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The Effect of α-Tocopherol on Polymerization of Methyl Methacrylate

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Photo- and thermal polymerizations of methyl methacrylate (MMA) in the presence of α-tocopherol were investigated in air or *in vacuo*. α-Tocopherol at higher concentrations inhibits both the photopolymerization of MMA sensitized by benzoin ethyl ether and the thermal polymerization induced by benzoyl peroxide, but at lower concentrations is able to initiate photopolymerization of MMA under aerobic conditions. Spectral data indicate that a fraction of α-tocopherol is incorporated in the produced polymer chain.

α-Tocopherol (αT) (Fig. 1) is known as an oil-soluble antioxidant vitamin, whose action *in vivo* is to quench radicals produced in biological membranes, particularly multivalent unsaturated fatty acid radicals induced through decompositions, and the excited singlet oxygen $^1O_2$. A lot of literature has reported this action,[1,2] but no report is found of the effect on vinyl polymerization. Because the antioxidant property of α-tocopherol is due to the production of semiquinone radical through oxidation of the hydroxyl group having an active hydrogen,[2,3] α-tocopherol is expected to be an inhibitor for vinyl polymerization. A high resolution electron spin resonance study has shown that 6-chromanyloxyl radical is produced by photolytic oxidation of α-tocopherol,[4] but the action of this radical on vinyl monomer has not yet been investigated. The present author has studied the effect of α-tocopherol on the polymerization of methyl methacrylate (MMA) and found that α-tocopherol at high concentrations inhibits the polymerization of MMA as expected but that it is effective at low concentrations for photoinitiation of MMA polymerization in the presence of air.

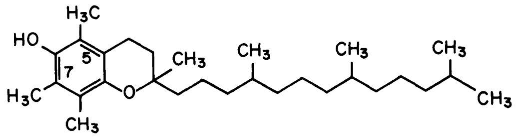

Fig. 1. Chemical structure of α-tocopherol.

Experimental

α-Tocopherol, benzoin ethyl ether (BEE), and benzoyl peroxide (BPO), all of reagent grade (Nakarai Chem. Co.), were used without further purification. MMA was distilled *in vacuo* before use. MMA was placed in a glass ampoule with or without solvent and kept at 25 °C in a thermostat for 30 min, the concentration of dissolved oxygen was confirmed to be 4.5×10^{-4} mol dm^{-3}, and then the ampoule was sealed in atomsphere.

A high pressure mercury lamp was used for photopolymerization and the lights below 300 nm wavelength were cut off with a glass filter (Toshiba, UV-30), if necessary. At a certain reaction time, the polymer solution was poured into methanol, and the conversion of polymer was estimated from the weight of the precipitant required.

Electron spectra were recorded on a Simadzu MPS-5000. Flash photolysis was conducted with a home-made apparatus consisting of a 1 cm$\phi\times$10 cm quartz sample tube, two main xenon lamps (Ushio FS-225HMA), a sub xenon flash lamp (Ushio FS-125B), and a spectroscope. The main lamps were

Table 1. Effects of addition of α-tocopherol on the polymerization of methyl methacrylate[a)]

	No.	Air	Reaction temp	Reaction time	Filter[b)]	Concn of initiator		Concn of α-tocopherol	Conversion of polymer
			°C	h		mol dm^{-3} (BPO)	(BEE)	mol dm^{-3}	%
Photo	1	none	30.6	5.0	none	0	0	0	7.7
	2	none	30.6	3.7	cut	0	0	0	0.0
	3	none	30.6	3.7	cut	0	0	1.45×10^{-4}	1.0
	4	none	30.6	5.0	none	0	0	1.76×10^{-3}	6.4
	5	none	30.6	5.0	none	0	0	4.64×10^{-3}	0.0
	6	+	20	0.5	none	0	4.17×10^{-2}	0	22.3
	7	+	20	0.5	none	0	4.17×10^{-2}	6.37×10^{-4}	15.3
	8	+	20	0.5	none	0	4.17×10^{-2}	6.96×10^{-3}	0.0
	9	+	30.6	4.8	none	0	0	0	0.0
	10	+	30.6	6.3	none	0	0	3.86×10^{-5}	6.4
	11	+	30.6	4.8	none	0	0	9.28×10^{-3}	0.0
	12	+	30.6	4.8	cut	0	0	3.86×10^{-5}	2.1
Thermal	13	none	78	0.25		2.48×10^{-2}	0	0	9.0
	14	none	78	0.25		2.48×10^{-2}	0	3.86×10^{-5}	8.5
	15	none	78	0.25		2.48×10^{-2}	0	4.64×10^{-3}	0.0
	16	+	80	0.25		4.13×10^{-2}	0	0	0.2
	17	+	80	0.25		4.13×10^{-2}	0	4.63×10^{-3}	0.3

a) Light intensity I=80 mW cm^{-2}. b) Cut off below 300 nm.

put parallel with the sample tube, and the sub lamp and spectroscope were put on the elongation of the center axis of sample tube. The sample was kept at room temperature. The concentration of O_2 in MMA was measured with an oxygenelectrode (Yellow Spring Instrument Co., Inc.). The viscosity of polymer acetone solution was measured with an Ubelohde viscosimeter at 30 °C.

Results and Discussion

As generally known, MMA monomer is caused to polymerize *in vacuo* by a radical produced by absorption of ultraviolet light below 300 nm wavelength, but the polymerization is hard to proceed under aerobic conditions because the radical is quenched by oxygen. The results of Table 1 were obtained when MMA was photochemically or thermally polymerized in the presence of α-tocopherol under aerobic or anaerobic conditions. Table 1 indicates that α-tocopherol at higher concentrations inhibits the polymerization of MMA by quenching the initiator radical or monomer radical as expected (Nos. 8 and 15). The mechanism of inhibition is thought to be as follows:

$$C_6H_5COOOCOC_6H_5 \xrightarrow{k_d} 2C_6H_5CO_2\cdot, \qquad (1)$$

$$C_6H_5CO_2\cdot + M \longrightarrow C_6H_5CO_22M\cdot, \qquad (2)$$

$$M_x\cdot + M \xrightarrow{k_p} M_{x+1}\cdot, \qquad (3)$$

$$2C_6H_5CO_2\cdot \xrightarrow{2k_t} \text{nonradical products}, \qquad (4)$$

$$M_x\cdot + M_y\cdot \longrightarrow M_x + M_y \text{ or } M_{x+y}, \qquad (5)$$

$$C_6H_5CO_2\cdot + M\cdot \longrightarrow C_6H_5CO_2M, \qquad (6)$$

$$C_6H_5CO_2\cdot + \alpha T \longrightarrow C_6H_5COOH + \alpha T\cdot, \qquad (7)$$

$$C_6H_5CO_2\cdot + \alpha T \xrightarrow{k_{inh}} \text{nonradical products}, \qquad (8)$$

where M is the monomer and R_i is the rate of initiation. The inhibition rate is expressed by

$$R_{inh} = \frac{k_p[M]R_i}{k_{inh}[\alpha_T]}. \qquad (9)$$

Plots of conversion *vs.* reaction time are shown in Fig. 2 for various α-tocopherol concentrations. The value of R_{inh} is close to zero, so that k_{inh} is much larger than k_p.

MMA does not polymerize without α-tocopherol under aerobic conditions, but MMA is photopolymerized in the presence of a small amount of α-tocopherol under an aerobic condition ($[O_2]=4.5\times10^{-4}$ mol dm^{-3}); that is to say, light and α-tocopherol are main initiators for these polymerization reactions. The effect of α-tocopherol on the conversion is shown in Fig. 3. Here, α-tocopherol inhibits to less than 10% of MMA conversion when the α-tocopherol concentration is 1.2×10^{-3} mol dm^{-3} as seen from Fig. 1 and the effect of inhibition may be ignored. The conversion increases in proportion to the square root of the amount of α-tocopherol below 5×10^{-3} mol dm^{-3}, which indicates that this reaction is on the bimolecular termination mechanism. The logarithm of the conversion is proportional to the logarithm of the intensity of light (the slope is 0.61 as seen from Fig. 4). This fact also supports that this reaction is on the bimolecular termination mechanism.

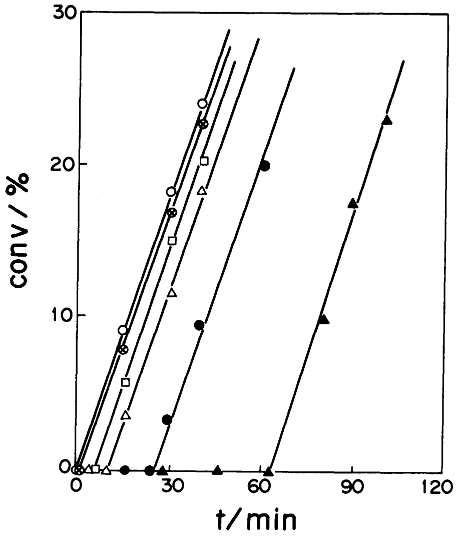

Fig. 2. The relation between conversion and reaction time, concentration of benzoyl peroxide is 2.40×10^{-2} mol dm^{-3} under anaerobic conditions, temperature is 70 °C, -O-: $[\alpha T]=0$, mol dm^{-3}, -X-: $[\alpha T]=3.86\times10^{-5}$, -□-: $[\alpha T]=2.32\times10^{-4}$ mol dm^{-3}, -Δ-: $[\alpha T]=6.01\times10^{-4}$ mol dm^{-3}, -●-: $[\alpha T]=1.5\times10^{-3}$ mol dm^{-3}, -▲-: $[\alpha T]=4.0\times10^{-3}$ mol dm^{-3}.

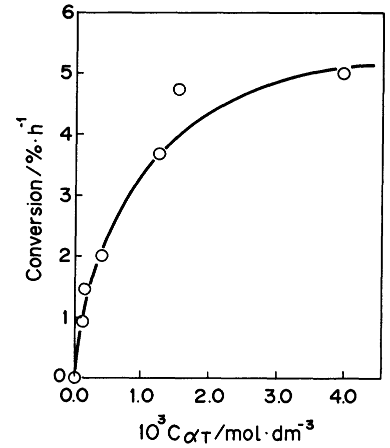

Fig. 3. The relationship between conversion and concentration of α-tocopherol at 30 °C under aerobic conditions.
$I=80$ mW cm^{-2}.

Next, the conversion was measured at various concentrations of monomer in benzene as a solvent. The results obtained conclude that the conversion is proportional to the concentration of monomer (the slope is 1.19 as seen from Fig. 5). This fact allows the polymerization rate R_p to be written as

$$R_p\,\alpha\,I^{1/2}C_{MMA}C\alpha_T^{1/2}, \qquad (10)$$

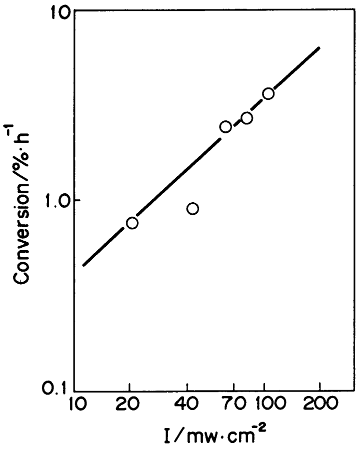

Fig. 4. Plots of conversion *vs.* intensity of light at 30.6 °C under aerobic conditions. Concentration of α-tocopherol is 6.44×10^{-4} mol dm^{-3}.

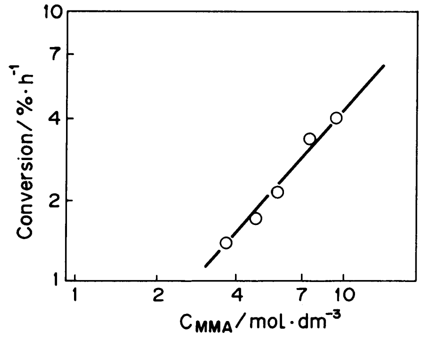

Fig. 5. Plots of conversion *vs.* monomer concentration at 30.6 °C under aerobic conditions. Concentration of α-tocopherol is 6.44×10^{-4} mol dm^{-3}. Intensity of light is 100 mW cm^{-2}.

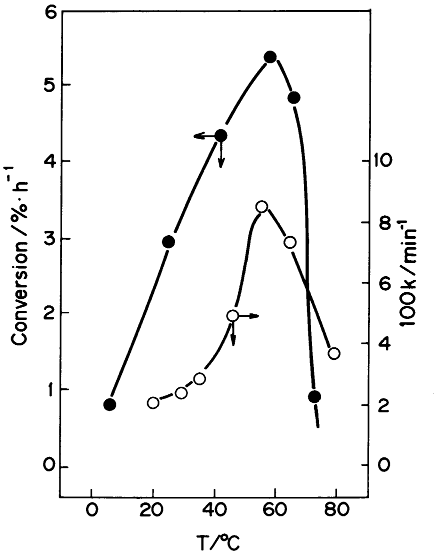

Fig. 6. Temperature dependence of conversion and the photooxidation rate constant. Concentration of α-tocopherol is 6.44×10^{-4} mol dm^{-3}, intensity of light is 100 mW cm^{-2}.
-●-: conversion of MMA, -O-: photooxidation rate of α-tocopherol.

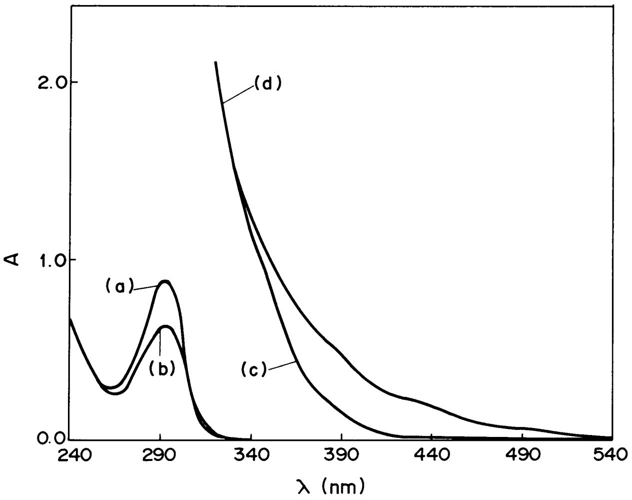

Fig. 7. Spectra of α-tocopherol and photooxidated products.
(a) 2.58×10^{-4} mol dm^{-3} α-tocopherol in methanol, (b) Photoirradiatted (a) for 1.5 h, (c) 3.63×10^{-2} mol dm^{-3} α-tocopherol in methanol, (d) Photoirradiatted (c) for 2 h.

where I is the intensity of light, C_{MMA} is the concentration of monomer, and $C_{\alpha\mathrm{T}}$ is the concentration of initiator. The temperature dependence of the conversion was also examined (Fig. 6). The conversion reaches a maximum at 50 °C and decreases sharply above 50 °C. The Arrhenius relation holds in the temperature range 5 —50 °C; the activation energy ΔE is estimated as about 33.9 kJ mol^{-1}.

The effect of α-tocopherol as photoinitiator was studied under aerobic conditions. When a methanol solution of α-tocopherol was photoirradiated under aerobic conditions, the optical density at 293 nm decreased with time (Fig. 7). This reaction was found to be first order in α-tocopherol with a rate constant k of 0.024 min^{-1} at 30 °C under aerobic conditions. In contrast, k is 6.4×10^{-3} min^{-1} under anaerobic conditions and 3.9×10^{-3} min^{-1} with the light cut off below 300 nm under aerobic conditions. These results indicate that this reaction needs both oxygen and ultraviolet light. As can be seen from Fig. 6, k and the conversion of MMA decrease above 50 °C. At first glance, the decrease in the conversion might be considered to result from both the increase in the quenching rate of α-tocopherol radical with temperature and the secrease in the concentration of α-tocopherol radical which initiates the polymerization. However, this mechanism cannot interpret the decrease in the oxidation rate of α-tocopherol above 50 °C. Thus the phenomenon cannot be interpreted with our present knowledge.

Flash photolysis of an α-tocopherol solution in ethanol was examined. Transient spectra were found at 356 nm between 10 and 100 µs and the vanishing rate constant was obtained as 1.55×10^{4} s^{-1}. It may be thought that the species concerned is the triplet state of semiquinone radical (6-chromanyloxyl radical) of α-tocopherol, because it is generally considered that even the triplet state of chlorophyll a, of which the residence time of the triplet state is the longest among popular molecules is quenched by electron acceptors to a residence time of 10^{-4} s (for example, the quenching rate constant of the triplet state of okitacene is $3.1\times10^5\,s^{-1}$).[5] This radical was observed by laser flash photolysis coupled with time resolved ESR.[6]

The mechanism of the photopolymerization of MMA with α-tocopherol is given as follows on the basis of the results obtained:

$$\alpha T \xrightarrow{h\nu} \alpha T\cdot, \tag{11}$$

$$\alpha T\cdot + O_2 \longrightarrow \alpha TO_2\cdot, \tag{12}$$

$$\alpha TO_2\cdot \xrightarrow{k_q} Q(\alpha T\text{-}O_2\text{-}\alpha T), \tag{13}$$

$$\alpha TO_2\cdot + MMA \xrightarrow{k_i} \alpha TO_2\text{-}MMA\cdot, \tag{14}$$

$$MMA_x\cdot + MMA \xrightarrow{k_p} MMA_{x+1}\cdot, \tag{15}$$

$$MMA_x\cdot + MMA_y\cdot \xrightarrow{k_t} MMA_{x+y} \text{ or } MMA_x + MMA_y. \tag{16}$$

The rate of initiation is expressed as

$$v_i = \frac{k_i C_{MMA}}{(k_i C_{MMA}+k_q)} \phi I[1-\exp(-\varepsilon C_{\alpha T} l)], \tag{17}$$

where ϕ is the quantum yield for producing α-tocopherol., Q is the subproduct of the reaction, l is the length of the reactor, and ε is the molecular extinction coefficient. When $C_{\alpha T}$ is small (the light is not perfectly absorbed), Eq. 17 can be reduced to

$$v_i = \frac{k_i C_{MMA}}{(k_i C_{MMA}+k_q)} \phi I \varepsilon C_{\alpha T} l. \tag{18}$$

Further, if $k_i C_{MMA} > k_q$, the following equation is obtained which agrees with the experimental Eq. 1:

$$R_p = \frac{k_p C_{MMA}}{(2k_t)^{1/2}} \phi^{1/2} I^{1/2} C_{\alpha T}^{1/2} (\varepsilon l)^{1/2}. \tag{19}$$

$\alpha TO_2\cdot$ may be a derivative from the 6-chromanyloxyl radical. The chromanyloxyl radical formed would be stabilized by radical delocalization and the most reactive site of the delocalized radical seems to be the C-5 position.[7] Then the initiation point of polymerization may be the C-5 position. Because the polymerized poly(methyl methacrylate) has an absorption band above 400 nm even after purification, it is thought that the oxidative product of α-tocopherol is present at the end of the produced poly(methyl methacrylate). The molecular weight of the polymer produced in the presence of α-tocopherol as a photoinitiator was investigated; the molecular weight was measured by the viscometric method.[8] The results are shown in Table 2, revealing that the presence of α-tocopherol suppresses the increase in the molecular weight.

Table 2. Molecular weight of the poly(methyl methacrylate) produced with α-tocopherol as initiator[a)]

$C_{\alpha T}$ / mol dm^{-3}	$[\eta]_{sp}$[b)]	$\bar{M}_v$
none	2.00	10.0×10^5
3.66×10^{-5}	1.78	8.6×10^5

a) Bulk polymerization under aerobic conditions, with irradiation by a mercury lamp (80 mW cm^{-2}). b) Measured at 30 °C in acetone with an Ubelohde viscocimeter.

Table 3. Comparison of various vinyl monomers polymerized with α-tocopherol

Temperature is 30.6 °C and lighe intensity is 80 mW cm^{-2} under aerobic conditions

Monomer	$C_{\alpha T}$ / mol dm^{-3}	Conversion / %h^{-1}
Methyl methacrylate	none	0.7
	4.33×10^{-4}	2.0
Styrene	none	0.6
	5.71×10^{-4}	2.2
Ethyl cinnamate	none	0.005
	7.33×10^{-4}	0.052

The effect of α-tocopherol as an initiator on other vinyl monomers were studied. It has been found that α-tocopherol can initiate styrene as well as MMA but hardly initiate ethyl cinnamate (Table 3).

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