

Photopolymerization of Methyl Methacrylate with *N*-Benzylpyridinium Bromide and Chloride in the Presence of 1,2-Dibromoethane and Carbon Tetrachloride

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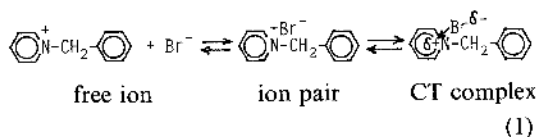
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ABSTRACT: The photopolymerization of methyl methacrylate (MMA) with *N*-benzylpyridinium bromide (BPB) and chloride (BPC) in the presence of carbon tetrachloride and 1,2-dibromoethane was carried out in dichloromethane and the accelerating effect of the haloalkanes on the photopolymerization was studied according to the spectroscopic and kinetic methods. In the absence of haloalkane, BPC photodecomposed to the *N*-benzylpyridinyl radical and halogen atom as well as BPB. The halogen atom initiated the polymerization, but the *N*-benzylpyridinyl radical contributed to its termination rather than initiation. When carbon tetrachloride and 1,2-dibromoethane were added to the polymerization system, they reacted rapidly with the *N*-benzylpyridinyl radical to reproduce BPC and BPB, respectively.

KEY WORDS Photopolymerization / Methyl Methacrylate / *N*-Benzylpyridinium Bromide / *N*-Benzylpyridinium Chloride / Carbon Tetrachloride / 1,2-Dibromoethane /

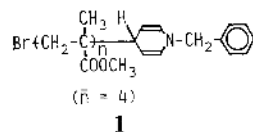
In a previous paper,¹ the authors reported that the photopolymerization of methyl methacrylate (MMA) was sensitized by *N*-benzylpyridinium bromide (BPB) in methanol and was accelerated by the addition of tetraethylammonium bromide (TEAB). Spectroscopic and kinetic studies of the polymerization indicated that there exists an equilibrium among free ions, ion pair and a CT complex of BPB as shown in eq 1, and that the increase of Br⁻ concentration by the addition of TEAB shifts the equilibrium to the right with increasing concentration of the CT complex of BPB which is responsible for the photopolymerization. The CT



complex of BPB photodecomposed to form both bromine atoms and *N*-benzylpyridinyl radicals; the latter disappeared by a fast reaction with methanol and the former initiated the polymerization yielding poly(methyl methacrylate) (PMMA) with high mo-

lecular weight.

In dichloromethane, however, the *N*-benzylpyridinyl radical reacted with a growing radical to terminate the polymerization and only oligo(methyl methacrylate) (OMMA) shown by structure 1 was



obtained. Since *N*-ethyl-4-carbomethoxy-pyridinyl radical was reported to react rapidly with carbon tetrachloride,² it should be expected that *N*-benzylpyridinyl radical may be captured by carbon tetrachloride even in dichloromethane.

In the present study, the photopolymerization of MMA with BPB in dichloromethane was carried out in the presence of several kinds of haloalkanes. Among them, carbon tetrachloride and 1,2-dibromoethane yielded PMMA with relatively high molecular weight up to high conversion. It is suggested that these two haloalkanes effectively captured the pyridinyl radical to reproduce *N*-benzyl-

pyridinium chloride (BPC) and BPB, respectively. Kinetic and spectral studies on the photopolymerization of MMA with BPC in the presence of carbon tetrachloride and 1,2-dibromoethane are also described.

EXPERIMENTAL

Materials

MMA was purified by the usual method just before use. BPB and BPC were prepared by the Menshutkin reaction. Carbon tetrachloride, methylene chloride, 1,2-dibromoethane and ethyl bromide were purified by the usual methods. Carbon tetrabromide was recrystallized from an ethanol-water mixture, mp 367–368 K.

Electronic Spectra

Electronic spectra were recorded on a Japan Spectroscopic Company Model UVIDEC-1 spectrophotometer and measured in a quartz cell having a 10 mm path length.

Photopolymerization

MMA, BPB, and haloalkanes were placed in a hard glass ampoule which was degassed, filled with nitrogen, and then sealed under vacuum. After irradiation in the same apparatus as described in the preceding paper,¹ the contents of the ampoule were poured into methanol and the precipitated polymer was filtered and dried *in vacuo*. When no precipitate was obtained, all the contents of the ampoule were evaporated *in vacuo* to dryness.

Molecular Weight

The molecular weight of PMMA was determined by gel-permeation chromatography (GPC) or viscometry. Gel-permeation chromatogram was measured on a Yanagimoto High Performance Chromatograph Model L-2000 equipped with a column Shodex A803, using tetrahydrofuran as an eluent. The molecular weight of PMMA was estimated from the elution volume of the polymer on the basis of a comparison with that of a standard polystyrene. The intrinsic viscosity of PMMA was measured by an Ubbelohde dilution viscometer in benzene at 303 K, and its molecular weight was calculated by the same equation³ used in the preceding paper.¹

RESULTS AND DISCUSSION

Photopolymerization of MMA with BPB in the Presence of 1,2-Dibromoethane and Carbon Tetrachloride

Photopolymerization of MMA with BPB was carried out in dichloromethane as a solvent, where a large excess of haloalkane such as carbon tetrabromide, 1,2-dibromoethane, ethyl bromide, carbon tetrachloride, and 1,2-dichloroethane was added in order to capture the *N*-benzylpyridinyl radical. For a comparison with the experiments above, photopolymerization was also carried out in dichloromethane in the presence of haloalkanes without BPB to confirm the photosensitivity of these haloalkanes themselves, and the results are shown in Table I.

In the absence of haloalkane, the photopolymerization of MMA with BPB was carried out in dichloromethane¹ and the conversion of MMA did not exceed 1% for an hour. The results shown in Table I, therefore, indicate that the photopolymerization of MMA with BPB in dichloromethane was accelerated by addition of three haloalkanes, carbon tetrabromide, 1,2-dibromoethane and carbon

Table I. Photopolymerization of MMA with BPB in the presence of haloalkanes

BPB	Haloalkanes	Conversion/% ^b		
		30 min	60 min	
mol dm ⁻³	mol dm ⁻³			
1 × 10 ⁻³	CBr ₄ ^a	0.01	10.87	20.90
	BrCH ₂ CH ₂ Br	1.16	3.97	7.85
	CH ₃ CH ₂ Br	1.33	1.06	1.36
	CCl ₄	1.04	8.77	11.44
	CICH ₂ CH ₂ Cl	1.27	1.05	1.32
None	CBr ₄ ^a	0.01	4.61	8.59
	BrCH ₂ CH ₂ Br	1.16	c	c
	CH ₃ CH ₂ Br	1.33	0.11	0.22
	CCl ₄	1.04	0.36	0.65
	CICH ₂ CH ₂ Cl	1.27	c	c

MMA, 5 cm³; haloalkane, 1 cm³; CH₂Cl₂ (solvent), 4 cm³; temp, 303 K.

^a 0.033 g of crystalline CBr₄ dissolved in 1 cm³ of CH₂Cl₂ was added.

^b Polymer was obtained by evaporation *in vacuo* to dryness, but in the absence of BPB, the polymer was obtained by precipitation with methanol.

^c There was no precipitate by the addition of methanol.

tetrachloride. Carbon tetrabromide was reported to serve as a photosensitizer and a chain transfer agent for the polymerization of MMA,⁴ and the present results also demonstrated a large photosensitizing effect of carbon tetrabromide. Accordingly, the accelerating effects of haloalkanes on the photopolymerization of MMA with BPB in dichloromethane was studied only with 1,2-dibromoethane and carbon tetrachloride in detail.

In the presence of 1,2-dibromoethane, the photopolymerization of MMA in dichloromethane gave a linear conversion-time relation over a wide range of conversions as shown in Figure 1 and also a PMMA whose number average molecular weight (M_n) was determined by GPC to be 26,000. These results distinctly differed from those obtained in the absence of an effective haloalkane and gave a non-linear conversion-time relation and a PMMA with low molecular weight ($M_n=4,400$). These facts suggested that the photopolymerization of MMA with BPB in the presence of 1,2-dibromoethane is not a dead-end one accompanied by termination by the *N*-benzylpyridinyl radical.

In the presence of carbon tetrachloride, the photopolymerization of MMA with BPB in dichloromethane was remarkably accelerated, but did not give a linear conversion-time relation at the initial stage. The molecular weight distributions of PMMA obtained after 10, 30 and 60 minutes were measured by GPC as shown in Figure 2. These results suggest that there exists a different mechanism of initiation from that of the initial stage.

The absorption spectra of BPB and BPC measured in a MMA-CH₂Cl₂ (1:1, v/v) mixture are shown in Figure 3 and both spectra showed substantially no change by the addition of 1,2-dibromoethane or carbon tetrachloride without irradiation. In the absence of an effective haloalkane, the absorption spectrum of BPB in the polymerization system was found to be accompanied by a complicated spectral change in a wavelength region longer than 400 nm by irradiation. The dotted line in Figure 3 shows the spectrum obtained after irradiation for one hour. The details are described in the preceding paper.¹

In the presence of 1,2-dibromoethane, the spectrum of BPB did not indicate any change by irradiation, but in the presence of carbon tetrachloride, the spectrum of BPB remarkably changed during irradiation and finally coincided with that of

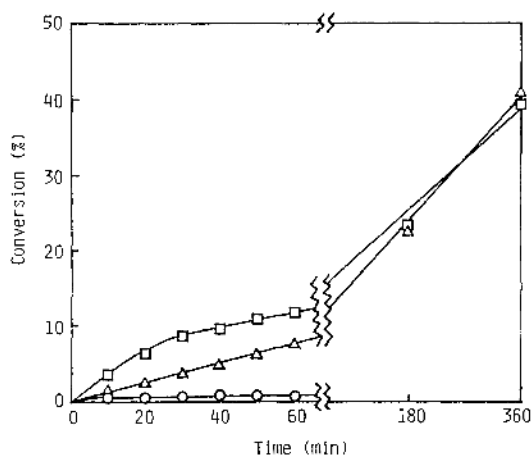


Figure 1. Conversion-time relations for the photopolymerization of MMA with BPB in dichloromethane in the presence of 1,2-dibromoethane and carbon tetrachloride: BPB, 1×10^{-3} mol dm⁻³; MMA, 5 cm³; Δ , CH₂Cl₂, 4 cm³ and BrCH₂CH₂Br, 1 cm³ (1.16 mol dm⁻³); \square , CH₂Cl₂, 4 cm³ and CCl₄, 1 cm³ (1.04 mol dm⁻³); \circ , CH₂Cl₂, 5 cm³.

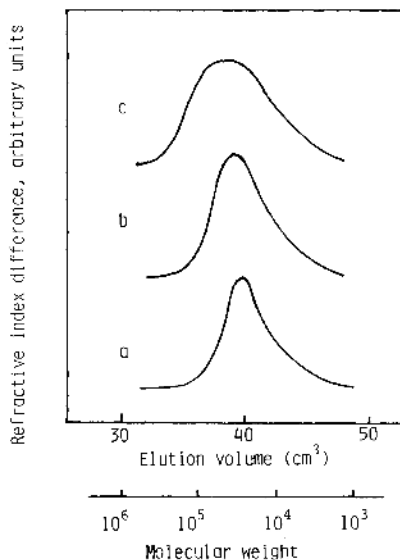


Figure 2. Gel-permeation chromatogram for PMMA obtained by photopolymerization of MMA with BPB in dichloromethane in the presence of carbon tetrachloride: MMA, 5 cm³; CCl₄, 1 cm³ (1.04 mol dm⁻³); CH₂Cl₂ (solvent), 4 cm³; time, (a) 10, (b) 30, (c) 60 min; GPC column, Shodex A802-A803-A805; eluent, THF.

BPC in MMA-CH₂Cl₂ before irradiation (Figure 4).

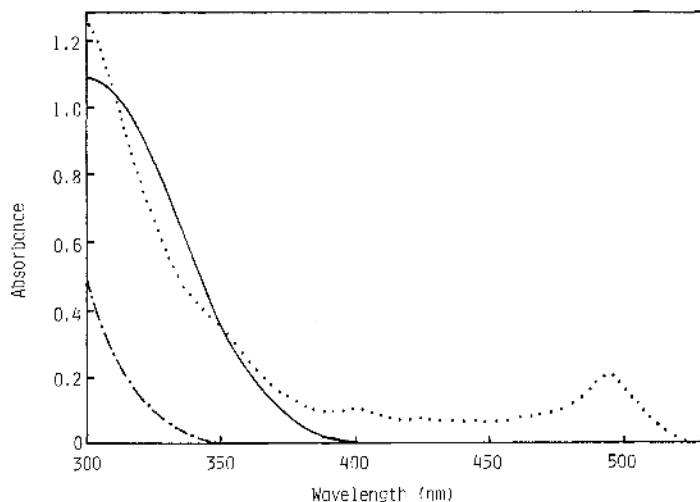


Figure 3. Absorption spectra of BPB (—) and BPC (---) in MMA-CH₂Cl₂ (1:1, v/v); BPB or BPC, 1×10^{-3} mol dm⁻³. The dotted line (····) show the spectrum of the BPB solution after irradiation for one hour under vacuum.

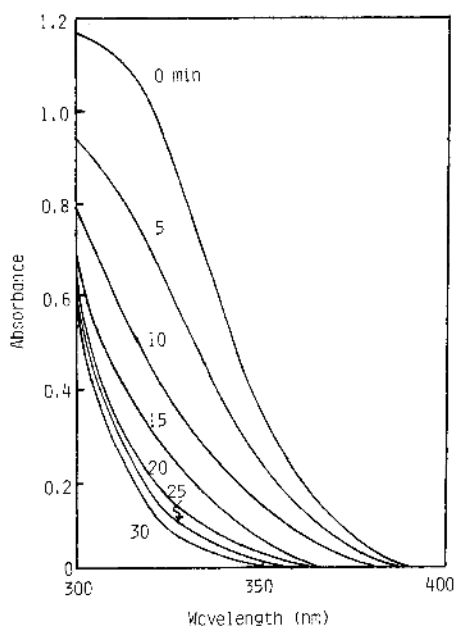
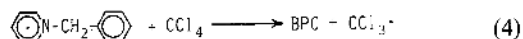
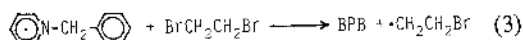
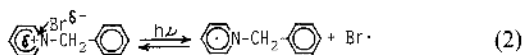


Figure 4. Spectral change found during the irradiation for the polymerization system of MMA-BPB-CCl₄: MMA, 5 cm³; CH₂Cl₂ (solvent), 4 cm³; CCl₄, 1 cm³ (1.04 mol dm⁻³); BPB, 1×10^{-3} mol dm⁻³.

From the spectral changes of BPB in MMA-CH₂Cl₂-CCl₄ it may be deduced that BPB was transformed to BPC by irradiation. This is sup-

ported by the conversion-time relation for the photopolymerization of MMA with BPB in CH₂Cl₂-CCl₄ and CH₂Cl₂-BrCH₂CH₂Br, and can be satisfactorily explained by the following eq 2-4.



In the presence of 1,2-dibromoethane, the *N*-benzylpyridinyl radical produced by eq 2 reacted with 1,2-dibromoethane to reproduce BPB through eq 3 in competition with the reverse reaction of eq 2. BPB, therefore, was not consumed during irradiation and the conversion linearly increased with time. As a result, termination with the pyridinyl radical was suppressed and the molecular weight of the polymer was much larger than that without 1,2-dibromomethane.

In the presence of carbon tetrachloride, BPB would be changed to BPC by eq 2 and 4 at the initial stage and consequently, the photopolymerization of MMA would be induced by BPC-CCl₄ system, as will be fully described in the next section in detail.

Photopolymerization of MMA with BPC in the Presence of 1,2-Dibromoethane and Carbon Tetrachloride

The effects of haloalkanes on the photopolymerization of MMA with BPC were also examined in a manner similar to the case of BPB, and the results are shown in Table II. Conversion-time relations for the photopolymerization of MMA with BPC in dichloromethane in the presence of 1,2-dibromoethane and carbon tetrachloride are shown in

Table II. Photopolymerization of MMA with BPC in the presence of haloalkanes

Haloalkanes	mol dm ⁻³	Conversion, % ^b	
		30 min	60 min
CBr ₄ ^a	0.01	5.44	12.56
BrCH ₂ CH ₂ Br	1.16	2.88	4.99
CH ₃ CH ₂ Br	1.33	1.18	1.65
CCl ₄	1.04	2.82	5.41
ClCH ₂ CH ₂ Cl	1.27	1.16	1.89
CH ₂ Cl ₂	—	0.87	1.50

MMA, 5 cm³; haloalkane, 1 cm³; CH₂Cl₂ (solvent), 4 cm³; BPC, 1 × 10⁻³ mol dm⁻³; temp, 303 K.

^a 0.033 g of crystalline CBr₄ dissolved in 1 cm³ of CH₂Cl₂ was added.

^b Polymer was obtained by precipitation with methanol.

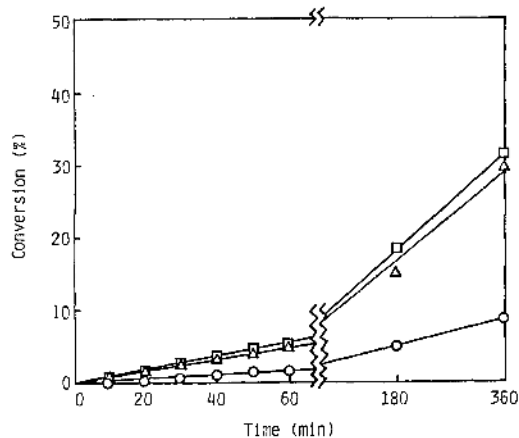


Figure 5. Conversion-time relation for the photopolymerization of MMA with BPC in dichloromethane in the presence of 1,2-dibromoethane and carbon tetrachloride: BPC, 1 × 10⁻³ mol dm⁻³; MMA, 5 cm³; △, CH₂Cl₂, 4 cm³ and BrCH₂CH₂Br, 1 cm³ (1.16 mol dm⁻³); □, CH₂Cl₂, 4 cm³ and CCl₄, 1 cm³ (1.04 mol dm⁻³); ○, CH₂Cl₂, 5 cm³.

Figure 5 along with that in the absence of effective haloalkane. Even in the absence of an effective haloalkane, the conversion-time relation was linear, and the molecular weight of the obtained PMMA was determined by viscometry to be 136,000. It seems that BPC photodecomposed more slowly than BPB due to the absorption maximum at a shorter wave length and the CT band with smaller intensity than that of BPB. In the presence of 1,2-dibromoethane and carbon tetrachloride, the photopolymerization

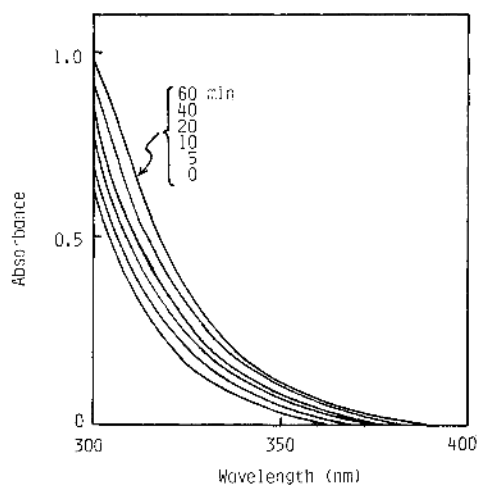


Figure 6. Spectral change found during irradiation for the photopolymerization system of MMA-BPC-BrCH₂CH₂Br: MMA, 5 cm³; CH₂Cl₂ (solvent), 4 cm³; BrCH₂CH₂Br, 1 cm³ (1.16 mol dm⁻³); BPC, 1 × 10⁻³ mol dm⁻³.

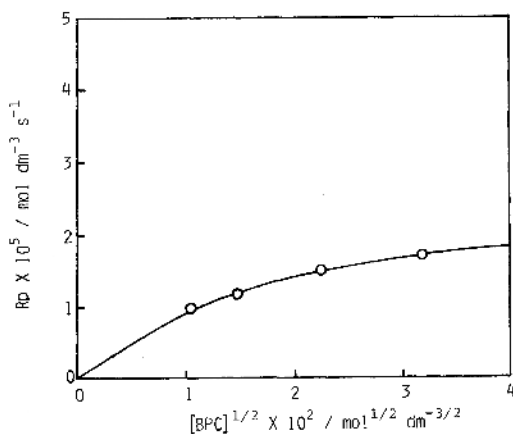


Figure 7. R_p vs. $[BPC]^{1/2}$ for the photopolymerization of MMA with BPC in dichloromethane: MMA, 5 cm³; CH₂Cl₂, 5 cm³; BPC, 1 × 10⁻³ mol dm⁻³.

of MMA with BPC gave linear conversion-time relations over a wide range of conversions and remarkably large rates of polymerization as shown in Figure 5. The molecular weights of PMMA obtained in the case of BPC- CCl_4 system were determined by viscometry to be 160,000 and in the case of BPC- $\text{BrCH}_2\text{CH}_2\text{Br}$ system to be 90,000. The smaller molecular weight in the latter case was probably derived from the termination with the pyridinyl radical occurred somewhat in competition with the reaction of eq 3.

The spectral change in BPC by irradiation was also measured for the polymerization system of MMA- CH_2Cl_2 - $\text{BrCH}_2\text{CH}_2\text{Br}$ as shown in Figure 6. In the wavelength region from 300 to 350 nm, the intensity of the absorption band increased with irradiation time and this suggests that BPC changed gradually into BPB during the polymerization.

The results in Figure 5 make it possible to study kinetically the photopolymerization of MMA with BPC. In the absence of effective haloalkane, the plot of R_p vs. $[\text{BPC}]^{1/2}$ was not linear as shown in Figure 7. As in the case of BPB,¹ it may be considered that the CT complex of BPC photodecomposed to chlorine atoms and *N*-benzylpyridinyl radicals; the former initiated the polymerization of MMA and the latter terminated it. In the presence of carbon tetrachloride, the photopolymerization of MMA with BPC proceeded much faster than in the absence of carbon tetrachloride, although the photosensitivity of carbon tetrachloride itself was

rather small as shown in Table I. As described before, carbon tetrachloride could react with *N*-benzylpyridinyl radical to produce BPC and $\text{CCl}_3\cdot$, and the latter would initiate the polymerization as well as chlorine atoms.

In consideration of the small rate of polymerization by carbon tetrachloride itself (R_{p0}), the rate of polymerization of MMA with BPC- CCl_4 system should be expressed by $(R_p^2 - R_{p0}^2)^{1/2}$, where R_p is the apparent total rate of polymerization. In Figure 8, the slope of the plot of $\log(R_p^2 - R_{p0}^2)^{1/2}$ vs. $\log[\text{CCl}_4]$ was obtained as 0.03, implying that the rate of chain transfer reaction of eq 4 was very fast and the reaction of eq 4 was not a rate-determining step for the polymerization.

In order to examine the effect of light intensity on the rate of polymerization, photopolymerization was carried out by varying the emission area of the Chemical Lamp. The results showed that conversions linearly increased with irradiation time at every intensity of the light source (Figure 9) and that the rate of polymerization increased in proportion to the square root of the light intensity (Figure 10). $(R_p^2 - R_{p0}^2)^{1/2}$ is also plotted against $[\text{BPC}]^{1/2}$ in Figure 11. The linear relation between $(R_p^2 - R_{p0}^2)^{1/2}$ and $[\text{BPC}]^{1/2}$ was in distinct contrast to the nonlinear one in the absence of carbon tetrachloride. The molecular weight of PMMA obtained by the BPC- CCl_4 system was measured by viscometry, and the reciprocal of the degree of polymerization ($1/\bar{P}_n$) was also plotted against R_p in

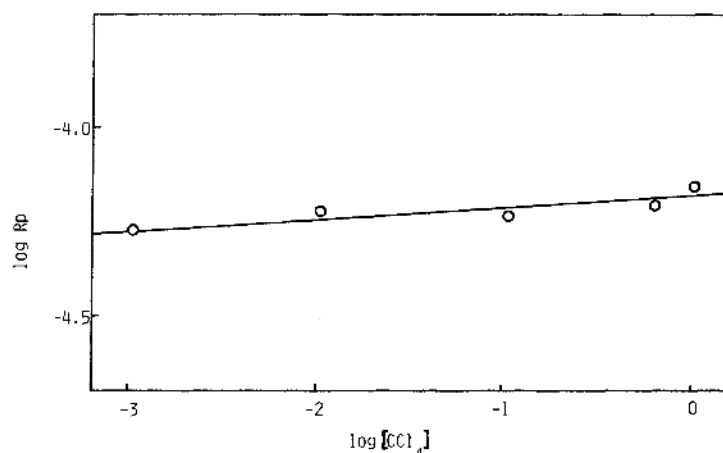


Figure 8. $\log R_p$ vs. $\log[\text{CCl}_4]$ for the photopolymerization of MMA with BPC in the presence of carbon tetrachloride: MMA, 4.68 mol dm^{-3} ; BPC, $1 \times 10^{-3} \text{ mol dm}^{-3}$; solvent, CH_2Cl_2 .

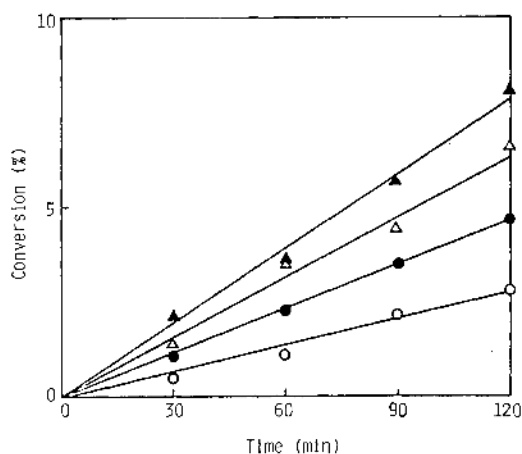


Figure 9. Effect of light intensity on the photopolymerization of MMA with BPC- CCl_4 system in dichloromethane: MMA, 5 cm^3 ; CH_2Cl_2 , 4 cm^3 ; PBC, $1 \times 10^{-3}\text{ mol dm}^{-3}$; temp, 303 K; relative light intensity, \circ , 1; \bullet , 2; \triangle , 4; \blacktriangle , 6.

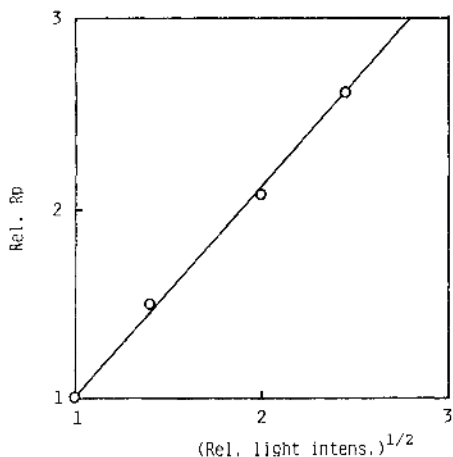


Figure 10. Relative R_p vs. $(\text{rel. light intens.})^{1/2}$ for the photopolymerization of MMA with BPC- CCl_4 system in dichloromethane.

Figure 12. The linear relation suggests that termination with the pyridinyl radical was suppressed completely. Elemental reactions for the photopolymerization of MMA with the BPC- CCl_4 system are therefore summarized as follows.

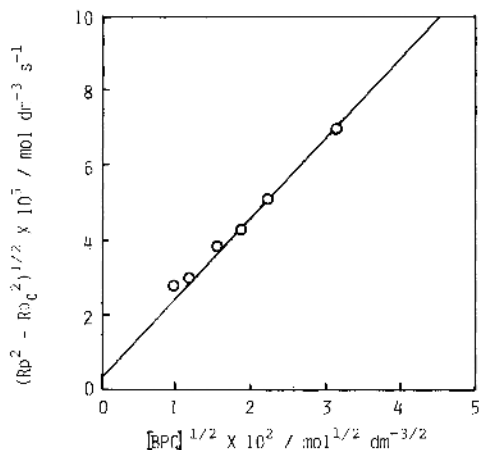
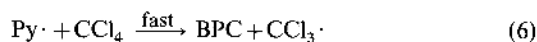
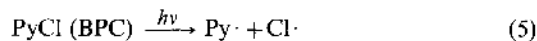


Figure 11. $(R_p^2 - R_{p0}^2)^{1/2}$ vs. $[\text{BPC}]^{1/2}$ for the photopolymerization of MMA with BPC in the presence of carbon tetrachloride.

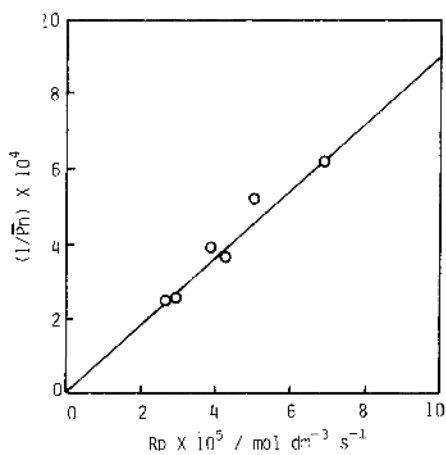
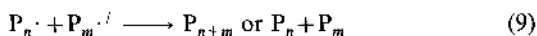
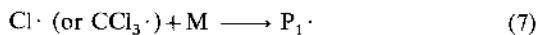


Figure 12. $1/\bar{P}_n$ vs. R_p for the photopolymerization of MMA with BPC in the presence of carbon tetrachloride.



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