

Photopolymerization of Methyl Methacrylate with 1-Benzyl-1,4-dihydronicotinamide in the Presence of Carbon Tetrachloride

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ABSTRACT: The photopolymerization of methyl methacrylate (MMA) with 1-benzyl-1,4-dihydronicotinamide (BNAH) was investigated in the presence of CCl_4 . The rate of photopolymerization of MMA with BNAH was remarkably accelerated by the addition of CCl_4 . The fluorescence spectra of BNAH in the presence of various concentrations of CCl_4 showed that the photoexcited BNAH (BNAH^*) was quickly quenched by CCl_4 . The spectral change of BNAH-CCl_4 system during UV-irradiation indicated that the absorption band (λ_{max} , 350 nm) of BNAH disappeared and the pyridinium band appeared at 260 nm. These results suggest that the polymerization is initiated by the following mechanism. Hydrogen transfers from BNAH^* to CCl_4 , and consequently 1-benzylnicotinamide radical (BNA^\bullet) and CCl_3^\bullet are generated. The BNA^\bullet quickly reacts with CCl_4 to produce 1-benzylnicotinamide chloride (BNA^+Cl^-) together with CCl_3^\bullet radical. The produced BNA^+Cl^- also photodecomposes into BNA^\bullet and Cl^\bullet radical. The CCl_3^\bullet and Cl^\bullet are able to initiate the polymerization. This photopolymerization could be performed in aqueous-organic two-phase system, and three components BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 were found to act as a cyclic phase-transfer photoinitiator system.

KEY WORDS Photopolymerization / Methyl Methacrylate / 1-Benzyl-1,4-dihydronicotinamide / 1-Benzylnicotinamide Chloride / Carbon Tetrachloride / Sodium Dithionite / Phase Transfer / Photoinitiator /

NAD^+ and NADH , coenzymes of alcohol dehydrogenase, play an important role in biological redox systems. The details of their reactions in biological redox systems, however, have not been clarified, and several compounds, such as 1-benzyl-3-carbamoylpyridinium salt (BNA^+) and 1-benzyl-1,4-dihydronicotinamide (BNAH), have been used as models of NAD^+ and NADH , respectively. The nonenzymatic reactions with these models are known to require a cofactor. For example, the reductions of carbonyl group with NADH models should be accelerated by metal ions, such as Mg^{2+} and Zn^{2+} .¹⁻³ NADH models could also be activated by irradiation with UV

light.⁴⁻⁶ As far as reported,^{7,8} a mechanism involving electron-proton-electron-transfer three-step processes may be dominant for nonenzymatic reaction with NADH models.

However, the actual features of the reaction with NAD^+ and NADH are still obscure. In the preceding paper,⁹ the authors carried out the photopolymerization of vinyl monomers in order to elucidate whether a radical intermediate was incorporated in the reaction system containing NADH . Methyl methacrylate (MMA) was photopolymerized well with BNAH and the polymerization was found to proceed in radical mechanism and to yield a low molecular weight polymer containing a

terminal BNAH residue.

In the present study, CCl_4 was added to the above polymerization system. 1-Benzylnicotinamide radical ($\text{BNA}\cdot$), generated in the photoinitiation step, attacked CCl_4 molecule rather than the MMA monomer and the growing polymer radical, yielding both BNA^+Cl^- and $\text{CCl}_3\cdot$ radical. The $\text{CCl}_3\cdot$ initiated the polymerization of MMA into high molecular weight polymer. MMA could also be photopolymerized with $\text{BNAH}-\text{CCl}_4$ in an aqueous-organic two-phase system. The details of the polymerization are presented in the following along with the photopolymerization of MMA with $\text{BNA}^+-\text{Na}_2\text{S}_2\text{O}_4-\text{CCl}_4$ in aqueous-organic two-phase system.

EXPERIMENTAL

Materials

MMA was purified by the usual method just before use. Water was deionized and distilled. 1-Benzylnicotinamide chloride (BNA^+Cl^-) and 1-benzyl-1,4-dihydronicotinamide (BNAH) were prepared by the procedure described in the literature.¹⁰ All other chemicals used in this study were of reagent grade.

Photopolymerization

Solution photopolymerization of MMA with $\text{BNAH}-\text{CCl}_4$ in dichloromethane was performed in a hard glass ampoule by irradiation with Toshiba Fluorescent Chemical Lamp FL-20SBL (20W, λ_{max} 360 nm). The detail procedure is described in the the previous paper.¹¹

Photopolymerization of MMA with $\text{BNA}^+-\text{Na}_2\text{S}_2\text{O}_4-\text{CCl}_4$ in aqueous-organic, two-phase system was performed by photochemical reaction apparatus, which was also described in detail in the previous paper.¹² A 150 cm^3 reaction vessel was charged with 20 cm^3 of MMA solution containing CCl_4 (10 mmol) and 80 cm^3 of aqueous solution containing BNA^+Cl^- (0.1 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (45 mmol) and Na_2CO_3 (45 mmol). The contents in the

reaction vessel had pure nitrogen bubbled through them followed by irradiation with a Fuji Glass High Pressure Mercury Lamp HL-100 (100 W). The reaction mixture was then poured into a large quantity of methanol and the precipitated polymer was dried *in vacuo*.

Measurements

UV and Fluorescence spectra were recorded on JASCO UVDEC-1 and JASCO FP-550 spectrometers, respectively.

RESULTS AND DISCUSSION

Photopolymerization of MMA with BNAH in the Presence of CCl_4

Photopolymerization of MMA with BNAH in the presence of CCl_4 proceeded faster than that with BNAH or CCl_4 alone (Figure 1) and yielded a polymer of high molecular weight ($\bar{M}_n \geq 100,000$). In order to clarify the effect of CCl_4 -addition on the polymerization system, fluorescence spectra of BNAH excited with 350 nm light were measured in the presence of

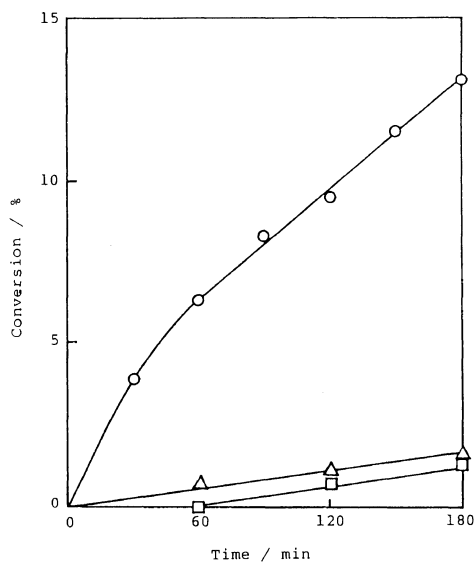


Figure 1. Photopolymerization of MMA with BNAH in the presence of CCl_4 : MMA, 5 cm^3 ; solvent, CH_2Cl_2 ; O, BNAH 1×10^{-3} mol dm^{-3} and CCl_4 1×10^{-2} mol dm^{-3} ; Δ, BNAH 1×10^{-3} mol dm^{-3} ; □, CCl_4 1×10^{-2} mol dm^{-3} ; temp, 303 K.

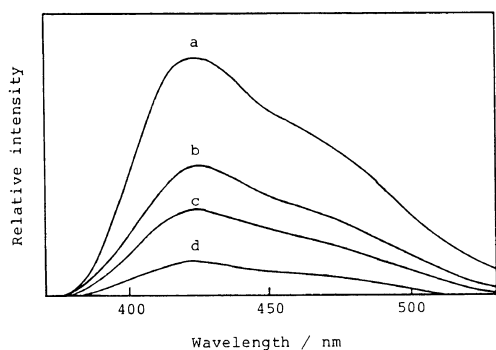


Figure 2. Fluorescence spectra of BNAH in CH₂Cl₂ in the presence of CCl₄: BNAH, 1×10^{-4} mol dm⁻³; CCl₄ (mol dm⁻³), a, 0; b, 0.10; c, 0.25; d, 0.50; λ_{ex} , 350 nm.

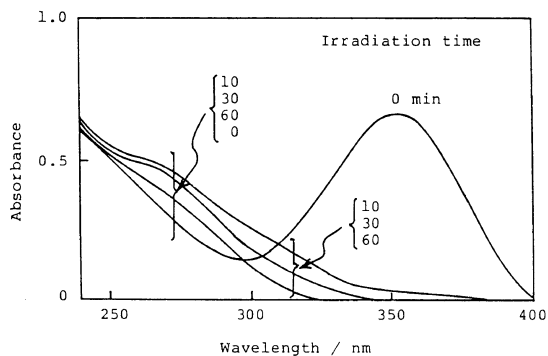
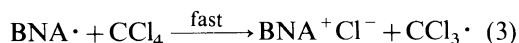
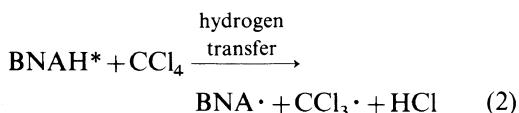


Figure 3. Spectral change by UV-irradiation for BNAH-CCl₄ system in CH₂Cl₂.

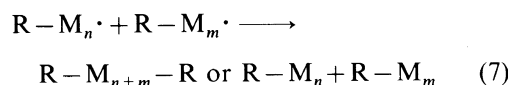
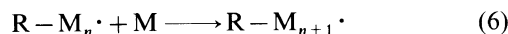
CCl₄. The spectra indicated that CCl₄ quenched the excited BNAH (BNAH*) (Figure 2). In the preceding paper,⁹ the authors reported that MMA was able to quench BNAH*. The former was found to quench the excited BNAH about ten times faster than the latter.

The possibility of producing BNA⁺Cl⁻ from BNAH in the photolysis of BNAH-CCl₄ system was examined by spectral change during UV-irradiation as shown in Figure 3. After 10 minutes-irradiation, the absorption band (λ_{max} 350 nm) of BNAH disappeared, whereas the bands of the pyridinium ring and pyridinium complex appeared at 260 and 320 nm, respectively. In the absence of CCl₄, such a spectral change was very slow.

These results suggest the following photo-initiation mechanism.



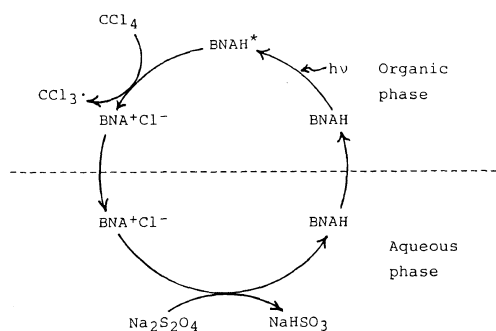
Equation 1 expresses photo-excitation of BNAH and eq 2 expresses hydrogen transfer from BNAH* to CCl₄. The generated *N*-benzylnicotinamide radical (BNA[•]) quickly reacts with CCl₄ to product BNA⁺Cl⁻ together with CCl₃[•] (eq 3). The CCl₃[•] is known to initiate the polymerization of MMA. The produced BNA⁺Cl⁻ also photoinitiated the polymerization of MMA in the presence of CCl₄ as well as 1-benzylpyridinium bromide¹¹ and chloride.¹³ The mechanism of photopolymerization with BNA⁺Cl⁻-CCl₄ may be expressed as follows:



Photopolymerization of MMA with BNA⁺Cl⁻-Na₂S₂O₄-CCl₄ in Aqueous-Organic, Two-Phase System

The photopolymerization described in the preceding section could be performed in an aqueous-organic two-phase system. BNA⁺Cl⁻ produced in organic phase may transfer to aqueous phase and if alkaline solution of Na₂S₂O₄ is present, it may be reduced to BNAH, which is able to transfer to the organic phase. Thus, the cyclic phase-transfer photoinitiator system shown in Scheme 1 is expected.

MMA was photopolymerized with BNA⁺Cl⁻-Ba₂S₂O₄-CCl₄ in an MMA-water two-phase system. The results in Table I show that



Scheme 1.

Table I. Photopolymerization of MMA with BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in aqueous-organic, two-phase system^a

| BNA^+Cl^- | CCl_4 | $\text{Na}_2\text{S}_2\text{O}_4$ | Na_2CO_3 | Conversion |
|---------------------------|----------------|-----------------------------------|--------------------------|------------|
| mmol | mmol | mmol | mmol | % |
| — | — | — | — | 1.10 |
| 1 | — | — | — | 0.66 |
| — | 36 | — | — | 0.21 |
| — | — | 90 | 90 | 3.29 |
| 1 | 36 | — | — | 0.33 |
| 1 | — | 90 | 90 | 1.20 |
| — | 36 | 90 | 90 | 5.12 |
| 1 | 36 | 90 | 90 | 19.57 |

^a MMA, 20 cm³; H₂O, 80 cm³; temp, 303 K; time, 1 h; blowing rate of N₂, 0.5 cm³ s⁻¹.

the photopolymerization proceeded slowly in the absence of any one of these three components.

In order to elucidate the mechanism kinetically, the photopolymerization of MMA with BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 was carried out at various feeding ratios of the initiator components. The results indicated the rate of polymerization (R_p) to be proportional to the square root of the concentration of each of the three initiator components, BNA^+Cl^- , $\text{Na}_2\text{S}_2\text{O}_4$, and CCl_4 (Figure 4—6). When BNA^+Cl^- was fed beyond 0.5 mmol, R_p did not increase and became constant (Figure 4). This implies that the entire amount of BNA^+Cl^- charged in aqueous phase is reduced to BNAH by $\text{Na}_2\text{S}_2\text{O}_4$ but that only a

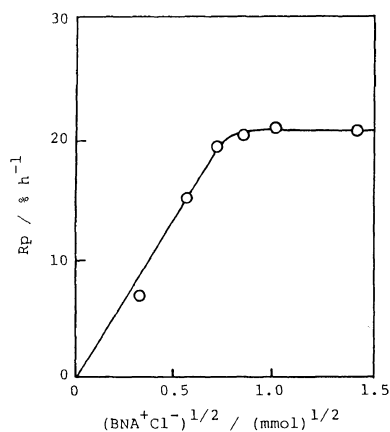


Figure 4. Relation of R_p vs. $(\text{BNA}^+\text{Cl}^-)^{1/2}$ for the photopolymerization of MMA with BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in aqueous-organic two-phase system: MMA, 20 cm³; H₂O, 80 cm³; $\text{Na}_2\text{S}_2\text{O}_4$, 45 mmol; Na_2CO_3 , 45 mmol; CCl_4 , 10 mmol; temp, 303 K.

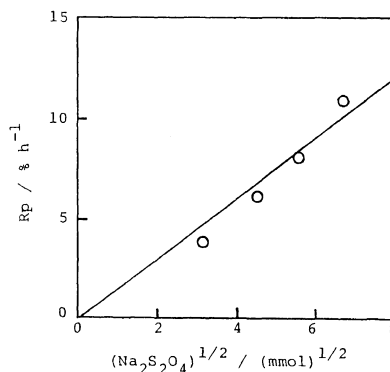


Figure 5. Relation of R_p vs. $(\text{Na}_2\text{S}_2\text{O}_4)^{1/2}$ for the photopolymerization of MMA with BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in aqueous-organic two-phase system: MMA, 20 cm³; H₂O, 80 cm³; BNA^+Cl^- , 0.1 mmol; Na_2CO_3 , 45 mmol; CCl_4 , 10 mmol; temp, 303 K.

constant part of produced BNAH is solubilized in the organic phase.

When BNAH was fed instead of BNA^+Cl^- in this two-phase system, the polymerization proceeded as well as with BNA^+Cl^- , and the relations of R_p vs. $(\text{BNAH})^{1/2}$ and R_p vs. $(\text{BNA}^+\text{Cl}^-)^{1/2}$ are compared in Figure 7. According to the experimental conditions, both linear relations of R_p vs. $(\text{BNAH})^{1/2}$ and $(\text{BNA}^+\text{Cl}^-)^{1/2}$ should have the same slope, but the slope of the former was far larger than that

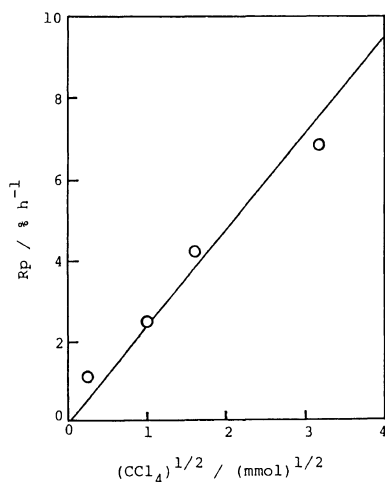


Figure 6. Relation of R_p vs. $(\text{Na}_2\text{CO}_3)^{1/2}$ for the photopolymerization of MMA with BNA^+Cl^- - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in aqueous-organic two-phase system: MMA, 20 cm³; H₂O, 80 cm³; BNA^+Cl^- , 0.1 mmol; $\text{Na}_2\text{S}_2\text{O}_4$, 45 mmol; CCl_4 , 10 mmol; temp, 303 K.

of the latter. As shown in Scheme 1, BNAH added to the organic phase was consumed by irradiation to BNA^+Cl^- , which was reduced to BNAH in the aqueous phase. In the stationary state of this cyclic phase-transfer initiation process, the concentration of BNAH is controlled by the experimental conditions. Therefore, at the initial stage of the polymerization, the concentration of BNAH in organic phase should be higher than that at the stationary state. On feeding much BNAH beyond 0.1 mmol, R_p decreased to a constant value. The apparent maximum of R_p implies that BNAH contributes not only to the initiation but also to the termination of what authors should specify as described in the preceding paper.⁹ The concentration of BNAH at the constant R_p seems to depend on the solubility of BNAH in the organic phase as mentioned above.

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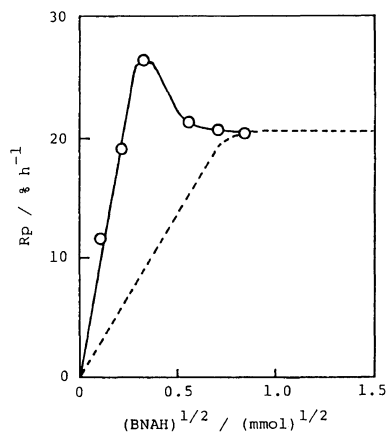


Figure 7. Relation of R_p vs. $(\text{BNAH})^{1/2}$ for the photopolymerization of MMA with BNAH - $\text{Na}_2\text{S}_2\text{O}_4$ - CCl_4 in aqueous-organic two-phase system: MMA, 20 cm³; H₂O, 80 cm³; $\text{Na}_2\text{S}_2\text{O}_4$, 45 mmol; Na_2CO_3 , 45 mmol; CCl_4 , 10 mmol; temp, 303 K. Dotted line indicates the relation of R_p vs. $(\text{BNA}^+\text{Cl}^-)^{1/2}$ in Figure 4.

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