:[8,11]



With regard to another polymer radical which has been trapped by *t*-BuNO, it is necessary to take account of the following possibility: a polymer radical produced by hydrogen abstraction from the α-methyl group of PMSt or the lateral polymer radical $P_n\cdot$ formed via the process in eq 3. If either radical is trapped by *t*-BuNO, the resulting nitroxide radical would show the same splitting with a_H of about 9 G (a triplet of triplets) as observed in the case that a hydrogen is abstracted from a *tert*-butyl group of *tert*-butylbenzene.[8] However, the line profile of a triplet of triplets is not found in the spectrum of Figure 4d, and therefore the above-mentioned possibility is reasonably excluded.

An alternative explanation for another polymer radical is the hydrogen abstraction from the phenyl ring of the polymer. The splitting pattern of the side peaks in Figure 4d resembles that of *tert*-butyl phenyl nitroxide radical and the value of the splitting constant is about 2 G, being close to $a_H^{p,o}$ of *tert*-butyl phenyl nitroxide radical. These findings imply a possibility of the hydrogen abstraction from the phenyl ring of the polymer. Because of less resolution of hyperfine splitting in the spectrum, however, no definite information on the presence of this polymer radical has been obtained in the present study.

Although chlorine atoms have not been observed in the spin trapping experiments of this work, they are likely to take part in the accelerating process. Chlorine atoms have been successfully trapped in γ-irradiated carbon tetrachloride by the use of phenyl *tert*-butyl nitrone as a trapping agent.[19] In addition, the radiolysis of chlorine-containing compounds is well-known to yield hydrogen chloride.[20] These observations suggest the formation of chlorine atoms from chlorine-containing compounds on γ-irradiation. It has been shown that the rate of chain scission of PMMA is greatly dependent on solvents when the polymer is exposed to γ-rays in dilute solutions.[21,22] The rate of chain scission is much accelerated in chlorine-containing solvents such as chloroform and carbon tetrachloride, while it is smallest in benzene. Taking account of concurrent degradation observed in the course of the chlorination of PMMA,[23] Henglein et al. ascribed the marked accelerating effect of the chlorine-containing compounds to a secondary reaction induced by chlorine atoms which are liberated from the solvents with γ-rays.[4c,22] They proposed that hydrogen abstraction from α-methyl groups by chlorine atoms was the primary process for the chain scission, followed by unimolecular decomposition of the resulting polymer radical.

An analogous situation for chlorine atoms would be also realized in the present study. Other factors involved in the degradation behavior of PMSt under γ-irradiation are the extent of radical production from additives and the reactivity on hydrogen abstraction of resultant radical species from the polymer. It seems most probable that the transient species of the degradation is the polymer radical II which has been detected in this work by spin trapping experiments. Extensive work is in progress to apply these experimental procedures to other degradation-type polymers.

Acknowledgment. We gratefully acknowledge Dr. M. Tabata of Hokkaido University for assistance in computer simulation of ESR spectra. We also thank Dr. T. Matsuyama of Kyoto University for helpful discussions during the course of experiments.

Registry No. PMSt (homopolymer), 25014-31-7; chlorobenzene, 108-90-7; carbon tetrachloride, 56-23-5; chloroform, 67-66-3; acetone, 67-64-1.

References and Notes

(1) Part 4 of the series "Photo- and Radiation-Induced Degradation of Vinyl Polymers in Solution".
(2) Present address: Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan.
(3) On leave from KemaNord AB, S-850 13, Sundsvall, Sweden.
(4) (a) A. Charlesby, "Atomic Radiation and Polymers", Pergamon Press, Oxford, 1960; (b) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Interscience, New York, 1962; (c) A. Henglein and W. Schnabel, "Current Topics in Radiation Research", M. Ebert and A. Howard, Eds., North-Holland Publishing Co., Amsterdam, 1966, Vol. II, Chapter 1; (d) M. Dole, Ed., "The Radiation Chemistry of Macromolecules", Academic Press, New York, 1973; (e) C. David, "Comprehensive Chemical Kinetics", C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, 1975, Vol. 14, Chapter 2; (f) W. Schnabel, "Polymer Degradation", Hanser, Munich, 1981, Chapter 5.
(5) A. A. Miller, E. J. Lawton, and J. S. Balwit, *J. Polym. Sci.*, **14**, 503 (1954).
(6) A. M. Kotliar, *J. Appl. Polym. Sci.*, **2**, 134 (1959).
(7) Y. Yamamoto, M. Himei, and K. Hayashi, *Macromolecules*, **9**, 874 (1976); *ibid.*, **10**, 1316 (1977).
(8) T. Ikeda, H. Yamaoka, T. Matsuyama, and S. Okamura, *J. Phys. Chem.*, **82**, 2329 (1978).
(9) E. G. Jansen, *Acc. Chem. Res.*, **4**, 31 (1971).

(10) J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley, New York, 1970, p 771.

(11) T. Ikeda, K. Kawaguchi, H. Yamaoka, and S. Okamura, *Macromolecules*, 11, 735 (1978).

(12) M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 395 (1970).

(13) Calculated from the figures presented in ref 4b, p 98.

(14) A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. von Voorst, *Tetrahedron Lett.*, 2115 (1966).

(15) K. U. Ingold, "Free Radicals", J. K. Kochi, Ed., Wiley, New York, 1973, Vol. 1, Chapter 2.

(16) J. E. Packer, D. B. House, and E. J. Rasburn, *J. Chem. Soc. B*, 1574 (1971).

(17) M. L. White and R. R. Kuntz, *Int. J. Chem. Kinet.*, 3, 127 (1971).

(18) Reliable determinations of the rate constant for hydrogen abstraction by trichloromethyl radicals have never been carried out in solution. However, the gas-phase data are reasonably assumed to be applicable to solution systems because benzene used as a solvent in this work is nonpolar and therefore the solvent effect on radical reactivity can be excluded.[15]

(19) Unpublished work of I. Lopp, cited in ref 9.

(20) A. Horowitz and L. A. Rajbenbach, *Int. J. Radiat. Phys. Chem.*, 5, 163 (1973).

(21) S. Okamura, T. Manabe, S. Futami, T. Iwasaki, A. Nakajima, K. Ohdan, H. Inagaki, and I. Sakurada, *Proc. U. N. Int. Conf. Peaceful Uses At. Energy, 2nd, 1958*, **29**, 176 (1958).

(22) A. Henglein, C. Schneider, and W. Schnabel, *Z. Phys. Chem. (Frankfurt/Main)*, 12, 339 (1957).

(23) W. Hahn and F. Grafmuller, *Makromol. Chem.*, 21, 121 (1956).

Substrate Effects on the Chemisorbed and Physisorbed Layers of Methacryl Silane Modified Particulate Minerals

Hatsuo Ishida* and James D. Miller

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. Received February 18, 1983

ABSTRACT: The substrate effects on the chemisorbed and physisorbed layers of [γ-(methacryloxy)propyl]trimethoxysilane (γ-MPS) modified particulate minerals were studied by diffuse reflectance Fourier transform infrared spectroscopy and gel permeation chromatography. The infrared measurements show that the adsorbed γ-MPS molecules exist as two well-defined layers on the substrate surface and that the relative proportion of these is influenced by the acid/base nature of the surface as well as the surface chemical functionality and the adsorbate loading. The acid/base nature of the particulate surface was characterized by measuring the pH of an aqueous slurry of each particulate, and the specimens examined gave values ranging from pH 1.9 through pH 12.4. The near-neutral pH substrates demonstrate the greatest proportion of chemisorbed silane. Gel permeation chromatography demonstrates that the physisorbed layers consist of unhydrolyzed or partially hydrolyzed monomers and polysiloxane oligomers or polymers with a molecular weight up to several thousand. The molecular weight of the oligomeric species is dependent on the long-range acid/base influence of the substrate surface and descends in the order neutral > basic ≥ acidic. This effect can be modeled by adjusting the pH of the treating solution and depositing oligomers in bulk form. The substrate characteristics determine the molecular structure of deposited trifunctional silanes by providing suitable or unsuitable sites for chemical reaction with the substrate, influencing the intramolecular condensation reaction, and determining the effective concentration and mobility of the adsorbate.

Introduction

Organofunctional silane coupling agents are used to modify the adhesive, chemical, rheological, and other properties of particulate polymer composites. Much of the early coupling agent technology centered on applications involving glass fibers or siliceous-type surfaces. More recently, considerable interest has developed in the use of coupling agents on other inorganic mineral substrates. While some of these are siliceous (e.g., clay) and analogies may be made with the glass-related research, others are not (e.g., calcium carbonate and alumina trihydrate).[1]

Deposition of organofunctional silanes is not similar to the modification of surfaces by most small organic molecules or monomers. Neither is it similar to the adsorption of polymeric materials. The organofunctional silanes used as coupling agents are trifunctional molecules capable of both reaction with the substrate surface and formation of complex polymeric networks upon deposition. A number of factors are known to influence the structure of adsorbed silanes on glass surfaces. These include the silane type, hydrolysis and drying conditions, heat treatment, and solution pH.[1] When the nature of surface-treated particulate substrates is studied, the most important independent variables are the substrate characteristics. Particulate minerals vary in chemical composition, surface charge, acid/base character, shape, size, surface area, and porosity.

Silane coupling agents are known to form chemisorbed and physisorbed layers on the surface of glass fibers.[2–4] The existence of physisorbed silane layers is not unique to the glass fiber surface. Dry-blended particulate minerals treated with silanes from either organic or aqueous solutions also give large amounts of physisorbed silane.[4,5] The physisorbed silanes play important roles as modifiers of the matrix interphase, influencing both the mechanical and rheological properties of the composite system. Recently, experimental observations have been made that can be attributed to the function of physisorbed silanes. An (aminopropyl)silane (γ-APS) treated aluminum oxide substrate with a polyethylene coating failed adhesively or cohesively depending on the heat treatment of the silane layers.[6] The failure mechanism was proposed to be a function of the degree of silane/matrix interpenetration and more recently, Kaul et al.[7] demonstrated direct evidence for interdiffusion between γ-APS and polyethylene in the same system. Improved peel strength was reported in all cases for this Al_2O_3/γ-APS/PE system[6] over the untreated substrate in spite of the lack of substantial

0024-9297/84/2217-1659$01.50/0 © 1984 American Chemical Society