

## Studies on Photopolymerization and Photocuring Initiated by Novel Dialkyl Peroxides Having Chromophore

Yoshiki HIGUCHI and Shuji SUYAMA\*

*Fine Chemicals & Polymers Research Laboratory, NOF Corporation,  
Taketoyo-cho, Chita-gun, Aichi 470-23, Japan*

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**ABSTRACT:** New dialkyl peroxides having an aryl ketone chromophore were synthesized by the reaction of *t*-butyl hydroperoxide with isopropylbenzene derivatives. These peroxides had UV absorption bands above 300 nm. The free radicals produced during photolysis effectively initiated the polymerization of methyl methacrylate (MMA) and multifunctional acrylates at room temperature. Photopolymerization rates were as fast as those by the known *t*-butyl peresters having a benzophenone chromophore. When acrylate resins were photocured with the dialkyl peroxides, the resulting coating exhibited no yellow coloration. The storage stability of the dialkyl peroxides was superior to that of the peresters.

**KEY WORDS** Photopolymerization / Photocuring / Photoinitiator / Dialkyl Peroxide / Peroxy Ester / Chromophore / Intramolecular Sensitization / Acrylate Resin / Methyl Methacrylate / Absorption / Spectrum /

Photoinitiators have been used in various fields, *e.g.*, printing, coating, electronic industries, and so on. Photoinitiators, such as benzoin ethers, substituted acetophenones, aromatic ketones, azo compounds, and oximes, are well-known.<sup>1</sup> Organic peroxides are also possible photoinitiators, but the dioxy bonds of the conventional organic peroxides were not cleaved by irradiation with near UV light, because they have no light absorption above 300 nm.

Some organic peroxides having UV absorption bands above 300 nm have been recently developed. Leffler *et al.*<sup>2</sup> prepared a series of benzoyl substituted benzoyl peroxides and showed that these peroxides were photolyzed with quantum yields of approaching unity. Since an intermolecular system, benzoyl peroxide plus benzophenone, gave low quantum yield, they concluded that the photosensitized decomposition of benzoyl sub-

stituted benzoyl peroxides mainly occurred by an intramolecular process. Neckers *et al.*<sup>3-5</sup> synthesized several peresters containing a benzophenone chromophore, and showed that the quantum yields at 366 nm were near unity and the free radicals produced during the photolysis efficiently initiated the polymerization of methyl methacrylate (MMA).

Recently, we successfully synthesized a new type of dialkyl peroxide having a benzophenone chromophore, 4-(1-*t*-butyldioxy-1-methylethyl)benzophenone (**1**), and studied the photolysis.<sup>6</sup> It was shown that the laser flash photolysis of **1** in CCl<sub>4</sub> gave long-lived transient absorptions in the region of 300—400 nm, and T-T absorption due to benzophenone chromophore at 600 nm. The quantum yield of the photolysis at 365 nm was 0.96. Thus, we expected that the dialkyl peroxides having a chromophore act as useful photoinitiators in analogy with Leffler's diacyl

\* To whom all correspondence should be addressed.

peroxides and Neckers' peroxyesters. In this article, we report the photoinduced polymerization of MMA, epoxy acrylate, urethane acrylate, and ester acrylate resins by *t*-butyl alkyl peroxides having a benzophenone or a acetophenone chromophore, and the results are compared with the known *t*-butyl peresters having a benzophenone chromophore.

## EXPERIMENTAL

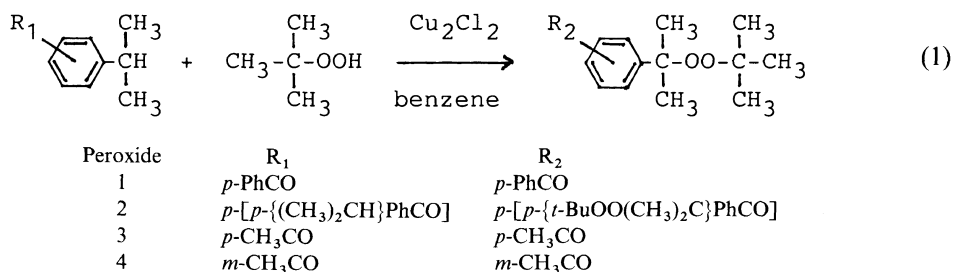
### Materials and Monomer

4-*t*-Butyldioxy-carbonyl benzophenone (BPE) and 3,3',4,4'-tetrakis(*t*-butyldioxy-carbonyl) benzophenone (BTTB) were prepared by methods described in literatures.<sup>3,7</sup> 2-*t*-Butyldioxy-2-phenylpropane (BCP, NOF Corporation), *t*-butyl hydroperoxide (NOF Corporation), and benzophenone (BP) were commercially available, and used as received. Ester acrylate resin used was a mixture of oligoester acrylate (Aronix M-8060, Toa Gousei Chemical Industry Co.) and 2-hydroxy-3-phenoxypropyl acrylate (Aronix M-

5700, Toa Gousei Chemical Industry Co.) at 40:60 percent by weight. Epoxy acrylate resin used was a mixture of diacrylate ester of bisphenol A type epoxy resin (Ripoxy SP-1509, Showa Highpolymer Co.), trimethylolpropan triacrylate, ethylcarbitol acrylate, and *N*-vinylpyrrolidone at 50:20:20:10 percent by weight. Urethane acrylate resin used was a mixture of bifunctional aromatic type urethane acrylate (Aronix M-1100, Toa Gousei Chemical Industry Co.), tetrahydrofurfuryl acrylate, and 2-hydroxyethyl methacrylate at 50:25:25 percent by weight. Methyl methacrylate and the other monomers were purchased from Tokyo Kasei Co., purified in an usual manner and stored under nitrogen.

### Synthesis of Peroxides 1—4

The dialkyl peroxides 1—4 were prepared by the redox reaction<sup>8</sup> of *t*-butyl hydroperoxide with the corresponding isopropylbenzene derivatives, readily available through a Freidel-Crafts reaction between acyl chlorides and cumene. The reaction scheme is as follows:



A mixture of *t*-butyl hydroperoxide 0.4 mol, corresponding isopropylbenzene derivatives 0.1 mol (0.05 mol in the case of **2**), and a catalytic amount of cuprous chloride (Wako Co.) in benzene 50 ml was stirred at 70°C under nitrogen. After 20—30 hours, the reaction mixture was washed with 3% aq. HCl solution, 5% NaOH solution, and water. After evaporation of benzene under vacuum, a viscous liquid was obtained, and purified by the column chromatography over silica gel

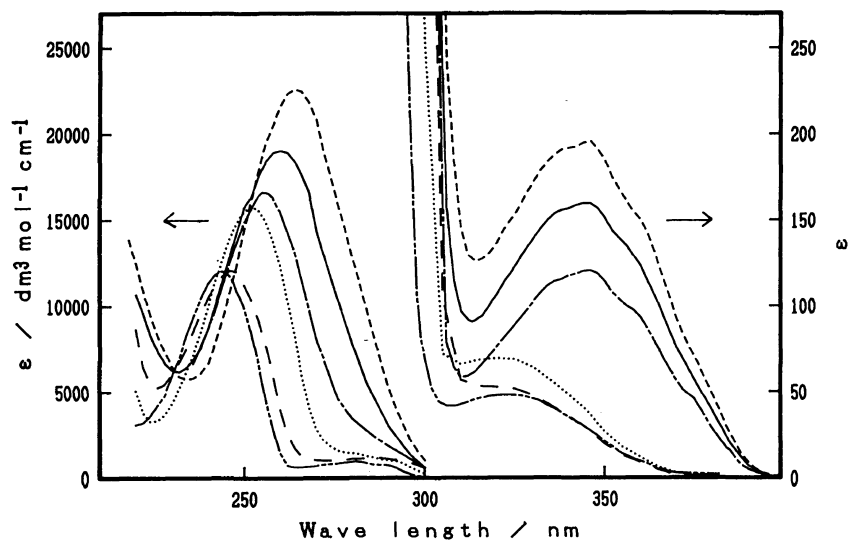
with hexane. A white powder (**1—3**) and liquid (**4**) were obtained. Their structures were ascertained as follows. The <sup>1</sup>H NMR spectra showed characteristic absorptions at 1.24—1.27 ppm (s, *t*-butyl group) and at 1.57—1.65 ppm (s, dimethyl). The IR spectra showed absorptions at 1660 cm<sup>-1</sup> (C=O of benzoyl group), 1690 cm<sup>-1</sup> (C=O of acetyl group), and 870—880 cm<sup>-1</sup> (O—O bond). Elemental analyses are shown in Table I. The absorption spectra are shown in Figure 1. The

**Table I.** Properties of the peroxides

Peroxide	mp	MS	IR	<sup>1</sup> H NMR
	C°	<i>m/z</i>	cm <sup>-1</sup>	$\delta$ , ppm
<b>1</b>	49	312 (M <sup>+</sup> )	1660 (C=O) 870 (O-O)	1.27 (9H, s, <i>t</i> -Bu), 1.62 (6H, s, CH) 7.4—8.2 (9H, m, aromatic)
<b>2</b>	89	442 (M <sup>+</sup> )	1660 (C=O) 870 (O-O)	1.27 (18H, s, <i>t</i> -Bu), 1.60 (12H, s, CH <sub>3</sub> ) 7.5—7.9 (8H, dd, aromatic)
<b>3</b>	27	250 (M <sup>+</sup> )	1690 (C=O) 875 (O-O)	1.23 (9H, s, <i>t</i> -Bu), 1.57 (6H, s, CH <sub>3</sub> ) 2.59 (3H, s, acetyl), 7.5—8.0 (4H, dd, aromatic)
<b>4</b>	liq.	250 (M <sup>+</sup> )	1690 (C=O) 880 (O-O)	1.24 (9H, s, <i>t</i> -Bu), 1.60 (6H, s, CH <sub>3</sub> ) 2.60 (3H, s, acetyl), 7.3—8.1 (4H, m, aromatic)

## Elementally analysis

Peroxide	Found		Calcd		$\lambda_{\max}$ nm	log ( $\epsilon$ )
	C%	H%	C%	H%		
<b>1</b>	76.8	7.7	76.9	7.7	260	4.27
					344	2.20
<b>2</b>	73.2	8.9	73.3	8.7	264	4.34
					345	2.29
<b>3</b>	71.9	9.1	72.0	8.9	252	4.20
					320	1.84
<b>4</b>	71.3	9.2	72.9	8.9	247	4.08
					320	1.72


**Figure 1.** Absorption spectra in 1,4-dioxane. —, 1; ---, 2; ·····, 3; — · —, 4; — — —, benzophenone; — — — —, acetophenone.

absorption maxima in the range 240–270 nm and absorption bands in the range 320–350 nm are attributed to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition, respectively. The extinction coefficients of  $n$ - $\pi^*$  are larger than those of corresponding aromatic ketones.

#### Measurement

IR and  $^1\text{H}$  NMR spectra were measured with a JASCO A-3 and a JEOL JNM-GSX270 spectrometers, respectively. Mass spectra and UV spectra were measured with a JEOL JMS-DX300 mass spectrometer, and a Shimadzu UV-2200 VIS spectrophotometer, respectively. GPC analysis was performed with a Shimadzu LC-6A. The columns used were Shodex KF-80M columns, Shimadzu HSG-10S column, and a Shimadzu HSG-15SH column. Melting points were measured with a Yanaco micro melting apparatus.

#### Photopolymerization of MMA

The photopolymerization of MMA was carried out using merry-go-round equipped with a 400 W high pressure mercury arc lamp. The wavelength of irradiation was 365 nm, which was isolated by a Toshiba glass filter UVD-36A. A solution of photoinitiator and MMA was added in a quartz ampule, purged with nitrogen, and then irradiated at 20°C. After the irradiation, the polymers were precipitated in methanol and analyzed gravimetrically. Molecular weight of poly(MMA) was measured by GPC.

#### Photocuring of Acrylate Resin

UV curing of three types of resin, ester acrylate, epoxy acrylate, and urethane acrylate, was carried out under the following conditions. Acrylate resin containing 2 wt% of photoinitiator was coated on glass plate with applicator (100  $\mu\text{m}$  of thickness), and irradiated with belt conveyer type UV cure derive equipped with 2 kW high-pressure mercury arc lamp. The pass times on the belt conveyer were determined by measuring the

hardness of the surface of the resin. The irradiation energy at 365 nm per pass was about 80  $\text{mJ cm}^{-2}$ .

#### Thermal Decomposition

A solution of the peroxides 0.05  $\text{mol dm}^{-3}$  in cumene was placed in Pyrex tube, and sealed under vacuum. The thermolysis rates were determined by measuring the disappearance of the peroxides by HPLC.

#### Storage Stability

Each ester acrylate resin containing 2 wt% of peroxide was placed at 60°C in the dark. Shelf lives of the resins were represented by the days to gelation.

## RESULTS AND DISCUSSION

#### Polymerization of MMA

Photopolymerizations of MMA were carried out at room temperature by irradiation with 365 nm light using the newly developed dialkyl peroxides **1**–**4** and compared with polymerizations using *t*-butyl peresters having a benzophenone moiety developed by Neckers<sup>3</sup> and researchers of NOF Corporation.<sup>7</sup> The results are listed in Table II. All four dialkyl peroxides **1**–**4** effectively initiated the photopolymerization of MMA. This is the first example that dialkyl-type peroxides initiate photopolymerization by the irradiation at such longer wavelength.

To elucidate the mechanism, the polymerization of MMA was carried out using a mixture of equimolecular 2-*t*-butyldioxy-2-phenylpropane (BCP) and benzophenone. It was found that the polymerization rate by the intermolecular sensitized system was much slower than by the sole use of **1** (Table II). This indicates that these dialkyl peroxides mainly initiate the polymerization of MMA by intramolecular photosensitized mechanism.

The higher polymerization rate with **1** is consistent with the higher photolysis quantum yield of **1** ( $\phi = 0.96$  in  $\text{CCl}_4$ )<sup>6</sup> then that of

**Table II.** Photopolymerization of MMA

Run	Initiator	$\epsilon^a$ at 365 nm	Initial concn	Polymerization rate, $R_p \times 10^4$	Molecular weight, $\times 10^{-3}$	
		$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	$\text{mol dm}^{-3}$	$\text{mol dm}^{-3} \text{s}^{-1}$	$\bar{M}_n$	$\bar{M}_w$
1	<b>1</b>	101	0.01	8.5	16.5	31.9
2	<b>2</b>	124	0.01	11.0	15.3	29.1
3	<b>2</b>		0.005	10.7	18.6	34.4
4	<b>3</b>	6	0.01	5.7		
5	<b>4</b>	4	0.01	3.9		
6	BPE	100	0.01	8.9	15.7	32.7
7	BTTB	121	0.01	12.0	22.0	41.8
8	BTTB		0.0025	10.7	28.2	51.9
9	BCP/BP		0.01/0.01	0.9		

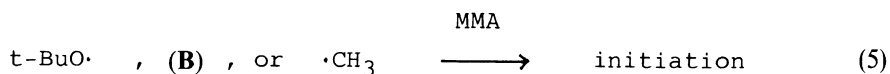
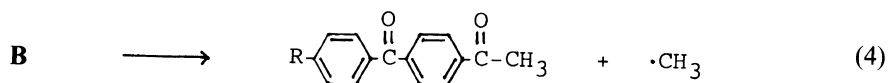
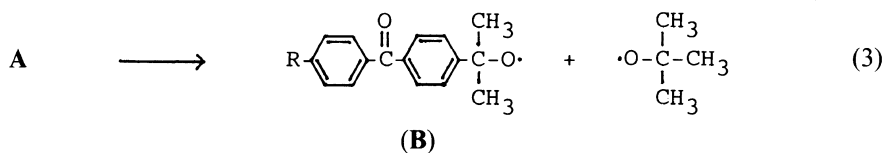
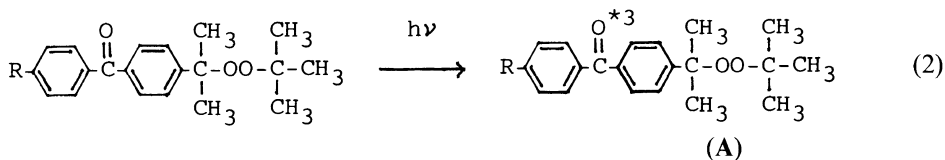
<sup>a</sup> Extinction coefficient in 1,4-dioxane.

benzophenone sensitized decomposition of BCP ( $\phi = 0.05$  in  $\text{CCl}_4$ ).

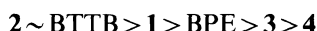
Another interesting aspect was that the rate of photopolymerization ( $R_p$ ) with dialkyl peroxides (**1** and **2**) was comparable to that of peresters having the same chromophore (BPE and BTTB). It is worth noting that the dioxy bonds of these dialkyl peroxides are not attached to a conjugated system in contrast

to the dioxy bond of the known perester initiators which are directly attached to the chromophore. Thus, we propose that the excited triplet energy of the chromophore is transferred to the dioxy bonds of the dialkyl peroxides through  $\sigma$  bonds or space.

A likely scheme leading to polymerization is as follows:

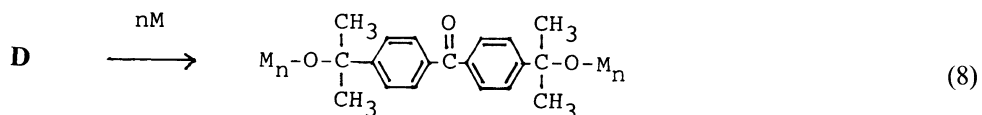
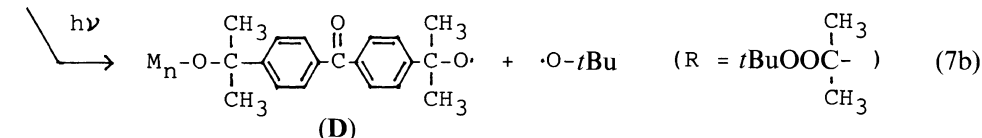
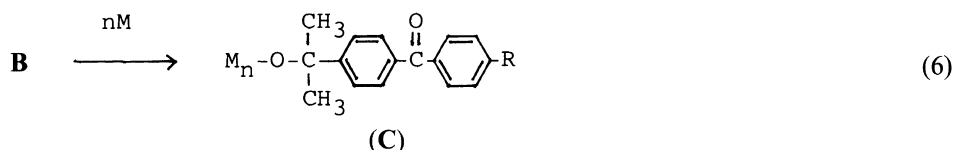


The order of  $R_p$  at the same initial initiator concentration was as follows:



$R_p$  using the peroxides with benzophenone derivatives (**1** and **2**) were higher than the peroxides with acetophenone derivatives (**3** and **4**). This is explained by differences in absorbance (i.e.,  $\epsilon \times [I]$ )<sup>9</sup>.

The effect of the number of reactive sites on the  $R_p$  and molecular weight was studied.  $R_p$  and molecular weight were compared at the same active oxygen concentration. It is interesting that  $R_p$  and  $\bar{M}$  using 0.005 M of diperoxide **2** (Run 3) were higher than those using 0.01 M of monoperoxide **1** (Run 1). The results are explained by the following equation.



here, M donates MMA. In the case of bifunctional peroxide **2** ( $\text{R} = t\text{BuOOC}(\text{CH}_3)_2$ ), the polymer **C** formed according to eq. 6 absorbs another photon and subsequently decomposes to *t*-butoxy radical and alkoxy radical **D** (eq 7b). The radical **D** further initiates the polymerization to give a high polymer having two  $M_n$ . The polymer **C** formed with monoperoxide **1** also absorbs another photon, but further polymerization by the excited polymer **C** does not occur because of the absence of a labile dioxy bond in the polymer. Eventually, alternative deactivation may be a major path (eq 7a) and lowers polymerization efficiency.

#### UV Curing of Acrylate Resins

UV curing of ester acrylate, epoxy acrylate, and urethane acrylate resins by these dialkyl

peroxides was carried out and compared with that by the known perester having a chromophore. The results are shown in Table III. In connection with  $\epsilon$ , dialkyl peroxides with acetophenone chromophore (i.e., **3** and **4**) exhibited lower curing efficiency than other photoinitiators. The use of the known peresters caused yellowing of the coatings. The cured resins with the present dialkyl peroxides exhibited no yellowing of coatings. To reduce the influence of oxygen on curing, an ester acrylate resin containing **1** or BPE was covered with PET film during irradiation. The curing results are shown in Table IV. The pass times of dialkyl peroxides were dramatically reduced and were nearly the same as those of BPE.

The effect of added triethanol amine was

**Table III.** Photocuring of acrylate resin

Initiator	Pass times			Yellowing of coating <sup>a</sup>
	Acrylate resin			
	Ester	Epoxy	Urethane	
<b>1</b>	11	5	14	○
<b>2</b>	11	6	17	○
<b>3</b>	25	15	49	○
<b>4</b>	29	15	60	○
BPE	8	5	13	×
BTTB	4	4	13	×

<sup>a</sup> ○, no yellowing; ×, yellowing.

**Table IV.** Photocuring of ester acrylate resin in the presence of amine or in the absence of O<sub>2</sub>

Initiator	Pass times			In the absence of O <sub>2</sub>
	Triethanol amine/wt%			
	0	0.5	2	
<b>1</b>	11	9	4	3–4
BPE	7	6	3–4	3

**Table V.** Thermal decomposition rates and parameters<sup>a</sup>

	Temp/°C	<b>1</b>	BCP
Thermal decomposition rate constant, $k_d \times 10^6/s^{-1}$	110	—	4.7+0.1
	120	13.9+0.2	16.9+0.3
	130	44.5+0.8	51.6+2.4
	140	135.7+3.5	161.1+3.3
	150	398.8+8.6	—
Activation enthalpy/kJ mol <sup>-1</sup>		151.5+0.2	151.4+0.9
Activation entropy/JK <sup>-1</sup> mol <sup>-1</sup>		45.1+1.2	46.1+4.5

<sup>a</sup> Initial concn. of peroxides were 0.05 mol dm<sup>-3</sup> in cumene.

also examined. The pass times decreased with increasing triethanol amine. This effect is due to the oxygen trapping by the amine.<sup>10,11</sup>

### Storage Stability

To examine the thermal stability of **1**, thermolysis of **1** was carried out in cumene under vacuum. The thermolysis rates, as deter-

**Table VI.** Shelf lives of resins with various peroxides at 60°C

Initiator	Shelf life
	Days to gelation
<b>1</b>	>100
<b>2</b>	>100
BPE	6
BTTB	3

mined by measuring the disappearance of **1** by HPLC, satisfied first-order kinetics (over two half-lives reaction). The resulting rate constants and activation parameters are listed in Table V and compared with the results of BCP. The thermolysis rates were slightly lower than BPC. This is consistent with the general trend that the electron withdrawing groups retard the decomposition of dioxy bonds.<sup>12</sup>

The half life of **1** was 49.4 hours at 110°C, which is much longer than the reported value of BPE (6.7 hours at 110°C).<sup>3</sup> Therefore, the newly developed dialkyl peroxide is thermally more stable than the known peresters. In fact, the shelf lives of the dialkyl peroxides were superior to those of the known peresters (Table VI).

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