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Photosensitized degradation and crosslinking of linear aliphatic polyesters studied by GPC and ESR

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Abstract

Photosensitized reaction on aliphatic polyesters, 3g4 and $M_2$3g4, prepared from succinic acid and propanediol derivatives were investigated by spectrophotometry, GPC, and electron spin resonance (ESR) methods. From change of GPC curves for 3g4 polyester doped with *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) as a photosensitizer, it was confirmed that not only degradation but also crosslinking reaction occurred for 3g4, $M_2$3g4, and poly(lactic acid), by UV irradiation. By detailed analysis of ESR spectra, it was confirmed that several radical species are produced through photosensitized reaction; TMPD radical cation, ester radial anion of polyester, main chain alkyl radical at the center of diol component, and acyl-type radical. Although there was no direct evidence for producing the main chain scission radical for 3g4 and $M_2$3g4, it was strongly suggested that the photosensitized degradation and the crosslinking reactions were originated from the ester radical anion that was produced by electron capturing. © 2002 Published by Elsevier Science Ltd.

Keywords: Photosensitized reaction; Electron spin resonance; Aliphatic polyester

1. Introduction

Direct irradiation on polymer material using UV light and high-energy sources such as X-ray, γ-ray, and electron beam largely changes both physical and chemical properties of the polymer through chemical reactions. The reaction proceeds via an energy or an electron transfer reaction, which results in degradation, crosslinking, and functionalizing of polymer. Such a pathway of polymer reaction can be depressed by adding photochemical compound into the polymer matrix, e.g. stabilizer for durability, and also can be changed to different reaction route.

In the previous paper [1,2], we have investigated the effects of photochemical additive, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), on photoreaction of poly(methyl methacrylate) (PMMA) and poly(L-lactic acid) (PLLA). Through electron spin resonance (ESR) measurement, it was found that photoionization of TMPD in the polymer matrix by UV irradiation produces several radical species that cause decomposition of polymer main chain. The key species in this photosensitized reaction is the ester radical anion on the polymer chain [3]. The ester radical anion is produced by electron capturing and indicates a Lorentzian singlet of ESR signal around $g = 2.003-2.004$. Many ESR studies concerning with radiation effects on PMMA and aliphatic ester compounds, including polyesters for implant materials, have been already reported [4–9]. Those reports also showed existence of the ester radical anion of matrix polymer after irradiation and decomposition reaction of polymer.

In this paper, we represent the photosensitized degradation of several aliphatic polyesters via the anionic reaction process. Two of the polyesters were prepared from succinic acid and propanediol derivatives, and doped with TMPD as photosensitizer. Commercial polyesters, poly(lactic acid)s, were also used to compare the results. Sample films were irradiated with UV light at 77 K and investigated by spectrophotometry, GPC, and ESR measurements. All polymers have the same ester linkage in the main chain, but indicated different results depending on each structural difference.

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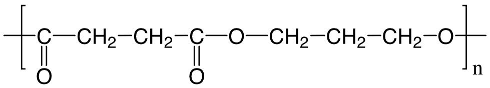
2. Experimental

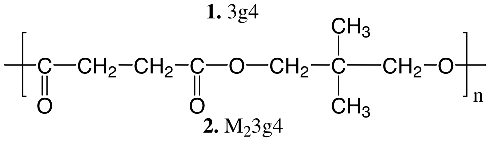
2.1. Materials

Aliphatic polyesters, **1** 3g4 and **2** $M_2$3g4, were prepared by typical melt polycondensation method using succinic acid and diols, propanediol and 2,2-dimethylpropanediol, respectively. Titanium tetraisopropoxide (10 wt%) was used as a catalyst. Each monomer compound was used as received from company. For the first stage of polymerization, mixture that consists of succinic acid, excess amount of diol, and 10 wt% of catalyst, were heated at 190–230 °C for 6 h in nitrogen gas stream. The later stage of polycondensation was carried out under vacuum condition keeping the pressure below 0.5 Torr at 230 °C for 4 h. The polyesters obtained were purified by repeated precipitations from chloroform solution with methanol and dried under vacuum at 50 °C for 1 day. Chemical structures for those polyesters were confirmed by NMR measurement. Poly(L-lactic acid) (**3** PLLA, D/L = 0:100) and poly(D,L-lactic acid) (**4** PDLLA, D/L = 25:75), provided by Shimadzu Corporation (Lacty), were purified by repeated reprecipitation. Photosensitizer, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (**5** TMPD, Aldrich), was purified twice by sublimation method under 10 mmHg at 40 °C.



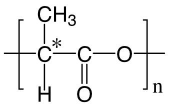
$$\left[-\mathrm{C(=O)-CH_2-CH_2-C(=O)-O-CH_2-CH_2-CH_2-O}-\right]_n$$

1. 3g4



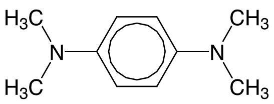
$$\left[-\mathrm{C(=O)-CH_2-CH_2-C(=O)-O-CH_2-C(CH_3)_2-CH_2-O}-\right]_n$$

2. $M_2$3g4



$$\left[-\mathrm{\overset{*}{C}H(CH_3)-C(=O)-O}-\right]_n$$

3. PLLA, **4.** PDLLA



5. TMPD

2.2. Preparation of samples

All sample films were prepared by casting method on glass plates from chloroform solution of corresponding polyesters. TMPD was dissolved into the solution just before the casting to avoid oxidation of TMPD. The films were dried in vacuum at room temperature for 10 h and then at 30 °C for 1 day. Thickness of the sample films was ca. 50 μm. Concentration of TMPD in each film was set at 3.0×10^{-2} mol/l (ca. 0.4 wt%). For spectrophotometric measurement, the sample film was cut into 9 mm by 50 mm strip shape and placed in a thin rectangle quartz cell under 10^{-5} Torr, which has 1 mm light-path length. For GPC and ESR measurement, the film was cut into 2 mm by 20 mm strip and 10–20 of them were placed in a spectral high purity silica ESR tube (5 mm o.d.) and sealed under 10^{-5} Torr at room temperature.

2.3. Photoirradiation

For UV irradiation, Xe–F pulsed excimer laser (Lambda Physik, $\lambda_c = 351$ nm, 1 Hz) and Xe/Hg continuous wave lamp (Oriel Instruments, 500 W, $\lambda_c = 356$ nm, $\lambda_{1/2} = 17$ nm, with some filters) were used [2]. For spectrophotometry, the sample cell was fixed and irradiated in a rectangle quartz Dewar cell filled with liquid nitrogen. For ESR measurement, the sample tube was set in a round Dewar flask filled with liquid nitrogen and rotated during the irradiation so as to be irradiated from all directions.

2.4. Measurements

Thermal characterizations of polyesters were done by DSC measurement (Perkin Elmer, DSC 7). Absorption spectra of sample film were measured at 77 K using UV–VIS spectrophotometer (Hitachi, UV3300) with quartz Dewar cell. A dry nitrogen gas was flowed over the Dewar cell to avoid making dew on the surface. ESR measurements were carried by X-band spectrometer (JEOL, JES-TE300) to detect radical species in the sample. The standard Mn^{2+} sample was used for magnetic field standard ($g = 2.00648$). Most of the ESR spectra were taken with the power of the microwave set to 1.00 mW. However, the power was reduced down to 0.02 mW in some cases to investigate saturation effect on the ESR signals. GPC measurements (Shodex GPC system, THF solvent with Tosoh TSKgel KF802 + KF806 at 40 °C, or chloroform solvent with TSKgel G2500H_8 + G4000H_8 at 40 °C) were done to measure change of molecular weight of the polyesters before and after UV irradiation, using poly(styrene) as molecular weight standard. All the polymer samples for GPC measurement were annealed at room temperature for more than 30 min before dissolving into THF. The weight- and number-average molecular weights for all samples before and after UV irradiation were calculated from the GPC curves. In this paper, for the sake of easy comparison of molecular weight changes among different polymer samples, the abscissa axes of molecular weight for GPC curves are normalized with the maximum position of the molecular weight of original unirradiated polymer sample.

3. Results

3.1. Thermal characterization

Thermal properties of polyester sample films before irradiation are measured by DSC and those glass transition temperatures (T_g) and melting points (T_m) are summarized in Table 1. For 3g4 and $M_2$3g4 polyesters, the T_gs were

Table 1
Thermal properties of polyesters

Polyester	T_g (°C)	T_m (°C)
3g4	−32.9	–
$M_2$3g4	−20.2	–
PLLA	55.7	169.8
PDLLA	50.9	–

below −20 °C and no melting point was seen in the DSC curve. In comparison with the result for PLLA that is well known as crystalline polyester, no melting point was observed for PDLLA. This result shows that PDLLA used in this paper is amorphous co-polyester. No significant peak due to TMPD crystal ($T_m \sim 50$ °C) was observed in every sample. This indicates that no crystallization of TMPD molecules occurred in the sample films during both the casting and the drying processes.

3.2. GPC measurements

Fig. 1 shows the GPC curves for 3g4 doped with TMPD before UV irradiation and after 1 and 2 cycles of irradiation–annealing process. The UV irradiation by Xe lamp and the succeeding thermal annealing were done at 77 K for 40 min and at 20 °C for 20 min, respectively.

The peaks of GPC curves in Fig. 1 shifted to lower molecular weight after repeating the irradiation–annealing process. These shifts indicate that degradation reaction of 3g4 occurred by photoirradiation and annealing. The changes of average molecular weight of 3g4 were calculated from the GPC curves, as shown in Table 2.

Generally, no photochemical reaction is expected for 3g4 by photoirradiation with $\lambda_c = 356$ nm because 3g4 is transparent in the region of $\lambda > 300$ nm. Thus, this degradation reaction for 3g4 is considered as a photosensitized reaction owing to adding TMPD into the polymer matrix. Such a photosensitized degradation observed here was reported also for poly(methyl methacrylate) (PMMA) [1] and poly(L-lactic acid) (PLLA) [2].

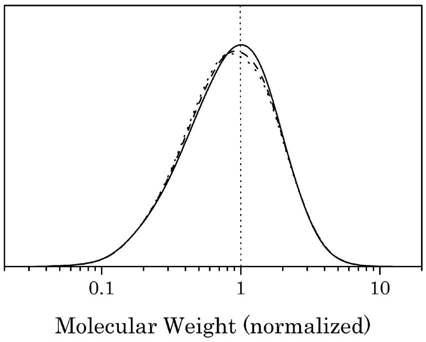


Fig. 1. GPC curves of 3g4 doped with TMPD. (a) — before UV irradiation, (b) – – – after 1 cycle of UV irradiation at 77 K for 40 min and thermal annealing at 20 °C for 20 min, and (c) · · · · after 2 cycles.

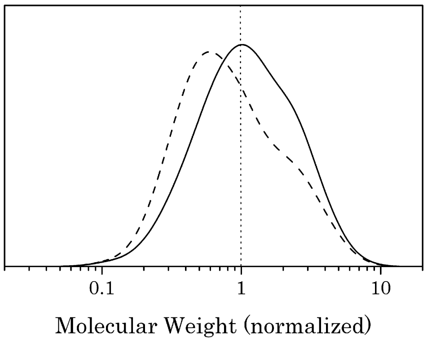


Fig. 2. GPC curves of $M_2$3g4 doped with TMPD. (a) — before UV irradiation, (b) – – – after UV irradiation at 77 K for 20 min and thermal annealing at 20 °C for 10 min.

Fig. 2 shows the GPC curves for $M_2$3g4 with TMPD before UV irradiation and after 2 cycles of irradiation–annealing processes. The UV irradiation and the thermal annealing were done at 77 K for 20 min and at 20 °C for 10 min, respectively. In spite of the shorter irradiation time for $M_2$3g4 than that for 3g4 film, the molecular weight of $M_2$3g4 after irradiation decreased more largely than that of 3g4.

When irradiation time was shortened for 3g4, quite different results were obtained. Fig. 3 shows the GPC curves for 3g4 doped with TMPD measured before UV irradiation and after 5, 10, and 15 cycles of irradiation–annealing processes. The UV irradiation and the thermal annealing were done at 77 K for 4 min and at 20 °C for 2 min, respectively. As shown in Fig. 3, the curve peaks moved to higher molecular weight according to the increase in the irradiation–annealing cycles. As shown in Table 2, the average molecular weights also increased. This indicates that crosslinking reaction occurred in 3g4 sample. The experimental differences between Figs. 1 and 3 are only the time for irradiation and annealing processes. Thus, it is considered that both degradation reaction and crosslinking reaction occur for 3g4 and the ratio of them depends on the experimental condition.

Fig. 4 shows the GPC curves for $M_2$3g4 doped with

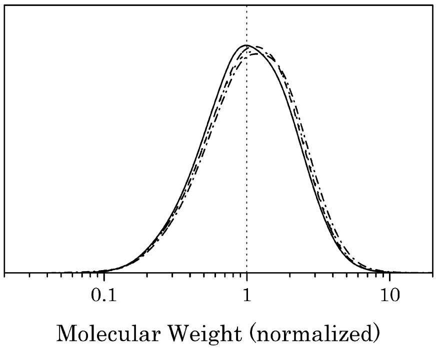


Fig. 3. GPC curves of 3g4 doped with TMPD. (a) — before UV irradiation, (b) – – – after 1 cycle of UV irradiation at 77 K for 4 min and thermal annealing at 20 °C for 2 min, (c) · · · · after 2 cycles, and (d) –·–·– after 3 cycles.

Table 2
Change of molecular weight of polyesters after UV irradiation and thermal annealing

Polyester	Irradiation (min)	Annealing		Cycle	M_n (× 10^4)[a]	M_w (× 10^4)[b]	M_w/M_n	ΔM[c]
		Temperature (°C)	Time (min)					
3g4				–	2.85	5.81	2.04	
	40	20	20	1	2.81	5.76	2.05	−
				2	2.80	5.71	2.04	−
				–	1.53	2.60	1.70	
	4	20	2	5	1.59	2.70	1.70	+
				10	1.59	2.72	1.72	+
				15	1.61	2.85	1.78	+
$M_2$3g4					1.72	3.37	1.96	
	20	20	10	2	1.34	2.87	2.14	−
				–	1.75	3.74	2.14	
	4	20	2	10	1.68	3.72	2.21	−
PLLA				–	7.73	27.4	3.54	
	2	40	3	1	7.05	23.1	3.28	−
				2	6.11	18.6	3.05	−
				3	6.03	20.1	3.33	−
	4			1	6.33	18.0	2.85	−
	8			1	5.76	16.2	2.82	−
PDLLA				–	5.21	11.6	2.23	
	2	40	3	1	5.08	11.3	2.22	−

[a] Number-average molecular weight.
[b] Weight-average molecular weight.
[c] Indicator, which roughly indicates the difference of average molecular weight between before and after irradiation; to higher (+) and to lower (−).

TMPD before UV irradiation and after 10 cycles of irradiation–annealing processes. The irradiation and the annealing were done at 77 K for 4 min, which was shorter than that in Fig. 2, and at 20 °C for 2 min, respectively. In spite of the same total irradiation time that was used in Fig. 2, only a little decrease of molecular weight is seen in Fig. 4. The average molecular weights for $M_2$3g4 in Fig. 4 also did not change as shown in Table 2.

Fig. 5 shows GPC curves for PLLA doped with TMPD measured after 1–3 cycles, that consisted of 2 min UV irradiation at 77 K and 3 min thermal annealing at 40 °C. The annealing process was done at 40 °C, in which the temperature is higher than that for 3g4 series, 20 °C. This is because the T_g of PLLA, 50 °C, is much higher than that of 3g4 and $M_2$3g4. The GPC curves of PLLA in Fig. 5 indicate decreases of molecular weight. Similar results were also obtained even when the irradiation time was enhanced from 2 to 4 min, or to 8 min. Those results of GPC measurement for PLLA are summarized in Table 2. PDLLA was also examined under the same condition as for PLLA. However, there was no apparent shift of GPC curves for irradiated PDLLA as seen in Table 2. From the viewpoint of molecular size level, PLLA and PDLLA are considered to have the same chemical reactivity, because both of them have the same chemical structures. Thus, the results of GPC

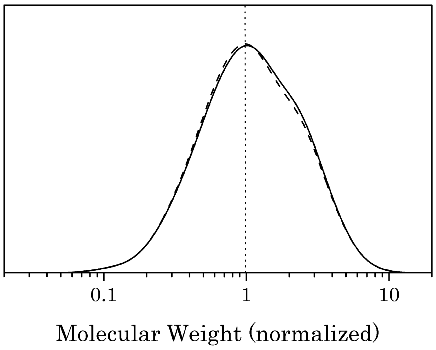


Fig. 4. GPC curves of $M_2$3g4 doped with TMPD. (a) — before UV irradiation and (b) – – – after 10 cycles of UV irradiation for 4 min at 77 K and thermal annealing at 20 °C for 2 min.

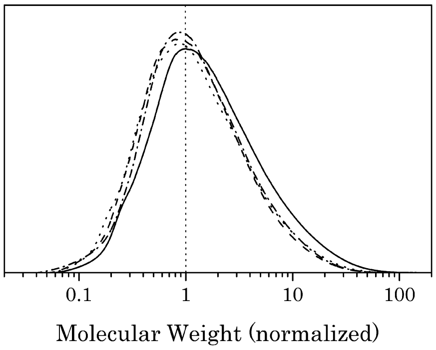


Fig. 5. GPC curves of PLLA doped with TMPD. (a) — before UV irradiation, (b) – – – after 1 cycle of UV irradiation at 77 K for 2 min and thermal annealing at 40 °C for 3 min, (c) · · · · after 2 cycles, and (d) –-–-– after 3 cycles.

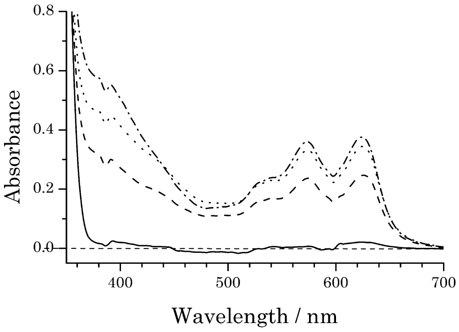


Fig. 6. Absorption spectra of PLLA doped with TMPD. (a) — before UV irradiation, (b) – – – after irradiation at 77 K for 30 s, (c) · · · · for 60 s, and (d) -·-·- for 120 s.

suggested that the difference of crystallinity of the polymer matrix strongly affects the polymer reaction process.

3.3. Absorption spectra

Originally, PLLA has no absorption band in the region from 300 to 800 nm. Fig. 6 shows the absorption spectra of PLLA doped with TMPD measured at 77 K before and after UV irradiation by Xe lamp at 77 K.

The strong absorption below 380 nm in Fig. 6(a) is due to the high molecular extinction coefficient of TMPD dispersed in PLLA matrix. After UV irradiation, a broad absorption band appeared from 350 to 700 nm is shown in Fig. 6. This absorption spectrum is assigned to $\mathrm{TMPD}^{+\bullet}$ radical [10,11]. Because of the high molecular extinction coefficient of $\mathrm{TMPD}^{+\bullet}$, it was difficult to find out other reaction products than $\mathrm{TMPD}^{+\bullet}$ in Fig. 6. The intensity of the $\mathrm{TMPD}^{+\bullet}$ absorption depended upon the irradiation time. Fig. 7 shows the growth curves of $\mathrm{TMPD}^{+\bullet}$ in PLLA and PDLLA during photoirradiation at 77 K. As shown in Fig. 7, $\mathrm{TMPD}^{+\bullet}$ increased at the same rate in both PLLA and PDLLA matrices. This indicates that there is no microscopic environmental difference in both PLLA and PDLLA matrices for TMPD photoionization reaction.

3.4. ESR measurements

For ESR measurement, both laser light and Xe/Hg lamp were used for photoirradiation. However, there was no large difference among those results, except the amount of produced radicals. This means that there is no fundamental difference of photochemical process between by laser light and by the Xe/Hg lamp.

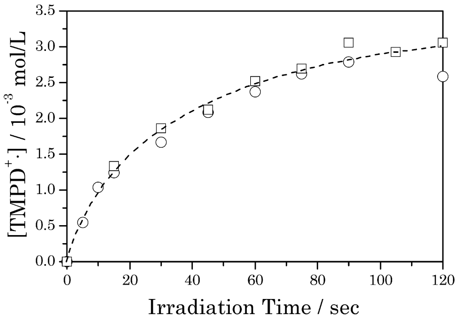


Fig. 7. Growth curve of $\mathrm{TMPD}^{+\bullet}$ in PLLA and PDLLA film. (a) ○, PLLA and (b) □, PDLLA. The irradiation was done at room temperature.

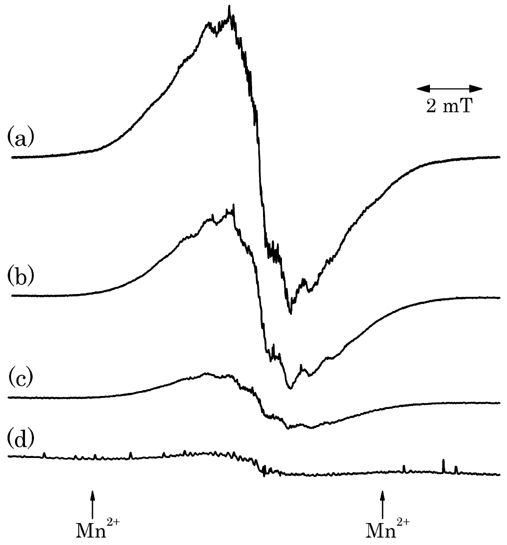


Fig. 8. ESR spectra of 3g4 doped with TMPD at 77 K. (a) After irradiation at 77 K for 4 min, (b) after succeeding thermal annealing at 0 °C for 2 min, (c) after further thermal annealing at 0 °C for 5 min and at 20 °C for 1 min, and (d) after further annealing at 20 °C for 5 min.

Fig. 8 shows ESR spectra of 3g4 doped with TMPD after irradiation by laser light at 77 K for 4 min and after succeeding thermal annealing at various temperatures. No apparent decay was observed by thermal annealing below − 80 °C, but the intensities of ESR spectra largely decreased by succeeding annealing at 0 and 20 °C, (b)–(d). These radical decays are considered the thermal recombination reactions that are caused by the thermally enhanced molecular motion of polymer chain. The spectrum of Fig. 8(c) after annealing at 20 °C is assigned to TMPD radical cation ($\mathrm{TMPD}^{+\bullet}$) that is produced by photoionization of TMPD at 77 K [1]. $\mathrm{TMPD}^{+\bullet}$ has been reported as a radical species that has long lifetime especially in polymer solid matrix [10,12]. As it can be seen by comparing Fig. 8(a) and (c), the ESR spectrum after irradiation (a) consists of

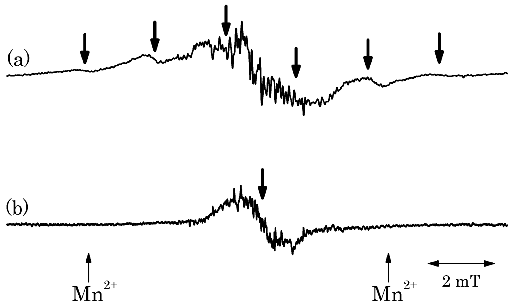


Fig. 9. Difference ESR spectra of 3g4 doped with TMPD in Fig. 8. (a) Obtained by subtracting (c) from (a) in Fig. 8, (b), (d) from (c) Fig. 8.

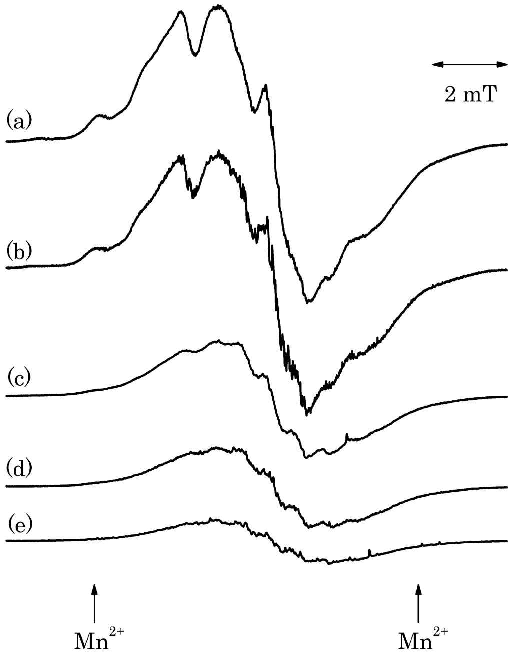


Fig. 10. ESR spectra of M_23g4 doped with TMPD at 77 K. (a) After irradiation at 77 K for 4 min, (b) after succeeding thermal annealing at 20 °C for 10 s, (c) for 1 min, (d) for 3 min, and (e) after further annealing at 40 °C for 3 min.

$TMPD^{+\cdot}$ and other radicals. These radial species other than $TMPD^{+\cdot}$ are polymer chain radicals, which are produced by capturing the electron ejected from TMPD during the UV irradiation at 77 K.

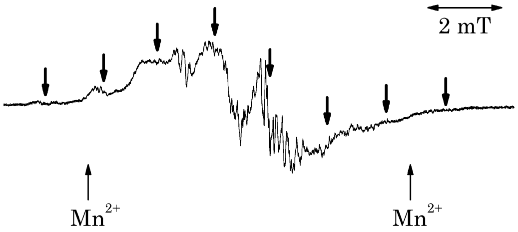


Fig. 11. Difference ESR spectrum of M_23g4 doped with TMPD in Fig. 10 obtained by subtracting (b) from (a).

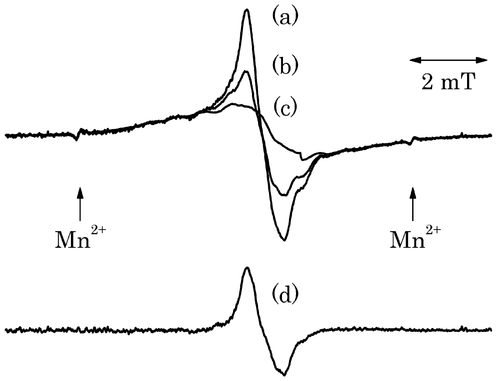


Fig. 12. ESR spectra of 3g4 with TMPD after irradiation at 77 K, measured with different microwave strengths. (a) 0.02, (b) 0.10, (c) 1.00 mW, and (d) difference spectrum between (a) and (b) obtained by subtraction (b) from (a).

Fig. 9(a) shows the difference spectrum between two spectra of Fig. 8(a) and (c), obtained by subtracting (c) from (a). Although there seem small noises around the center of magnetic field, six peaks with 2.0–2.1 mT intervals (down arrows) and a centered broad singlet are recognized in Fig. 9(a). Considering the chemical structure of 3g4 polyester, this set of six peaks with a little anisotropy feature is assigned to $-CH_2-\underset{\cdot}{C}H-CH_2-$ radical with hfcc ca. 2.1 mT for both H_α and H_β. Tsuji and Seiki, who investigated UV irradiated high density polyethylene using ESR method, concluded that $-CH_2-\underset{\cdot}{C}H-CH_2-$ shows six lines ESR spectrum with hfcc = 3.0 mT [13]. The difference of hfcc between Tsuji's result and our may be due to the structural difference of polymer, such as crystallinity and flexibility of polymer chain. Fig. 9(b) shows the difference spectrum between Fig. 8(c) and (d), which clearly indicates a broad singlet spectrum (at the down arrow). This singlet is also seen in Fig. 9(a). The g value of this singlet was estimated to be 2.001–2.002. Similar singlet was also observed by Ooi et al., who investigated γ-irradiated oligoesters [5]. They assigned the singlet, $g = 2.002$, to $-\underset{\cdot}{C}O$ radical. The singlet in Fig. 9(b) may also be assigned to $-\underset{\cdot}{C}O$ which was produced by decomposition of the ester linkage, –CO–O–. Thus, it was clarified by ESR measurement that three radical components are produced in 3g4 after UV irradiation at 77 K: $TMPD^{+\cdot}$, $-CH_2-\underset{\cdot}{C}H-CH_2-$, and $-\underset{\cdot}{C}O$.

Fig. 10 shows ESR spectra of M_23g4 after UV irradiation at 77 K and after succeeding thermal annealing at 20 °C. In Fig. 10(a), some characteristic peaks are seen on the wide spread spectrum. Fig. 11 shows the difference between Fig. 10(a) and (b) obtained by subtracting (b) from (a). No apparent signal of broad singlet, that is observed in Fig. 9(b), is seen in Fig. 11, however, a set of eight peaks with hfcc = 1.4–1.6 mT (down arrows) is superimposed on the wide spread signal of $TMPD^{+\cdot}$.

The set of eight peaks in Fig. 11 with small anisotropic features may be assigned to $-CH_2-\underset{\cdot}{C}(CH_3)-CH_2-$ radical. Hama et al. [14] reported that the UV irradiation of isotactic polypropylene produces the main chain tertiary radical, $-CH_2-\underset{\cdot}{C}(CH_3)-CH_2-$, which shows nine peaks

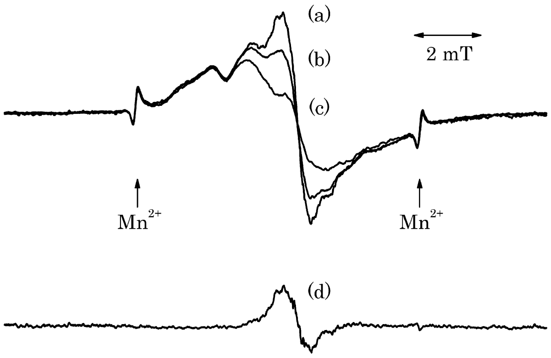


Fig. 13. ESR spectra of M_23g4 with TMPD after irradiation at 77 K, measured with different microwave strengths. (a) 0.02, (b) 0.10, (c) 1.00 mW, and (d) subtracted spectrum between (a) and (b).

with hfcc = 2.15 mT intervals. As already-mentioned earlier about the main chain radical of 3g4, the disagreement about $-CH_2-\dot{C}(CH_3)-CH_2-$ between Hama's result and ours may be also due to the difference of polymer structure. According to the chemical structure of M_23g4, $\cdot CH_3$ radical should be produced when $-CH_2-\dot{C}(CH_3)-CH_2-$ is produced, resulting a set of four peaks with 2.2 mT intervals [1]. However, no ESR signal of $\cdot CH_3$ was observed.

Fig. 12(a)–(c) shows ESR saturation effects on irradiated 3g4 sample measured by different strength of microwave, 0.02–1.00 mW. There was a large difference between them. Generally, intensity of ESR signal increases in proportion to the square root of incident microwave power. However, too much power causes saturation of ESR signal in relation to the relaxation time of radical species. As shown in Fig. 12(d) that is obtained by subtracting (b) from (a), the saturated component is a singlet.

Fig. 13 shows the saturation effect on photoirradiated M_23g4 sample and the difference spectrum between two of them. M_23g4 also shows the same saturation effect as observed for 3g4 in Fig. 12. For both 3g4 and M_23g4, the saturated components show the same Lorentzian singlet with hfcc ~ 1 mT and g values of them are 2.0038 and 2.0034, respectively. These properties of the shape and the saturation effect for both singlets are very similar to the singlet which is observed for photoirradiated PMMA film, $g = 2.0037$ [1]. This singlet of PMMA was assigned to a radical anion of ester group on PMMA side chain. 3g4 and M_23g4 also have ester linkages in those main chain. Thus, those singlet in Figs. 12 and 13 should also be assigned to the ester radical anions. According to the report about γ-irradiated oligoesters by Ooi et al. [5], the ester radical anion produced by γ-irradiation indicates a doublet ESR signal, which disagrees with our observation and assignment results. They concluded that the doublet comes from the hindered rotation of methylene group adjacent to CO group of ester group. This discrepancy may come from the structural differences, because the oligoesters are crystalline while our polyesters are amorphous. More analysis taking into account of the steric structure of radical is needed.

4. Discussion

As shown in Table 1, the T_g for 3g4 and M_23g4 were 20–30° below 0 °C. Thus, the radical reactions on 3g4 and M_23g4 polymer chains are considered to have finished by thermal annealing at 20 °C due to the large molecular motion. Such a radical decay processes by thermal annealing were observed by ESR spectra in Figs. 8 and 10. On the other hand, no apparent spectral change was seen by the thermal annealing at − 80 °C for both 3g4 and M_23g4 after irradiation. This suggests that the radical products in 3g4 and M_23g4 are polymeric species and the radical reaction are strongly depressed below T_g due to the frozen molecular motion of polymer chain.

From the results of the molecular weight changes as shown in Table 2, it is clear that not only main chain scission reaction but also crosslinking reaction occurred through the photosensitized reaction. There seems a common tendency in those results; if the irradiation time is shorter, the degradation of polymer is more depressed even though the total of the irradiation time is the same. Especially for 3g4 sample, the average molecular weight did not decrease but increased by shortening the irradiation time to 4 min.

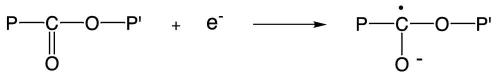
PLLA and PDLLA samples showed different molecular weight changes under the same irradiation condition although these polymers have the same chemical formulae; for example, as shown in Table 2, a large decrease of molecular weight by 40 min irradiation is only seen for PLLA, but not for PDLLA. As shown in Fig. 7, there is no difference of $TMPD^{+\cdot}$ growing for both PLLA and PDLLA samples. Thus, the difference of the GPC results between them should be due to structural difference that comes from crystallinity, etc. Such a structural dependency on polymer reaction was also reported by Babanalbandi et al. [8], who investigated the G values for radical formation in poly(lactic acid)s with different tacticity by γ-irradiation at room temperature. They found that decreasing the crystallinity of poly(lactic acid) leads to a small increase of G value. They also found that the G value for the scission, $G(S)$, are the same for both PLLA and PDLLA, but, for the crosslinking, $G(X)$, is higher for PLLA than PDLLA. This discrepancy between their result and ours may be due to the differences in irradiation temperature and the amount of produced radicals.

According to the previous studies on PMMA and PLLA [1,2], the reaction processes in photosensitized reaction for ester compounds are generally expressed by Schemes 1–3.

As already shown in Section 3.4, several kinds of radical species were found for 3g4 and M_23g4; $TMPD^{+\cdot}$, $-O-\dot{C}O^{-}-$, $-CH_2-\dot{C}H-CH_2-$, $-CH_2-\dot{C}(CH_3)-CH_2-$, and $-\dot{C}O$. The production of the ester radical anion $-O-\dot{C}O^{-}-$ was confirmed for 3g4 and M_23g4 by ESR saturation effect as shown in Figs. 12 and 13. However, it should be noted that the scission radical $\cdot P'$ was not observed for 3g4 and M_23g4 after UV irradiation at 77 K. According

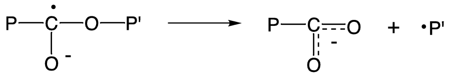
$$TMPD \xrightarrow[2h\nu]{} TMPD^{+\cdot} + e^-$$

Scheme 1.



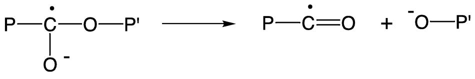
$$P-C(=O)-O-P' + e^- \longrightarrow P-\dot{C}(O^-)-O-P'$$

Scheme 2.



$$P-\dot{C}(O^-)-O-P' \longrightarrow P-C(\overset{-}{\cdots}O)\overset{-}{\cdots}O + \cdot P'$$

Scheme 3.



Scheme 4.

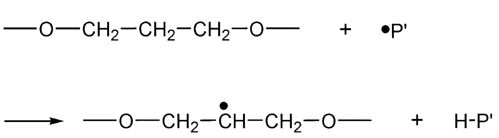
to Scheme 3, production of ·P′ is strongly expected when —O—C̣O$^-$— decomposes. In the case of PLLA, the main chain scission radical ·P is clearly observed by ESR method [2]. Moreover, for PMMA, radical production of $\cdot CH_3$ by ester side group dissociation was also observed [1]. However, in ESR spectra of Fig. 9(b), −C̣O radical was observed after irradiation. Although those ESR intensity of −C̣O in the spectrum is very low, these signals suggest that the main chain decomposition occurs at −CO−OR− linkage during the photosensitized reaction and that the ester radical anion should be the origin of the decomposition (Scheme 4).

In this time, the main chain radical $-CH_2-\dot{C}H-CH_2-$ and $-CH_2-\dot{C}(CH_3)-CH_2-$ were observed for 3g4 and $M_2$3g4, respectively. As shown in Table 1, T_g of PLLA is much higher than 3g4. Therefore, it seems reasonable to assume that the main chain scission radical of 3g4 has very high reactivity even at 77 K and disappeared by dehydrogenation during the irradiation process (Scheme 5).

Such a dehydrogenation reaction on the main chain is also confirmed in the case of UV irradiated polyethylene [13].

5. Conclusion

Spectrophotometry, GPC, and ESR methods were applied to investigate the photosensitized reaction of aliphatic polyester 3g4, $M_2$3g4, and poly(lactic acid)s doped with photosensitizer TMPD. In the GPC curves between before and after UV irradiation, not only the degradation reaction but also the crosslinking reaction of polymer was clearly observed for 3g4 polyester. Although no shift of GPC curve to higher molecular weight was observed for other polyesters, it is suggested that there is a similar possibility of crosslinking reaction for other



Scheme 5.

polyesters also. From the detailed analysis of ESR spectra, it was confirmed that some radical species from polyester are produced during the photosensitized reaction; the ester radial anion produced by electron capturing, the main chain alkyl radicals at the center of diol component produced by dehydrogenation, and the acyl-type radical produced by main chain scission. Although there was no large amount of radical species by main chain scission, it was strongly suggested that photosensitized degradation and crosslinking reactions are originated from the ester radical anion.

References

[1] Sakai W, Tsuchida A, Yamamoto M, Yamauchi J. J Polym Sci, Part A: Polym Chem 1995;33:1969–78.
[2] Sakai W, Kinoshita M, Nagata M, Tsutsumi N. J Polym Sci, Part A: Polym Chem 2001;39:706–14.
[3] Sakai W, Tsuchida A, Yamamoto M, Yamauchi J. Macomol Rapid Commun 1994;15:551–7.
[4] Nozawa Y. Bull Chem Soc Jpn 1970;43:657–62.
[5] Ooi T, Mimura K, Hama Y, Shinohara K. J Polym Sci, Polym Chem 1976;14:813–24.
[6] Mäder K, Domb A, Swartz HM. Appl Radiat Isot 1993;47(11/12):1669–74.
[7] Pomerantz TC, Hill DJT, O'Donnell JH, Pomery PJ. Radiat Phys Chem 1995;45(5):737–44.
[8] Babanalbandi A, Hill DJT, O'Donnell JH, Pomery PJ, Whittaker A. Polym Degrad Stab 1995;50:297–304.
[9] Babanalbandi A, Hill DJT, O'Donnell JH, Pomery PJ. Polym Degrad Stab 1996;52:59–66.
[10] Yamamoto M, Tsuchida A, Nakano M. MRS Int Meet Adv Mater 1989;12:243–8.
[11] Lewis GN, Bigeleisen J. J Am Chem Soc 1943;65:520–6.
[12] Dolan E. J Chem Phys 1962;37:2508–9.
[13] Tsuji K, Seiki T. Polym J 1971;2(5):606–22.
[14] Hama Y, Ooi T, Shiotsubo M, Shinohara K. Polymer 1974;15:878.