

Chemiluminescence Parameter for the Degradation of Polyolefins

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ABSTRACT: The chemiluminescence time-courses of various polymer materials under heating in air or inert gas were observed and simulated on the basis of kinetic analysis. Chemiluminescence parameters, such as peak-top intensity, integrated intensity during measurement, steady state intensity, and chemiluminescence decay rate, were found to strongly correlate with the stability of polymer materials, judging from correspondence with the results of durability tests on the same materials. The relationship between the chemiluminescence and the structural characteristics of the polymer was also investigated.

KEY WORDS Chemiluminescence Parameter / Degradation / Durability / Heating / Kinetic Analysis / Polypropylene / Polyethylene /

Generally, the degradation of polymer materials is caused by various factors such as heat, UV light, irradiation, ozone, mechanical stress, microbes, and promoted by oxygen, humidity, strain, etc. The durability of polymers was evaluated by tests under thermal aging, out-door exposure, UV irradiation, repeated stress and so on.

These tests commonly need much time, *e.g.*, 100—1000 hours for heat resistance test and a few month for out-door exposure test. On the other hand, chemiluminescence (CL) measurement is sensitive to catch the very first stage of oxidation of polymers and does not require so long time to obtain the information. Since the preceding studies of CL in polymers^{1,2} appeared, many applications for various polymers have been reported.³⁻¹⁷ However, very few papers can be seen in which the results of CL measurement are discussed in connection with the results of actual durability tests. From this point of view, in this work, we investigated the CL phenomena induced by heat and propose CL parameters to evaluate the stability of polymer materials.

EXPERIMENTAL

Materials

Polypropylene (PP; Sumitomo Noblen, $M_w = 2.0 \times 10^5$) and polyethylene (PE; Sumikathene-L, $M_w = 1.3 \times 10^5$) used in this study are commercial products of Sumitomo Chemical Co., Ltd. They were purified, as occasion demands, by reprecipitation using xylene/methanol mixture. The additives such as antioxidants, were mixed into PP in molten state by using a Brabender Plasticorder. Sample specimens were hot-press molded to a sheet of $3 \times 3 \text{ cm}^2$ and 0.5—1 mm in thickness. Samples having different thermal history were obtained by heating at 200°C in air during different period.

Measurement

CL was measured with a single photon counting method using a Chemiluminescence Analyzer OX-7-TC (Tohoku Electronic Industry Co., Ltd.) equipped with a micro computer. Sample temperature was controlled with a Temperature Processor Controller TLD-47 (Tohoku Electronic Industry Co.,

Ltd.). Argon gas or air was selected as the atmosphere in the sample cell according to the kind of measurement. The CL intensity was measured as a function of time. The gate times for the measurement were 1, 10, and 30 s, and normalized as cps. The spin-spin relaxation time (T_2) was measured using a pulsed NMR spectrometer PC-120 (Bruker Co., Ltd.), equipped with a digital memory and micro computer. The free induction decay (FID) curves of PE were measured by the solid echo method and resolved into several components by the least square method.

RESULTS AND DISCUSSION

Kinetic Approach to Polymer Degradation

A simple scheme of oxidation process for polymer sample is shown in Figure 1. Radical species ($R\cdot$) produced by main chain scission or proton elimination which are caused by the action of heat, UV light, and mechanical stress partly react with O_2 and form peroxy radical ($ROO\cdot$). The activation energy of the $ROO\cdot$ formation reaction was estimated to be nearly equal to zero by Stivara.¹⁸ From studies on the oxidation of hydrocarbons,¹³ only the exothermic bimolecular reaction of $ROO\cdot$ is known to be able to excite a product ketone up to its first triplet state (RO^*). Visible light

is emitted as it returns to its ground state. According to Stivara,¹⁸ the activation energy of the $ROO\cdot$ bimolecular reaction (ΔE_b) was estimated to be *ca.* 12 kJ mol^{-1} , while the reaction between $ROO\cdot$ and R has a larger activation energy of *ca.* 29 kJ mol^{-1} . This suggests that contribution of the latter reaction can be neglected. Then, the intensity of light emitted, I_{CL} , will be proportional to the rate of the bimolecular reaction and overall efficiency, f (apparatus constants, yields of formation and emission of excited state),

$$I_{CL} = f \cdot k_b [ROO\cdot]^2 \quad (1)$$

where k_b is the rate constant of bimolecular reaction of $ROO\cdot$. In the absence of an inhibitor, the next equation is valid,

$$d[ROO\cdot]/dt = R_i - k_b \cdot [ROO\cdot]^2 \quad (2)$$

where R_i is the rate of generation of $ROO\cdot$, including the rates of generation of $R\cdot$ by heat, return from $R\cdot$ to R , and disappearance by recombination of $R\cdot$.

i) *CL under Heating in Inert Gas*

In the case of heating in inert gas, R_i is estimated to be zero. The temperature of the sample was increased at a rate of $20^\circ\text{C min}^{-1}$ from room temperature, and kept at 90°C . Then, we simulated the CL time-course using eq 1 and 2. In the simulation, it was assumed

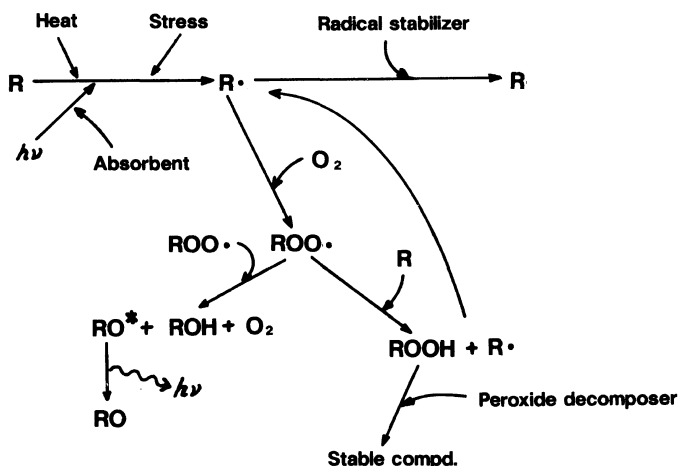


Figure 1. Simple scheme of oxidation and luminescence process for polymers.

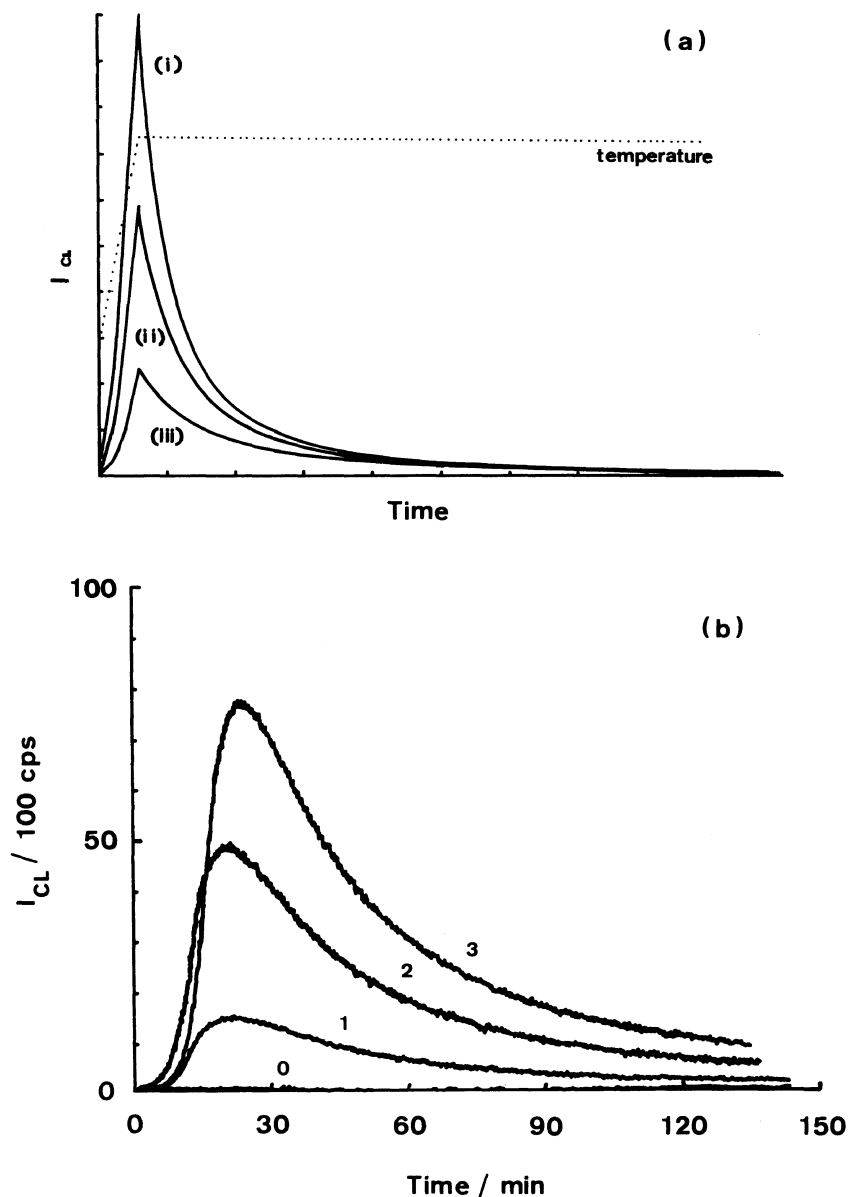


Figure 2. (a) Chemiluminescence time-course simulated by eq 1 and 2 in the text under oxygen free condition. $R_i=0$, (i) $C_0=1.0$, (ii) $C_0=0.7$, and (iii) $C_0=0.4$. Dotted line shows temperature. (b) Experimental chemiluminescence time-course of polyethylene having a different thermal history, measured at 90°C in argon gas. Samples were heated at 200°C in air during different period. Numerals denote heating period in hours.

that k_b was proportional to $\exp(-\Delta E_b/kT)$, where T is the absolute temperature and k is the Boltzmann factor. The rise and decay of the simulation curves, shown in Figure 2(a),

are caused by temperature change. The peak-top intensity and integrated intensity (area) of the CL time-course increase with increasing C_0 , which is the initial concentration

of $\text{ROO}\cdot$ and corresponds to the history of oxidation of the samples. Figure 2(b) shows the experimental CL time-courses of PE samples having different thermal histories, which were observed under heating in argon gas. The peak-top and area of the CL time-course of the samples obviously correspond to the thermal treatment period. This is in good agreement with the simulation described above. It is considered that the peak-top or area from this CL measurement can be used to indicate the oxidation history

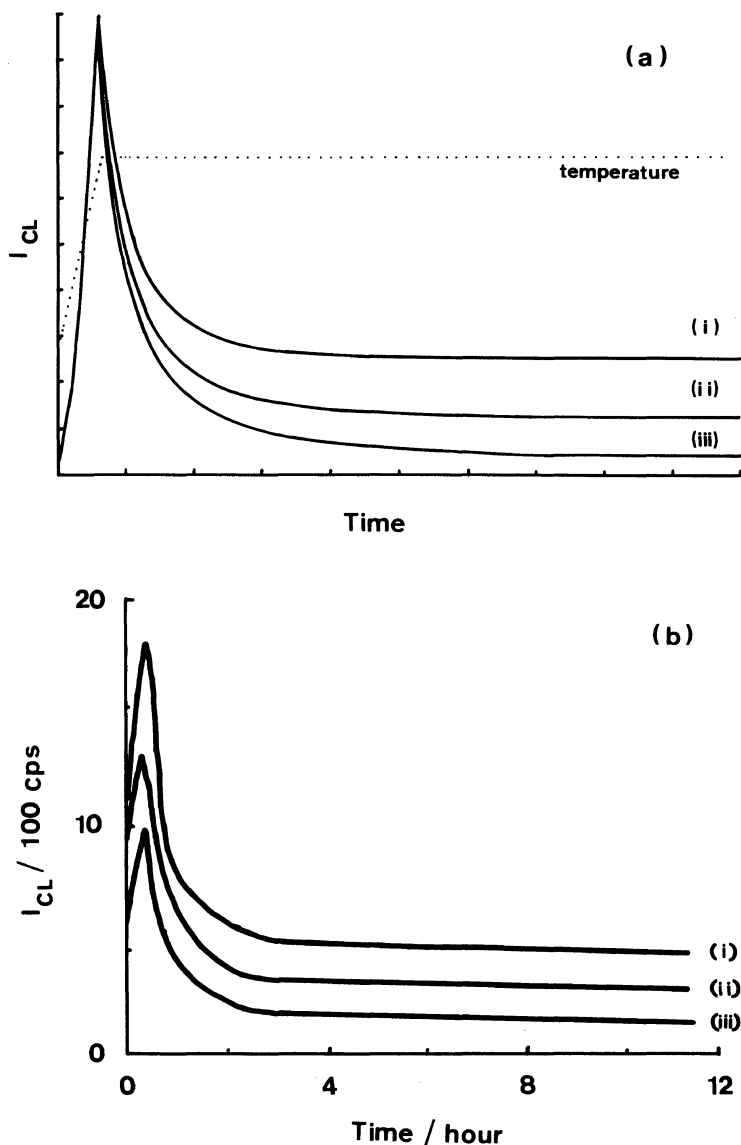


Figure 3. (a) Chemiluminescence time-course simulated by eq 1 and 2 in the text under oxidation condition in which R_i are (i) 0.03, (ii) 0.015, and (iii) 0.005, respectively. Dotted line shows temperature. (b) Observed chemiluminescence time-course of stabilized polypropylene measured at 150°C in air. Concentrations of the hindered phenols in polypropylene are: (i) PH-1, 250 ppm, (ii) PH-1, 1000 ppm, and (iii) PH-2, 1000 ppm.

of polymer materials.

ii) *CL under Heating in Air (O₂)*

Corresponding to the case of heating at a rate of 20°C min⁻¹ by 150°C in air (O₂), the CL time-course was simulated using eq 2, where C₀ is constant, R_i is proportional to exp(-ΔE_i/kT), and k_b is to exp(-ΔE_b/kT). ΔE_i, which is the activation energy of the generation of ROO·, may be nearly equal to ΔE_b. When the temperature of the sample and oxygen concentration were kept constant, it was found from the simulation that the CL intensity converged to some definite value during the time-course. In this steady state condition, d[ROO·]/dt in eq 2 is zero, and CL intensity in this condition (I_s) can be expressed as follows.

$$I_s = f \cdot k_b [\text{ROO}\cdot]^2 = f R_i \quad (3)$$

Equation 3 shows that I_s is proportional to the rate of generation of ROO· (R_i). In Figure 3(a), it is clear that I_s increases with increasing R_i. Thus, it is possible from I_s to evaluate the ease of oxidation of polymers and the ability of inhibitors as radical captor. Figure 3(b) show

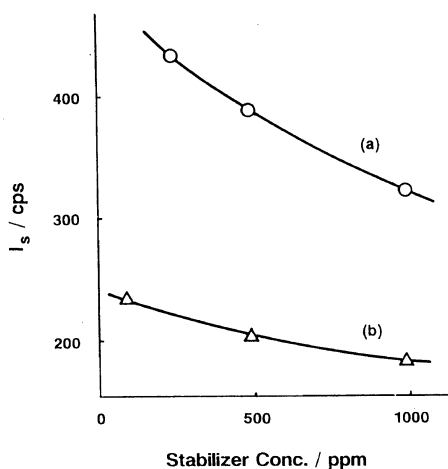


Figure 4. Stabilizer concentration dependence of steady state chemiluminescence intensity (I_s) for polypropylene at 150°C in air. (a), PH-1; (b), PH-2.

the observed CL time-courses of the stabilized PP sheets which contain hindered phenols. The CL intensity gradually came down to a constant value after passing through a maximum value at the initial stage. Since these CL decay curves were not influenced by the concentration of the hindered phenols, the hindered phenols do not seem to quench the excited triplet state of carbonyls. Thus, this constant value after about 4 hours was taken as I_s. Figure 4 shows the dependence of I_s on the concentrations of the hindered phenols. I_s decreased with increasing concentration of the hindered phenols, and the hindered phenol PH-2[†] was found to have stronger ability to catch radicals in PP than PH-1[†]. A reciprocal of Gear-Oven life¹⁹ of the same samples in air, which is one of the important parameters of durability, was found to have good linearity

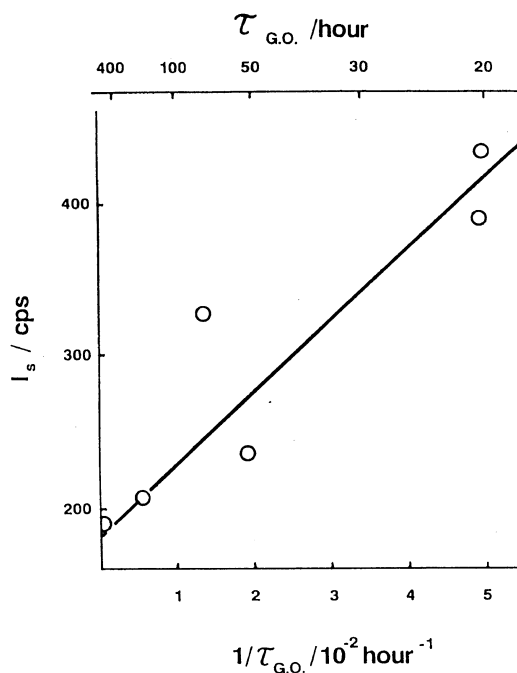


Figure 5. Relationship between reciprocal Gear-Oven life and steady state chemiluminescence intensity (I_s) of polypropylene at 150°C in air.

[†] PH-1, *n*-octadecyl-3-(4'-hydroxy-3',5'-di-*t*-butylphenolpropionate); PH-2, tetrakis-[methylene-3-(3',5'-di-*t*-butyl-4'-hydroxy-phenylpropionate)]methane

Table I. Steady state chemiluminescence intensity of polypropylene sheets containing various phenols

Specimens	Stabilizer ^a	G.O. life	I_s
		h	Count/30 s
1	a	530	3.8×10^3
2	b	1010	1.8×10^3
3	c	1320	1.7×10^3
4	d	2130	1.4×10^3

^a a, 3,4-dimethylphenol; b, 4-methyl-2,6-di-*tert*-butylphenol; c, 2-*tert*-butyl-4-methylphenol; d, 2,3,6-trimethylphenol.

Table II. Chemiluminescence decay rate and T_2 of polyethylene differing in thermal history

Heating period	CL decay rate	$T_2/\mu\text{s}$	
		Crystalline	Amorphous
h	$\text{cps}^{-1/2} \text{s}^{-1}$		
0	2.1×10^{-3}	13	53
1	1.5×10^{-3}	13	46
2	1.0×10^{-3}	12	41
3	0.8×10^{-3}	12	41

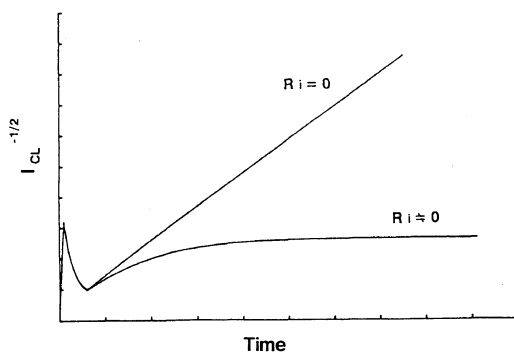
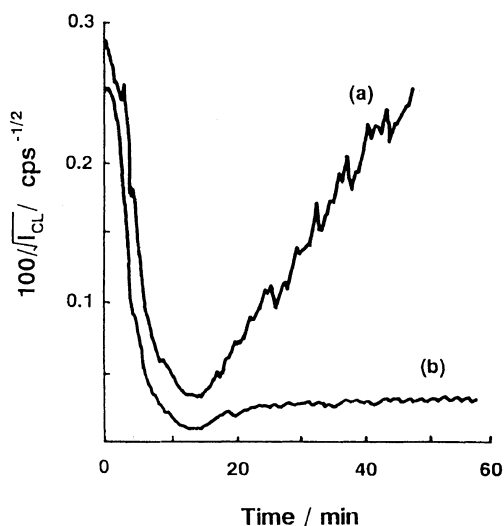
with I_s as shown in Figure 5. This indicates that the CL intensity at the steady state which is measured in air under heating corresponds to the rate of oxidative degradation. This is in good agreement with the simulation by eq 3. Table I shows I_s and Gear-Oven life for PP sheets containing various phenols.

The results indicate that 2,4,6-trimethylphenol is the most effective among the phenols shown in Table II to stabilize PP. Thus, CL measurement, especially I_s measurement, which takes only a few hours to obtain information on polymer durability, is more favorable to evaluate the ability of additives than a time consuming test such as the Gear-Oven life test which takes several hundred hours or more.

iii) *Chemiluminescence Decay* (non static second order kinetic analysis)

If R_i is zero, the differential eq 2 gives the following equation,

$$1/[\text{ROO}\cdot] = -k_b \cdot t + 1/C_0 \quad (4)$$

**Figure 6.** Simulated time-courses of the reciprocal of the square root of chemiluminescence intensity. $R_i=0$ and $R_i \approx 0$ correspond to conditions under inert gas and under air (O_2), respectively.**Figure 7.** $1/\sqrt{I_{\text{CL}}}$ vs. time plots of polypropylene measured at 150°C : (a), in argon gas; (b), in air.

where C_0 is the initial concentration of $\text{ROO}\cdot$. Substituting eq 4 in eq 1 gives the following expression.

$$1/\sqrt{I_{\text{CL}}} = \sqrt{k_b/f} \cdot t + 1/(\sqrt{f \cdot k_b} \cdot C_0) \quad (5)$$

This equation reveals that the reciprocal of the square root of the CL intensity is proportional to time (t).

Figure 6 shows the $1/\sqrt{I_{\text{CL}}}$ vs. t plots simulated by use of eq. 1 and 2. Good linearity is obtained between $1/\sqrt{I_{\text{CL}}}$ and t when R_i is

zero, while $1/\sqrt{I_{CL}}$ value saturates with increasing time when R_i is not zero. We confirmed this by measuring the CL of PP sheets heated at 150°C in air and in argon gas, which correspond to the cases of $R_i \neq 0$ and of $R_i = 0$, respectively. These $1/\sqrt{I_{CL}}$ vs. t plots for PP, which seem to be good agreement with simulation results, are shown in Figure 7. From

eq. 5 the slope in Figure 7 is considered to correspond to the square root of the bimolecular reaction rate of $ROO\cdot$. We may name this slope the CL decay rate in this paper. We replotted the results shown in Figure 2(b) into Figure 8, which shows that the CL decay rate of PE sheet decreases with the heating period. It may be supposed that the molecular

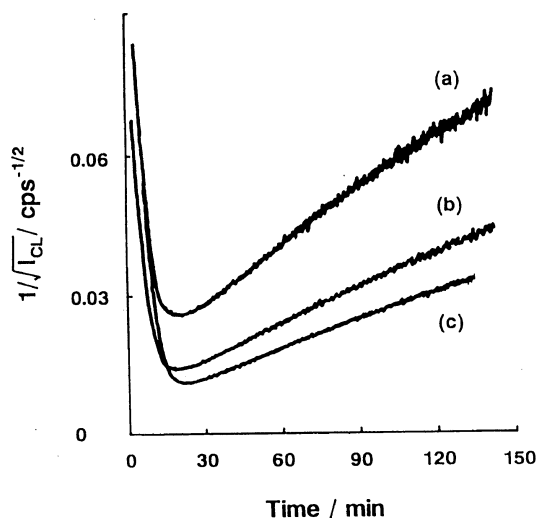


Figure 8. $1/\sqrt{I_{CL}}$ vs. time replots of polyethylene having a different thermal history in Figure 2(b) measured at 150°C in argon gas. Heating period: (a), 1 h; (b), 2 h; (c), 3 h.

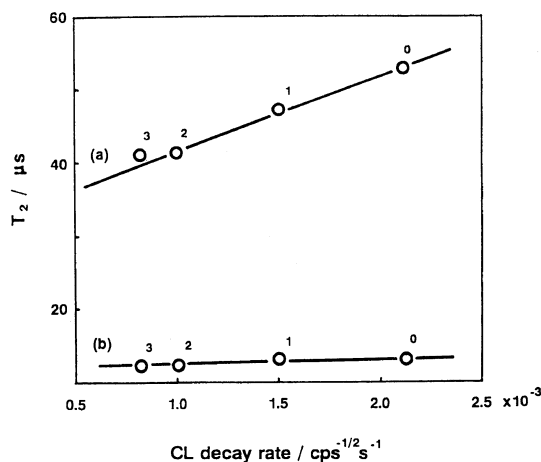


Figure 9. Relationship between chemiluminescence decay rate and T_2 of polyethylene having a different thermal history. Refer text and Figure 2(b). (a), amorphous phase; (b), crystalline phase. Numerals denote heating period in hours.

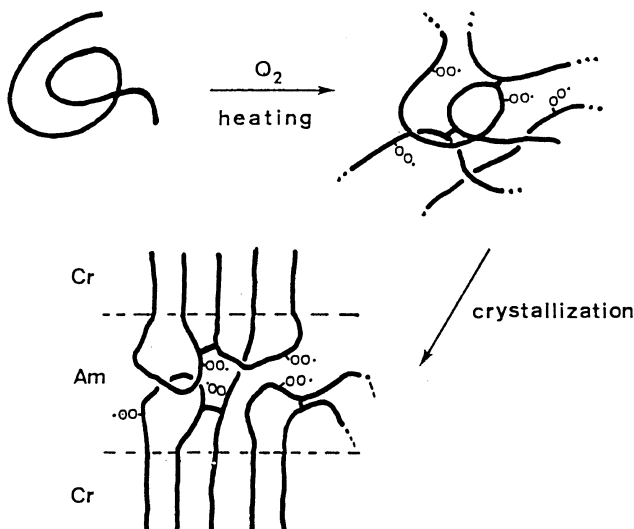


Figure 10. Structure change model of polyethylene when heated in air and recrystallized.

mobility of PE chain decreases with aging since the biomolecular reaction rate of ROO· decreased with crosslinking of molecules. To make sure of this assumption, measurement of ^1H spin-spin relaxation time (T_2) of PE sheets was carried out by a pulsed NMR spectroscopy at room temperature. The free induction decay (FID) obtained could be separated into this components. The short T_2 component is assigned to the crystalline phase and the long T_2 component to the disordered phase (amorphous phase) in the solid state of PE. The relationship between these T_2 values and CL decay rates is plotted in Figure 9. T_2 of the crystalline phase in PE was not altered by aging, while T_2 of the amorphous phase decreased with aging, suggesting that the mobility of amorphous molecular chains decreases. Changes in T_2 in the amorphous phase are in good agreement with the CL decay rate as shown in Table II. Since it is considered that both oxidation and crosslinking, generated at a molten state of PE, are condensed into the amorphous phase with crystallization, T_2 in the amorphous phase might correspond to the CL decay rate (Figure 10).

These experimental and theoretical results suggest that measurement of the CL decay rate in inert gas is useful to examine the degree of aging of polymer materials which age mainly by crosslinking.

NOMENCLATURE

I_{CL}	= chemiluminescence intensity [cps]
$[\text{ROO}\cdot]$	= peroxy radical concentration [mol l ⁻¹]
R_i	= rate of generation of ROO· [mol l ⁻¹ s ⁻¹]
k_b	= Rate constant of bimolecular reaction of ROO· [(mol l ⁻¹ s ⁻¹)]
f	= overall efficiency [cps s (mol l ⁻¹) ⁻¹]
I_s	= chemiluminescence intensity

	in steady state condition [cps]
C_0	= initial ROO· concentration [mol l ⁻¹]
$\sqrt{k_b/f}$	= CL decay rate [cps ^{-1/2} s ⁻¹]
T_2	= ^1H spin-spin relaxation time [μs]
ΔE_b	= activation energy of k_b [J mol ⁻¹]
ΔE_i	= activation energy of R_i [J mol ⁻¹]

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- Gear Oven Life is the time taken to generate crack on the surface of specimen under heating at 150°C. It was determined according to JIS K7212.