Plasma-Induced Surface Radicals of Low-Density Polyethylene Studied by Electron Spin Resonance[1]

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Received June 26, 1997; Revised Manuscript Received December 5, 1997

ABSTRACT: Plasma-induced low-density polyethylene (LDPE) radicals were studied in detail by electron spin resonance (ESR) by its comparison with ESR of high-density polyethylene (HDPE). The observed ESR spectra of plasma-irradiated LDPE are largely different in pattern from those of HDPE. The systematic computer simulation disclosed that such observed spectra consist of three kinds of radicals, midchain alkyl radical (1), allylic radical (2) as discrete radical species, and a large amount of dangling bond sites (DBS) (3) at an intra- and intersegmental cross-linked region. All these component radicals are essentially identical to those of HDPE. One of the most special features unique to plasma-irradiated LDPE, however, is the fact that thermally stable DBS (3) is a major component radical instead of a midchain alkyl radical in HDPE. This can be ascribed to the difference in polymer morphology between LDPE and HDPE: branched structure with a large amount of amorphous region for LDPE and linear structure with a large amount of crystalline region for HDPE. Since one of the characteristics of plasma irradiation is the fact that it is surface-limited, LDPE would undergo the radical formation preferentially on the surface-branched structural moiety followed by facile cross-link reactions resulting in the formation of DBS. Thus, the nature of radical formation of PE was found to be affected by the polymer morphology in a very sensitive manner.

Introduction

Polyethylene (PE), both LDPE[2] and HDPE,[3] is one of the most well-investigated polymers concerning radicals generated by high-energy radiation such as X-ray and γ-ray irradiation. A number of electron spin resonance (ESR) studies of radiation-induced radicals of PE have been reported.[2,3] This reflects, in part, interest in the high degree of technical importance of PE.

On the other hand, plasma irradiation can provide a different phase of study for polymer radicals. One of the characteristics of plasma irradiation is the effective energy transfer to a solid surface to create stable free radicals on a variety of polymer surfaces.[4]

One of the advantages of plasma irradiation over other types of radiation for the study of polymer radicals is that the radical formation can be achieved with a brief plasma duration by a simple experimental apparatus such as those we have devised.[5,6] This method makes it possible not only to study the polymer radicals without a significant change of polymer morphology but also to study the time-dependent ESR spectra following readily the ESR kinetics for the radical formation and its decay, so that we can carry out the systematic computer simulations with a higher credibility using variously prepared samples for one polymer.

As part of continuing work on elucidation of plasma-induced surface radicals, we recently reported the detailed ESR study on the nature of plasma-induced surface radicals of powdered HDPE coupled with the systematic computer simulations, and discussed the structure of radicals formed on its comparison with that of γ-irradiated HDPE.[5k]

In this paper, we report the first detailed account of an ESR study on plasma-induced LDPE radicals together with those of HDPE reported ealier,[5k] since the special features of LDPE radical formation would be best discussed by comparison with those of HDPE.

Experimental Section

Materials. LDPE (pellet) is commercially available, but the commercial LDPE shows the presence of unsaturated bonds (vinylene, carbonyl groups etc.) by FT-IR spectral measurements, as in the case of HDPE.[5k] Therefore, LDPE was purified by dissolving it (2 g) in hot xylene (50 mL, 100 °C) and then precipitating in a large excess of methanol (1 L). Precipitated LDPE was collected by filtration and dried in vacuo at 60 °C for 3 days. This procedure was repeated at least twice until the disappearance of unsaturated bonds was confirmed on the FT-IR spectral measurement. The LDPE thus obtained was screened with a 200 mesh sieve. The mean particle size was measured in ISOTON II (filtered solution based on 0.9% saline) (Nikkaki Inc.) by a Coulter counter (Model TA-2, Coulter Electronics Inc.), from which the specific surface area was determined: 1.51 cm^2/mg. The X-ray powder diffraction (XRD) pattern measurement (Rigaku RAD-1C) indicated ca. 40% crystallinity for the LDPE surface, deduced from a comparison of the integrated peak area of the crystalline peak and the halo pattern area of the amorphous region. The XRD spectra of LDPE are shown in Figure 1 together with that of HDPE (ca. 90% crystallinity). The degree of crystallinity remained unchanged before and after plasma irradiation for 20 min within the limits of detection by XRD measurement.

Plasma Irradiation and ESR Spectral Measurement. The unsaturated bond-free LDPE powder (20 mg) was placed in a specially designed ampule (30 mm i.d., 100 mm long) connected with a capillary tube (2 mm i.d.) at the uppermost part of the ampule, and the ampule was filled with argon gas and sealed (0.5 Torr). Then the plasma state of argon was sustained during agitation of the samples by a radio frequency discharge of inductive coupling at 13.56 MHz with a prescribed power and duration. The ESR spectral measurements were performed while turning the ampule upside down at appropriate intervals. The procedure was essentially the same as that reported earlier.[5k]

S0024-9297(97)00936-4 CCC: $15.00
Published on Web 04/29/1998

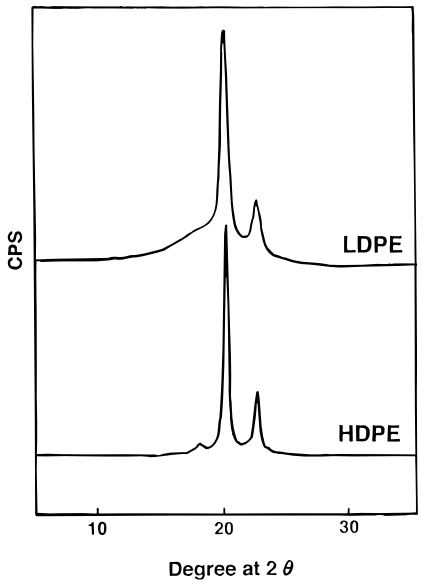

Figure 1. XRD spectra of LDPE and HDPE. The ratio in crystalline and amorphous regions is about 40:60 for LDPE and 90:10 for HDPE.

The ESR spectral intensity was determined by double integration. The radical concentration (spin number/cm^2) was calculated from the spectral intensities with the aid of calibration lines obtained from the spectral intensity of a poly(methyl methacrylate) (PMMA) powdered sample impregnated with DPPH. Measurements of g values were made relative to the fourth signal from the lower magnetic field ($g = 1.981$) of Mn^{2+} in magnesium oxide (MgO). ESR spectra were recorded by a JES-RE1X (JEOL) spectrometer with X-band and 100 kHz field modulation. Care was taken to ensure that no saturation occurred and that the line shape was not distorted by an excessive modulation amplitude. Thus, from a plot of the square root of the microwave power versus the signal peak height, a power level of 0.04 mW was chosen.

Computer Simulation of ESR Spectra. The computer simulations were performed with a 32-bit microcomputer (NEC PC9821Cx3). The simulated spectra were obtained from Gaussian functions by iteratively fitting spectroscopic parameters (g value, line width at half-height (HV), hyperfine splitting constant (HSC), and relative peak intensity) with observed spectra digitized through an A/D converter according to a nonlinear least-squares method.[5c] The simulation programs were fabricated so as to include the effect of g-factor anisotropy and/or α-hydrogen anisotropy on the line shape of the powder spectra according to Kneubühl's equation and Cochran's equation, respectively.[7] To assist the simulation procedure, we have also fabricated the program for obtaining the difference spectrum by subtracting one observed spectrum from another.

Results and Discussion

Observed Room-Temperature ESR Spectra of Plasma-Irradiated LDPE. The progressive changes of the room-temperature ESR spectral pattern of plasma-irradiated powdered LDPE with various plasma durations are shown in Figure 2, together with those of HDPE.[5k]

It is seen that several seconds of plasma irradiation is long enough to detect the radicals formed in LDPE as in the case of HDPE. The ESR spectra of plasma-induced radicals of LDPE, however, are largely different in pattern from the well-defined sextet-type spectrum of HDPE. The spectral pattern gradually changes as the plasma duration increases, especially characterized by an increase in the peak intensity of the central lines.

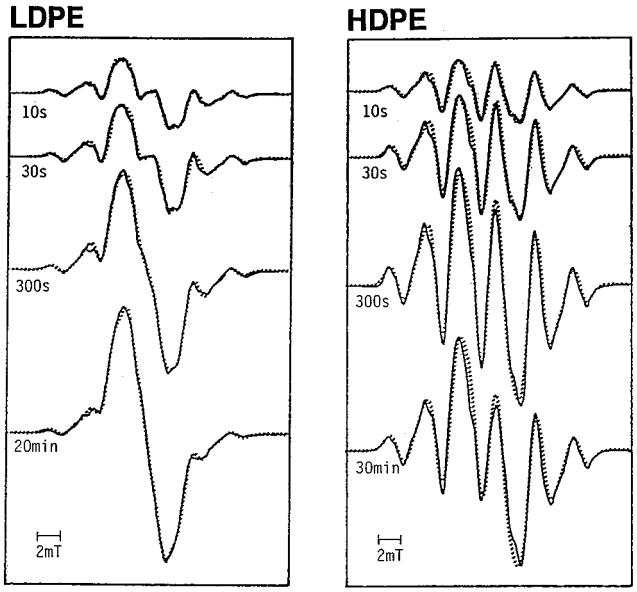

Figure 2. Observed ESR spectra of Ar-plasma-irradiated LDPE and HDPE powders for various durations together with the simulated spectra shown as dotted lines.

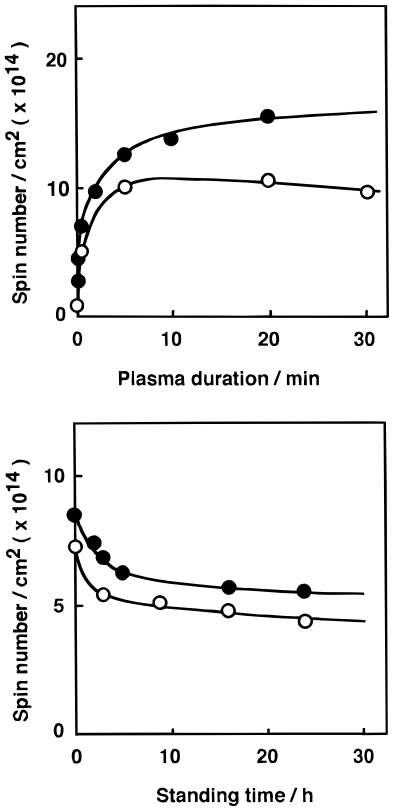

Figure 3. Progressive changes in total spin concentration per unit surface area of Ar-plasma-irradiated LDPE and HDPE powders determined by double integration as a function of plasma duration (A) and on standing anaerobically at room temperature (B): (●) LDPE; (○) HDPE.

We note that the main spectral features of LDPE plasma-irradiated for less than 30 s are superficially similar to that of HDPE obtained after plasma irradiation followed by standing for a long period of time at room temperature (vide infra, see Figure 4).

Figure 3 shows the comparison of the progressive changes of total radical concentrations (determined by double integration of the observed spectra) between

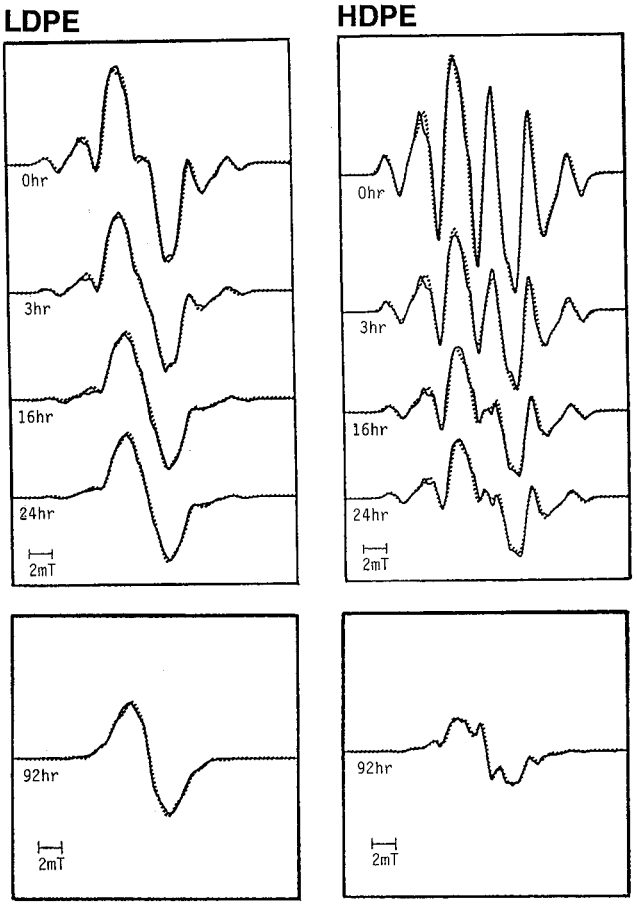

Figure 4. Progressive ESR spectral changes on standing anaerobically at room temperature of LDPE and HDPE plasma-irradiated for 3 min, respectively, together with the simulated spectra shown as dotted lines.

plasma-irradiated LDPE and HDPE as a function of plasma duration (A) and on anaerobic standing at room temperature (B).

It is apparent that the spectral intensity increases as the plasma duration increases, although it tends to level off in both cases, and the net effect of plasma irradiation on the radical formation in LDPE is larger than that in HDPE, while the decrease in the spectral intensity on standing at room temperature is only slightly larger in HDPE than in LDPE (Figure 3B). The ratio between LDPE and HDPE in the initial rate of radical formation per unit surface area was ca. 1.68:1 ($k = 2.59 \times 10^{15}$ spin cm^{-2} min^{-1} for LDPE and $k = 1.54 \times 10^{15}$ spin cm^{-2} min^{-1} for HDPE).

ESR Spectral Changes on Standing in Anaerobic Conditions at Room Temperature. Figure 4 shows a series of ESR spectra of LDPE plasma-irradiated for 3 min on standing at room temperature together with those of HDPE. It is seen that the spectral pattern of LDPE has gradually changed with a decrease in the total spectral intensity, but in a different manner from those of HDPE.[5k] On standing at room temperature for 92 h, the broad single line spectrum was finally obtained from LDPE, and after that, the spectral pattern persisted unchanged on further standing, which shows a considerable difference in pattern compared with that of HDPE shown in Figure 4. This indicates that not only the observed ESR spectra of plasma-irradiated LDPE consist of more than two-component spectra of the radicals with different thermal stabilities at room temperature but also the nature of radical decay in LDPE is different from that of HDPE, since the spectrum of plasma-irradiated LDPE is very much similar to that of HDPE plasma-irradiated for 3 min followed by standing at room temperature for 24 h (Figure 4).

Simulated Spectra. We recently reported that systematic computer simulations of the radicals formed in plasma-irradiated HDPE using isotropic lines have proven equally valid for providing a sufficiently fundamental insight into the nature of surface radicals formed in plasma-irradiated HDPE.[5k] Thus, we also simulated the present spectra of radicals formed in plasma-irradiated LDPE using isotropic lines, as in the case of HDPE.

The corresponding simulated spectra are shown as dotted lines in Figures 2 and 4, respectively. It can be seen that all the observed spectral features have been satisfactorily reproduced by the present simulations. Figure 5 shows representative component spectra of the simulated spectra for the radicals of plasma-irradiated LDPE. The simulated spectra consist principally of three kinds of component spectra: a sextet spectrum (I), a septet spectrum (II), and a smeared-out broad line (III). All the simulated spectra were obtained from the same component spectra with different ratios.

The ESR spectroscopic parameters for a representative selection of the component spectra, I, II and III, in the simulated spectra are listed in Table 1. An outline of a smeared-out broad line (III) ($g = 2.0024$) was approximated by a single broad line ($\sum H = 9.38$ mT) with a small amount of a triplet of doublets (2.23 and 1.44 mT). It should be noted that all these component spectra are essentially identical with those of HDPE.

Structural Assignment. In the studies of plasma-irradiated HDPE, the radical structures of the sextet spectrum (I), septet spectrum (II), and smeared-out broad line (III) have already been assigned to the midchain alkyl radical (1) (−CHĊHCHCHĊH−), the allylic radical (2), (−CHĊHCHCH=CHCHĊH−), and immobilized dangling bond sites (DBS) (3) at the surface cross-linked region, respectively, and the pathway for their radical formation has been established.[5k] Since all the component spectra in plasma-irradiated LDPE are essentially the same as those in HDPE, they can be assigned to the same component radicals as those in HDPE.

Figure 6 shows the progressive changes of three-component spectral intensities in the simulated spectra of LDPE in the course of plasma irradiation (Figure 6A) and on standing at room temperature (Figure 6B).

It is seen from Figure 6A that the spectral intensity of III parabolically increases as plasma duration increases, while the spectral intensities of I and II tend to level off for a short plasma duration. This captures the essential reason for the changes in the observed spectral pattern in the course of plasma irradiation (see Figure 2). A striking difference in the nature of radical formation between LDPE and HDPE is the fact that a smeared-out broad line (III) is a major component in LDPE from the beginning of plasma irradiation, whereas a sextet spectrum (I) of the radical (1) initially produced is a major component in HDPE, as reported previously.[5k] The result indicated that LDPE has a great propensity to undergo a rapid and facile surface cross-link reaction. This is understandable from the polymer morphology of LDPE, as illustrated in Figure 7, which possesses a large amount of branched structures favorable for a

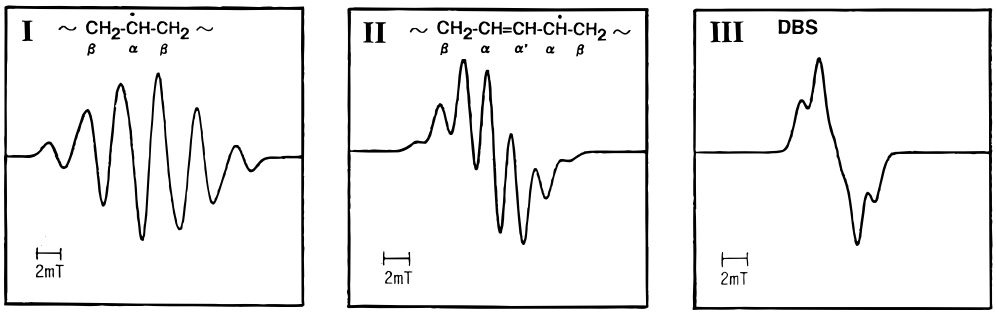

Figure 5. Representative spectral features for the three component spectra, **I**, **II**, and **III**, in the simulated spectra of plasma-irradiated LDPE.

Table 1. ESR Spectral Data for Component Radicals in Simulated Spectra of LDPE and HDPE[a]

		I	II	III
LDPE	g	2.0026	2.0024	2.0023
	A_α	2.18 (1H)	1.79 (2H)	
	$A_{\alpha'}$		0.58 (1H)	
	A_β	3.15 (4H)	1.86 (4H)	
HDPE	g	2.0037	2.0037	2.0036
	A_α	2.19 (1H)	1.77 (2H)	
	$A_{\alpha'}$		0.58 (1H)	
	A_β	3.22 (4H)	1.82 (4H)	

[a] Values of HSC are given in mT.

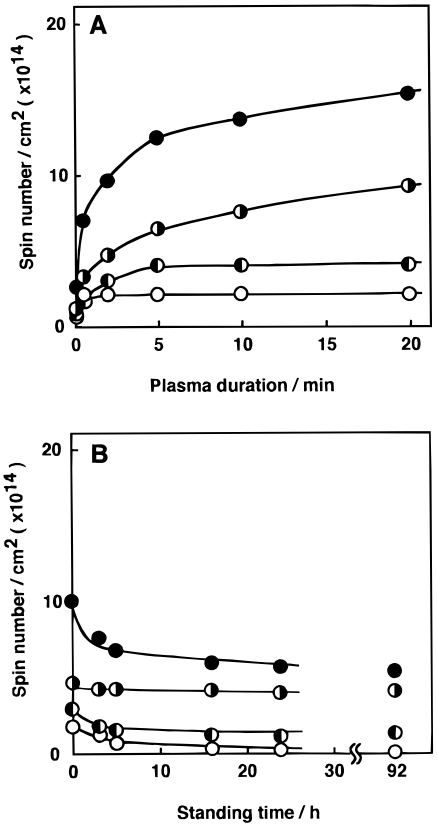

Figure 6. Simulated progressive changes in component spectra in Ar-plasma-irradiated LDPE powder: (A) on plasma duration; (B) on standing anaerobically at room temperature of the sample plasma-irradiated for 3 min. Key: (●) total; (○) sextet; (◐) septet; (◑) DBS.

surface cross-link reaction. A similar propensity has also been observed in some other polymers. For example, alkyl-substituted celluloses (ethylcellulose and (hydroxylpropyl)cellulose) had a great tendency to undergo a high cross-link reaction on its plasma irradiation so that the DBS was a major comoponent among three

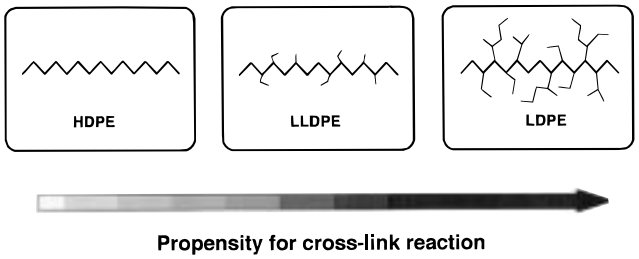

Figure 7. Three types of polymer morphology in polyethylene (PE). LLDPE stands for linear low-density polyethylene.

kinds of radicals formed, unlike nonsubstituted cellulose where a discrete hydroxyl−alkyl radical was a major component.[5o]

On the other hand, it is seen from Figure 6B that the sextet (I) and septet (II) spectra gradually decrease in intensity and the spectrum (I) finally disappears on standing at room temperature. The spectral intensity of III, however, remains nearly unchanged, demonstrating that the decrease in the total spectral intensity is caused by instability of two component spectra, I and II. Thus, the simulated spectrum (92 h standing) of LDPE shown in Figure 4 consists of a component spectrum of III contaminated with a small amount of II. A small amount of septet (II) is concealed from its appearance in the spectral feature due to a large line width of DBS, while the spectrum of HDPE plasma-irradiated for 3 min followed by standing for 92 h consists of the septet spectrum (II) as a major component.[5k] Then, the midchain alkyl radical (1) of the sextet spectrum (I) was also unstable in HDPE, which would be caused by the radical coupling and/or β-hydrogen elimination.

Conclusion

The conclusions drawn from the present study can be summarized as follows: It was found that even less than several seconds of plasma duration is long enough to produce a detectable amount of surface radicals of LDPE, and the radical concentration of LDPE observed at room temperature is greater than that of HDPE. The observed ESR spectra of plasma-irradiated LDPE are largely different from those of HDPE but are superficially similar to those of HDPE plasma-irradiated for less than 30 s followed by standing at room temperature for a long period of time.

The systematic computer simulation disclosed that such observed spectra consist of three kinds of radicals, midchain alkyl radical (1), allylic radical (2) as discrete radical species, and a large amount of DBS (3) at the surface cross-linked region. All these component spectra are essentially identical to those of HDPE.

One of the most special features unique to plasma-irradiated LDPE, however, is the fact that DBS (3) is a major component instead of the midchain alkyl radical (1) in HDPE. This can be reasonably ascribed to the difference in intrinsic polymer morphology between LDPE and HDPE: branched structure with a large amount of amorphous region for LDPE and linear structure with a large amount of crystalline region for HDPE. Since one of the characteristics of plasma irradiation is the fact that it is surface-limited, LDPE would undergo the radical formation preferentially on the surface-branched structural moiety followed by cross-link reaction resulting in the facile formation of DBS. Thus, the nature of radical formation of PE was found to be affected by the polymer morphology in a very sensitive manner.

We believe that LDPE radicals generated by any radiation method have never been studied before to such a detailed extent as those reported herein.

Finally, it should be noted that on the basis of the fact that the component spectra of plasma-irradiated LDPE were essentially identical with those in plasma-irradiated HDPE, the ESR spectral analyses of plasma-irradiated LDPE further reinforced our conclusion on HDPE that a smeared-out broad line (III) is a DBS (3) resulting from both intra- and intersegmental cross-link reactions, not a polyenyl radical.[5k]

Acknowledgment. This work was financially supported in part by a Grant-in-Aid of Scientific Research on Priority Areas from the Ministry of Education, Science, Sports, and Culture of Japan (Grant No. 08672479), which is gratefuly acknowledged.

References and Notes

(1) (a) Part of this work was presented at the Symposium of Plasmas and Polymers; ACS National Meeting, San Fransico, CA, 1997. (b) Kuzuya, M.; Kondo, S.; Sugito, M. *Polym. Prepr.* **1997,** *38* (1), 1049.

(2) (a) Ohnishi, S.; Ikeda, Y.; Kashiwagi, M.; Nitta, I. *Polymer* **1961**, *2*, 119. (b) Libby, D.; Ormerod, M. G. *J. Phys. Chem. Solids* **1961**, *18*, 316. (c) Tsuji, K.; Seiki, T. *J. Polym. Sci., Part B* **1969**, *7*, 839. (d) Tsuji, K. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 467. (e) Tsuji, K. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1407. (f) Basheer, R.; Dole, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 957.

(3) (a) Ohnishi, S.; Ikeda, Y.; Sugimoto, S.; Nitta, I. *J. Polym. Sci.* **1960**, *47*, 503. (b) Lawton, E. J.; Balwit, J. S.; Powell, R. S. *J. Chem. Phys.* **1960**, *33*, 395. (c) Kashiwabara, H. *J. Phys. Soc. Jpn.* **1961**, *16*, 2494. (d) Ohnishi. S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 254. (e) Kashiwagi, M. *J. Chem. Phys.* **1962**, *36*, 575. (f) Ohnishi, S.; Sugimoto, S.; Nitta, I. *J. Chem. Phys.* **1962**, *37*, 1283. (g) Salovey, R. *J. Polym. Sci.* **1962**, *61*, 463. (h) Ormerod, M. G. *Polymer* **1963**, *4*, 451. (i) Fallgatter, M. B.; Dole, M. *J. Phys. Chem.* **1964**, *68*, 1988. (j) Salovey, R.; Yager, W. A. *J. Polym. Sci., Part A* **1964**, *2*, 219. (k) Kusumoto, N.; Yamamoto, T.; Takayanagi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 1173. (l) Fujimura, T.; Tamura, N. *J. Phys. Chem.* **1975**, *79*, 1859. (m) Nunome, K.; Muto, H.; Toriyama, K.; Iwasaki, M. *Chem. Phys. Lett.* **1976**, *39*, 542. (n) Shimada, S.; Maeda, M.; Hori, Y.; Kashiwabara, H. *Polymer* **1977**, *18*, 19. (o) Shimada, S.; Hori, Y.; Kashiwabara, H. *Polymer* **1978**, *19*, 763. (p) Fujimura, T.; Hayakawa, N.; Kuriyama, I. *Polymer* **1978**, *19*, 1031. (q) Fujimura, T.; Hayakawa, N.; Kuriyama, K. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 945. (r) Fujimura, T.; Hayakawa, N.; Tamura, N. *J. Macromol. Sci., Phys.* **1979**, *112*, 1440. (s) Hori, Y.; Fukunaga, Z.; Shimada, S.; Kashiwabara, H. *Polymer* **1979**, *20*, 181. (t) De Vries, K. L.; Smith, R. H.; Fanconi, B. M. *Polymer* **1980**, *21*, 949. (u) Gvozdic, N.; Dole, M. *Radiat. Phys. Chem.* **1980**, *15*, 435. (v) Shimada, S.; Kashiwabara, H. *Polymer* **1981**, *22*, 1385. (w) Igarashi, M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2450. (x) Plonka, A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1011. (y) Hikmet, R.; Keller, A. *Radiat. Phys. Chem.* **1987**, *29*, 15. (z) Jones, R. A.; Taylor, D. J. R.; Stepto, R. F. T.; Ward, I. M. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 133. (aa) Feldman, V. I.; Sukhov, F. F.; Slovokhotova, N. A.; Zubov, A. Yu. *Int. J. Polym. Mater.* **1993**, *22*, 185. (ab) Chipara, M. I.; Ifrim, A.; Grecu, V. V.; Toacsan, M. I.; Pogrion, N. P.; Inoscu, A.; Chipara, M. D.; Romero, J. R. *Polym. Degrad. Stab.* **1994**, *43*, 165. (ac) Bhateja, S. K.; Duerst, R. W.; Aus, E. B.; Andrews, E. H. *J. Macromol. Sci. Phys.* **1995**, *B34*, 263.

(4) Hudis, M. *Techniques and Applications of Plasma Chemistry*; Hollahan, J. R., Bell, A. T., Eds.; Wiley: New York, 1974.

(5) (a) Kuzuya, M.; Koide, A.; Ito, A.; Noguchi, A. *Chem. Lett.* **1989**, 555. (b) Kuzuya, M.; Noguchi, A.; Ito, H.; Kondo, S.; Noda, N. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1. (c) Kuzuya, M.; Noguchi, A.; Ishikawa, M.; Koide, A.; Sawada, K.; Ito, A.; Noda, N. *J. Phys. Chem.* **1991**, *95*, 2398. (d) Kuzuya, M.; Ito, H.; Kondo, S.; Noda, N.; Noguchi, A. *Macromolecules* **1991**, *24*, 6612. (e) Kuzuya, M.; Kamiya, K.; Sawada, K. *Proc. Jpn. Symp. Plasma Chem.* **1991**, *4*, 317. (f) Kuzuya, M.; Ishikawa, M.; Noguchi, A.; Sawada, K.; Kondo, S. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 379. (g) Kuzuya, M.; Noda, N.; Kondo, S.; Washino, K.; Noguchi, A. *J. Am. Chem. Soc.* **1992**, *114*, 6505. (h) Kuzuya, M.; Kondo, S.; Ito, H.; Noguchi, A. *Appl. Surf. Sci.* **1992**, *60*, 416. (i) Kuzuya, M.; Kamiya, K.; Yanagihara, Y.; Matsuno, Y. *J. Plasma Sources Sci. Technol.* **1993**, *2*, 51. (j) Kuzuya, M.; Sawada, K.; Takai, T.; Noguchi, A. *Polym. J.* **1993**, *25*, 75. (k) Kuzuya, M.; Niwa, J.; Ito, H. *Macromolecules* **1993**, *26*, 1990. (l) Kuzuya, M.; Kondo, S.; Noguchi, A.; Xu, K. *J. Photopolym. Sci. Technol.* **1993**, *6*, 371. (m) Kuzuya, M.; Morisaki, K.; Niwa, J.; Yamauchi, Y.; Xu, K. *J. Phys. Chem.* **1994**, *98*, 11301. (n) Kuzuya, M.; Niwa, J.; Noguchi, T. *Polym. J.* **1995**, *27*, 251. (o) Kuzuya, M.; Yamauchi, Y.; Niwa, J.; Kondo, S.; Sakai, Y. *Chem. Pharm. Bull.* **1995**, *43*, 2037. (p) Kuzuya, M.; Sugito, M.; Kondo, S. *J. Photopolym. Sci. Technol.* **1996**, *9*, 261.

(6) (a) Kuzuya, M. *Trends Phys. Chem. (India)* **1991**, *2*, 39. (b) Kuzuya, M. *J. Photopolym. Sci. Technol.* **1992**, *5*, 407. (c) Kuzuya, M. *Yakugaku Zasshi* **1996**, *116*, 266.

(7) (a) Kneubühl, F. K. *J. Chem. Phys.* **1960**, 33, 1074. (b) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1961**, *34*, 1161.

MA9709361