CHEMISTRY LETTERS, pp. 555-558, 1989.

Nature of Free Radical Formation in Acrylic Resins by Plasma-Irradiation

Masayuki KUZUYA,* Atsuo KOIDE, Akiko ITO, and Akihiro NOGUCHI
Gifu Pharmaceutical University, 5-6-1, Mitahora-Higashi, Gifu 502

The room temperature ESR spectra of the radicals in four kinds of plasma-irradiated acrylic resins, PMMA, PMAA,and their copolymers, were studied. The spectra of the copolymers have shown unique patterns and the spectral intensity was proportional to the relative amount of carboxylic acid group in acrylic resins.

A number of electron spin resonance (ESR) studies of stable free radicals generated in acrylic resins through various sources such as γ-, X-, and UV-ray irradiation have been reported,[1] and all the spectra obtained at room temperature were similar and assigned to the terminating radical, $\sim CH_2-\dot{C}(COOR)(CH_3)$.[2] It has also been reported that plasma-irradiation of frozen vinyl monomers of methacrylic acid gave ESR spectrum which is by and large similar to those of γ-irradiated polymethacrylic acid.[3]

It is known that plasma-irradiation of inert gas conveniently produces a large amount of free radicals on the solid surface as well as to the formation of the surface layer with highly crosslinked network structure.[4] In fact, even several tens of seconds of plasma-irradiation are long enough to cause changes in the surface properties. And also, one of the characteristics of plasma-irradiation is the fact that it is surface-limited. Thus, plasma irradiation could provide a different phase of studies for radical formation on the solid surface. However, ESR studies of the radicals of polymethacrylic acid and its esters produced by plasma-irradiation have not been reported.

In order to investigate a specific effect of plasma-irradiation on the free radical formation on the solid surface distinct from those by other irradiation methods, we have carried out plasma-irradiation on four kinds of powdered acrylic resins such as polymethacrylic acid (PMAA) and its methyl ester (PMMA), and two types of the copolymers, MMA and MAA(6:4); Eudragit L100, and MMA and MAA (7:3); Eudragit S100,[5] and we report here the special features of the free radical formation studied by ESR spectral measurements.[6]

Plasma-irradiated samples of acrylic resins for ESR spectral measurements were prepared by the following method: Powdered acrylic resins (50 mg) were placed in a specially-designed ampule (30 mm i.d., 100 mm long) connected with capillary tube (2 mm i.d.) at the upmost part of the ampule and argon gas for plasmolysis (0.5 Torr) was impregnated and sealed. Then the plasma state of argon was sustained for 30 s with stirring of samples at room temperature by a radio frequency discharge of inductive coupling at 13.56 MHz with the supplied power (40 W) unless otherwise stated, and the ESR mesurements were performed

while turning the ampule upside down after plasma-irradiation, which is essentially the same procedure as that reported earlier.[7]

The room temperature ESR spectra of the free radicals of plasma-irradiated acrylic resins measured immediately (A), and two days (B) after plasma-irradiation are shown in Fig. 1. Argon, nitrogen and oxygen were used for plasmolysis, but the spectrum obtained was independent of the nature of the gas.

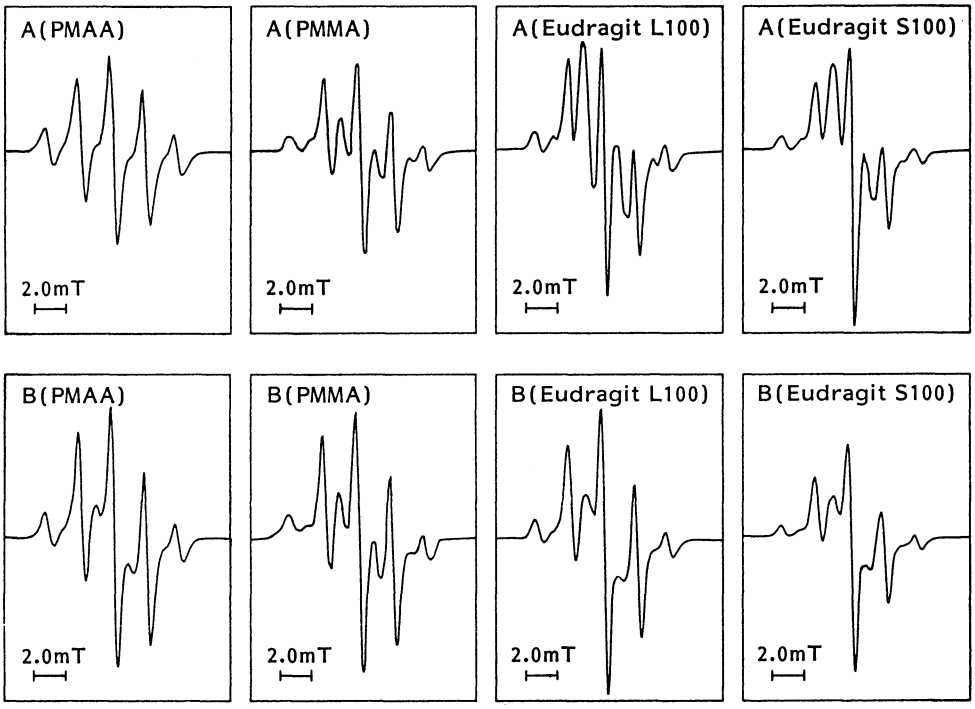


Fig. 1. The room temperature ESR spectra of powdered acrylic resins measured immediately (A) and two days (B) after plasma-irradiation.

The spectral features of (B) are similar, but not identical, to each other, which can be represented as a nine-line spectral feature consisting of two sets of lines, main five-lines and subsidiary four-lines. The spectra (B) in all cases persisted unchanged in shape for a long period of time at room temperature. This is a well known spectrum essentially identical with those obtained by other irradiation methods, and were assigned to a single terminating radical.[8-10] The interpretation of the spectrum has long been the subject of much discussion. The nine-lines spectrum has thus far been interpreted in several ways; overlap of the two conformations,[11-13] a Gaussian distribution around the most stable conformation,[14,15] and the exchange of two β-protons due to the hindered oscillation around the C-C bond.[16] Among these alternatives, the two conformation theory seems most acceptable.[13]

The spectra (A) in Fig. 1. exhibited further marked difference from each other, and the spectra from the copolymers, Eudragit L100 and S100, showed large deviation from the standard isotropic nine-lines spectrum. These spectral features have never been observed for methacrylate polymers by any irradiation method. This is a specially noteworthy feature, for it has been reported that the spectrum in question is unaffected by replacement of the ester alkyl groups.[17,18] Thus, it is strongly suggestive that some transient radicals besides the termi-

nating radical may be present (vide infra).

Since one of the characteristics of plasma-irradiation is surface-limited, the surface area of the samples is among the most important parameters to compare an efficiency of the radical formation with each other under a given set of plasma conditions. Thus, the mean particle size of each powdered sample was measured by Coulter Counter (Model TA-2, Coulter Electrics Inc. U.S.A.), from which the surface area was determined. The spectral intensity per unit surface area has been shown to be proportional to the relative amount of carboxylic group to the methyl carboxylate group in acrylic resins, as shown in Fig. 2., indicating that the former groups facilitate the radical formation.

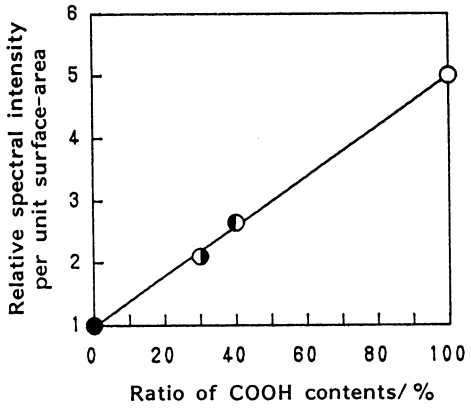


Fig. 2. Dependence of relative COOH contents on the radical formation in acrylic resins by plasma-irradiation. ●; PMMA, ◑; Eudragit S100, ◐; Eudragit L100, ○; PMAA.

Figure 3 shows the effect of plasma operational conditions on efficiency of the radical formation in Eudragit L100. Varying operational conditions such as plasma-supplied power, plasma-duration and argon pressure for plasmolysis was scarcely effected on the spectral patterns in each case, but they exerted a strong influence on the spectral intensity.

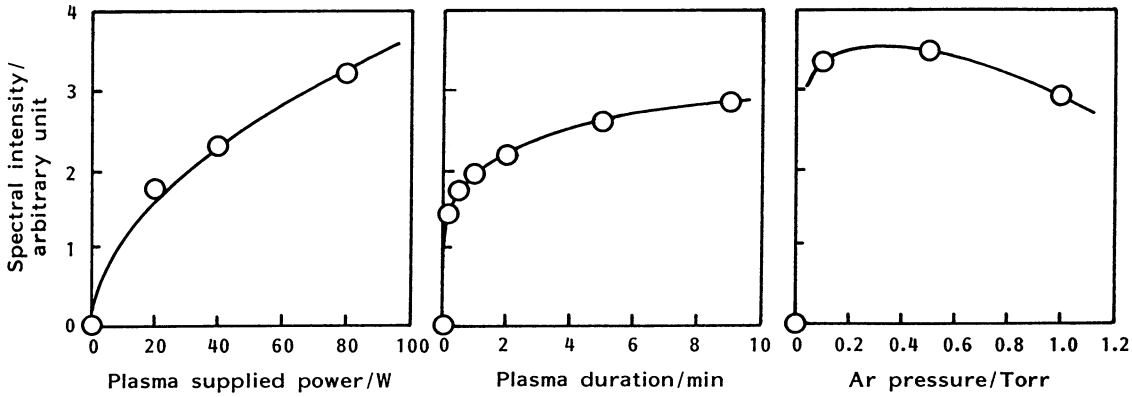
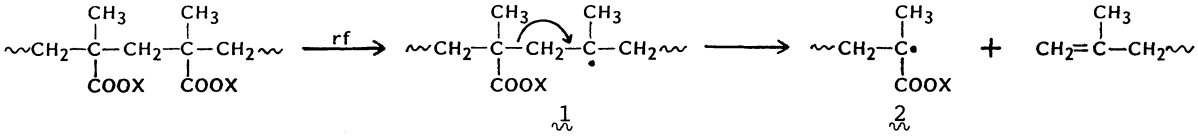


Fig. 3. The effect of plasma operational conditions on the radical formation in plasma-irradiated Eudragit L100.

It is seen that the spectral intensity was proportional to the plasma power, but the spectral shape remained constant, while the effect of plasma-duration were gradually levelled off, since the evoluted gas from the polymer makes the pressure raise and weaken a glow region of the plasma states in the

present closed system. The similar tendency has been observed for the effect of impregnated argon pressure; the radical formation decreased as argon pressure increases under the pressure of higher than 0.4 Torr.

Based on the experimental fact, the most probable mechanism by which the terminating radical, 2, has been formed by plasma-irradiation could involve an initial elimination of carboxyl group as shown in Scheme 1. The feasibility of the ensuing process can be rationalized in terms of c,d-substituent effect on the resulting radical, 2, (capto-dative concept).[19] If this mechanism is operative, a mid-chain radical, 1, is a possible species for the transient radicals involved in the spectra of Eudragit L100 or S100. We are actively elaborating these initial studies.



Scheme 1.

References

1) S.Ya.Pshezhetskii, A.G.Kotov, V.K.Milinchuk, V.A.Roginskii, and V.I.Tupikov, "EPR of Free Radicals in Radiation Chemistry," John Wiley & Sons, New York (1974).
2) M. Kamachi, Adv. Polym. Sci., 82, 207 (1987).
3) C.H.Bamford, A.D.Jenkins, and J.C.Ward, Nature (London), 186, 712 (1960).
4) M.Hudis, "Techniques and Application of Plasma Chemistry," ed by J.R. Hollahan and A.T.Bell, John Wiley, New York (1974).
5) All acrylic resins were commercially available, and for purification, were dissolved in chloroform, precipitated by pouring into methanol and dried in vacuo at 60 °C for 5 h.
6) The ESR spectra were recorded by a JES-RE1X (JEOL) spectrometer with 100 kHz field modulation, and the microwave power level was kept at 0.4 mW to eliminate saturation effects in the spectra.
7) M.Kuzuya, S.Nakai, T.Okuda, T.Kawaguchi, and Y.Yanagihara, J. Chem. Soc., Faraday Trans. 1, 83, 1579 (1987).
8) M.C.R.Symons, J. Chem. Soc., 1963, 1186.
9) H.Fischer, J. Polym. Sci., Part B, 2, 529 (1964).
10) P.Kourim and K.Vacek, Trans. Faraday Soc., 61, 415 (1965).
11) J.Sohma, T.Komaysu, and H.Kashiwabara, J. Polym. Sci., Part B, 3, 287 (1965).
12) J.A.Harris, O.Hinojosa, and J.C.Arthur,Jr., J. Polym. Sci. Polym. Chem. Ed., 11, 3215 (1973).
13) M.Kamachi, M.Kohno, D.J.Liaw, and S.Katsuki, Polym. J., 10, 69 (1978).
14) M.J.Bowden and J.H.O'Donnell, J. Phys. Chem., 72, 1577 (1968).
15) M.Iwasaki and Y.Sasaki, J. Polym. Sci., Part A-1, 7, 1537 (1969).
16) Y.Sasaki and M.Iwasaki, J. Polym. Sci., Part A-1, 7, 1749 (1969).
17) R.J.Abraham. H.W.Melville, D.W.Ovenall, and D.H.Whiffen, Trans. Faraday, Soc., 54, 1133 (1958).
18) I.S.Ungar, W.B.Gager, and R.I.Leininger, J. Polym. Sci., 44, 295 (1960).
19) H.G.Viehe, R.Merenyi, L.Stella, and Z.Janousek, Angew. Chem., Int. Ed. Engl., 18, 917 (1979).

(Received December 21, 1988)