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RADICAL TRANSFORMATION IN SOME GAMMA-IRRADIATED POLY-α-OLEFINS

Naoshi KUSUMOTO
Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University
Kumamoto 860

Some gamma-irradiated poly-α-olefins showed the change of ESR spectra from a complexed pattern to a simple singlet at room temperature. This was well elucidated by a reaction kinetic study on the assumption that short life radicals were transformed into stable ones.

It has been found that ESR spectrum of gamma-irradiated isotactic polyproyplene (IPP) changed from a complexed pattern to a simple singlet simultaneously with decreasing spectral intensity when it was kept at room temperature.[1,2] On the other hand, the spectral intensity of gamma-irradiated syndiotactic polypropylene(SPP) was found to decrease with constant line shape.[2] The decrease in the spectral intensity of SPP was elucidated by the second-order reaction mechanism of trapped radicals, but that of the IPP showed progressive departure with laps of time from the assumption of the second-order mechanism as shown in Figure 1. Therefore, it was implied that trapped radicals were partially transformed into another radical species which is stable at room temperature and shows the singlet spectrum, although another possibility that a weak singlet spectrum had originally been superimposed could be thought.

This singlet spectrum can be specified as the polyenyl type radical[3] which is formed by the dehydrogenation process.[4] Moreover, a similar change in ESR spectra was found for isotactic polybutene-1(PB1) and isotactic polypentene-1(PP1). The aim of this letter is, therefore, to ensure the implication mentioned above by the quantitative description of radical process.

Putting $\dot{A}$ and $\dot{B}$ as short and long life(polyenyl type) radicals, respectively, possible radical reaction processes are given as follow.

$$\dot{A} + \dot{A} \xrightarrow{k_1} 2A \tag{1}$$

$$\dot{A} \xrightarrow{k_2} \dot{B} \tag{2}$$

$$\dot{A} + \dot{B} \xrightarrow{k_3} AB \tag{3}$$

$$\dot{B} + \dot{B} \xrightarrow{k_4} 2B \tag{4}$$

The reaction rate constants k_3 and k_4 may be negligibly small compared with other constants here and the change of radical concentration for the radical $\dot{A}$ is

$$dC_a/dt = -(k_1C_a^2 + k_2C_a) \tag{5}$$

The solution of this equation for C_a is

$$C_a = -k_2C_{ao}/k_1[C_{ao} - (C_{ao} + k_2/k_1)\exp(k_2t)] \tag{6}$$

where C_{ao} is the initial radical concentration. The equation for the change of concentration of the radical $\dot{B}$ is

$$dC_b/dt = k_2^2C_{ao}/k_1[(C_{ao} + k_2/k_1)\exp(k_2t) - C_{ao}] \qquad (7)$$

The solution of this equation can be obtained assuming $k_1 \gg k_2$ as

$$C_b = [k_2C_{ao}/k_1(C_{ao} + k_2/k_1)]\ln[1 + k_1(C_{ao} + k_2/k_1)t] \qquad (8)$$

The whole radical concentration observed is

$$C = C_a + C_b \qquad (9)$$

IPP, SPP, PB1, and PP1 were irradiated in a vacuum by gamma-rays to the total dose of 10^7 rad at -196 °C. ESR was measured at 35 °C. For IPP and SPP k_1 was estimated from the slope of the curves in Figure 1 as 9.80×10^{-3} and 2.50×10^{-2} l/mol·sec, respectively. Substituting the value of k_1 into eq. (9) and changing the value of k_2 the best fit curve was obtained as shown in Figure 2. The best fit value of k_2 was 1.76×10^{-5} sec^{-1} for IPP. The calculated curve well agrees with experimental points. The same procedure was conducted for PB1 and PP1, and good agreements were obtained for both cases. The values of k_1 were 2.64×10^{-3} and 2.75×10^{-3} l/mol·sec for PB1 and PP1, respectively. Those of k_2 were 1.32×10^{-5} and 1.00×10^{-5} sec^{-1} for PP1 and PB1, respectively.

It should be also noted that polymers which have helical chain conformations showed the radical transformation, but no transformation in SPP with no helix.

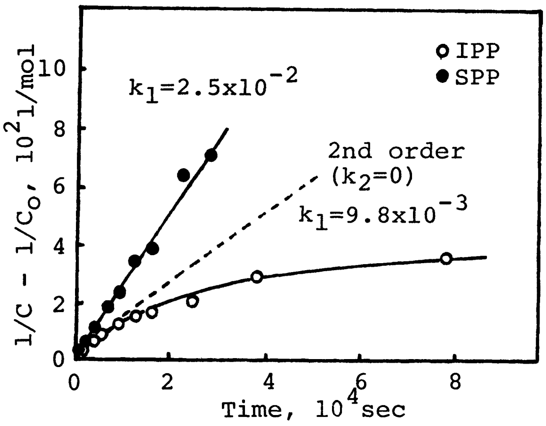

Figure 1. Time dependence of the reciprocal of radical concentration.

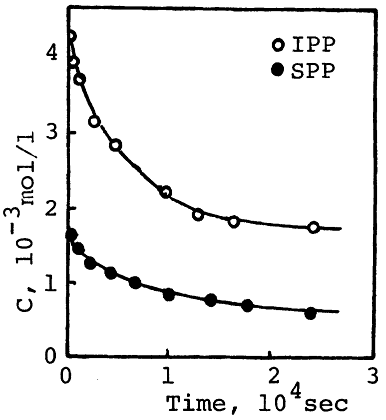

Figure 2. Time dependnece of radocal concentration.

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