

SHORT COMMUNICATIONS

Photopolymerization of Methyl Methacrylate with 1-Benzyl-1,4-dihydronicotinamide

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1-Benzyl-1,4-dihydronicotinamide (BNAH), a model of NADH (nicotinamide adenine dinucleotide) coenzyme, has often been used as a reductant for various substrates¹⁻⁷ and the reduction of some substrates with photo-activated BNAH reported.⁸⁻¹⁰ However, the exact mechanism for the reaction is still not completely understood, although a multi-step mechanism which involves electron-transfer, has recently been proposed.^{7,10} In the preceding paper,¹¹ we showed that BNAH photo-initiated the polymerization of methyl methacrylate (MMA). This is of interest, because elucidation of the mechanism for the polymerization may clarify the mechanism for the reduction with NADH. In the present paper, the photopolymerization of MMA with BNAH was kinetically studied, and the initiation mechanism is discussed.

The monomer, BNAH and solvent were placed in a hard glass ampoule, which was then degassed, filled with nitrogen, and sealed under vacuum. After irradiation by three Toshiba Fluorescent Chemical Lamps FL20SBL at 303 ± 0.5 K in the same apparatus used previously,¹² the contents were evaporated *in vacuo* to dryness. The conversion and molecular weight were determined by gravimetry and gel permeation chromatography

(GPC) (column, Shodex A802-A803-A805; eluent, THF), respectively. Photo-copolymerization of styrene (St) and MMA with BNAH was also carried out by a similar method.

As shown in Figure 1, MMA easily photopolymerized with BNAH in dichloromethane, but St more slowly. Acrylonitrile (AN), however, did not photopolymerize with BNAH. MMA also photopolymerized with BNAH in acetonitrile and methanol as well as dichloromethane. The copolymer composition curves of St and MMA in dichloromethane and methanol suggest a radical mechanism (Figure 2). The initial rate of polymerization (R_p) was measured from the linear conversion-time relation for the polymerization of MMA with BNAH, and the relation of R_p vs. $[\text{BNAH}]^{1/2}$ is shown in Figure 3. The number average degree of polymerization (P_n) of the polymer obtained was also determined by GPC and the relation of $1/P_n$ vs. $[\text{BNAH}]^{1/2}$ is shown in Figure 3. These relations are linear over a range of low concentration of BNAH, and therefore the polymerization may be a radical one. At a high concentration of BNAH, both R_p and P_n remarkably decreased. This suggests that BNAH contributes not only to the initiation but also to the termination of the photopolymerization of MMA.

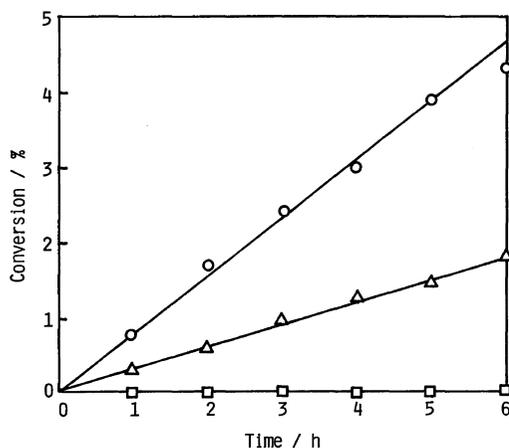


Figure 1. Photopolymerization of vinyl monomers with BNAH in CH_2Cl_2 : monomer, 5 cm^3 ; \circ , MMA; \triangle , St; \square , AN; CH_2Cl_2 , 5 cm^3 ; BNAH, $1 \times 10^{-3}\text{ mol dm}^{-3}$; temp, 303 K.

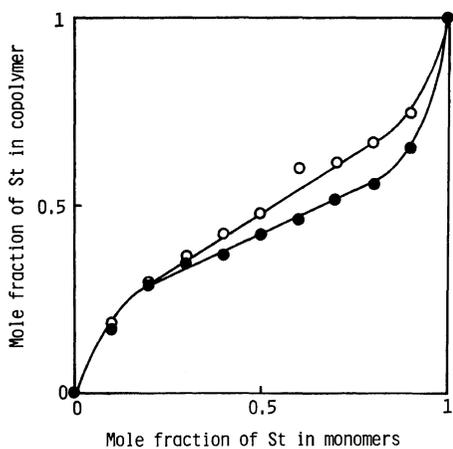


Figure 2. Photo-copolymerization of St and MMA with BNAH in CH_2Cl_2 (\bullet) and CH_3OH (\circ).

To clarify the detailed initiation mechanism of the photopolymerization of MMA with BNAH, we measured the fluorescence spectra of BNAH in the presence of MMA. Stern-Volmer plots obtained by measurements in dichloromethane, acetonitrile and methanol, showed that MMA acted as a quencher, and that the action was affected by the polarity of the solvent (Figure 4). According to Stern-Volmer plots in Figure 5, the rate of quenching increases in the order of AN, MMA and St;

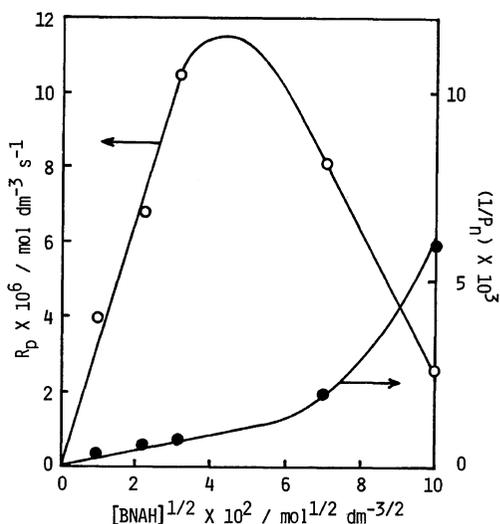


Figure 3. R_p and $1/P_n$ vs. $[\text{BNAH}]^{1/2}$ for the photopolymerization of MMA with BNAH in CH_2Cl_2 .

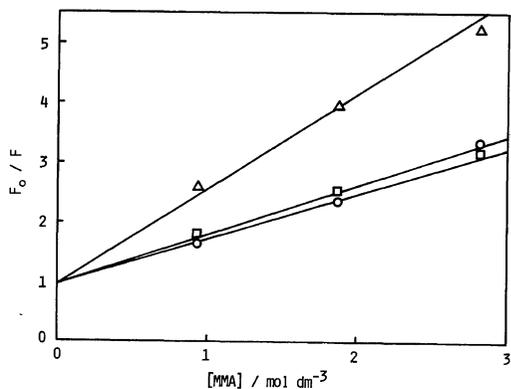


Figure 4. Stern-Volmer plots for the fluorescence of BNAH (ex. 350 nm, em. 420 nm) in CH_2Cl_2 (\circ), CH_3CN (\triangle) and CH_3OH (\square) in the presence of MMA.

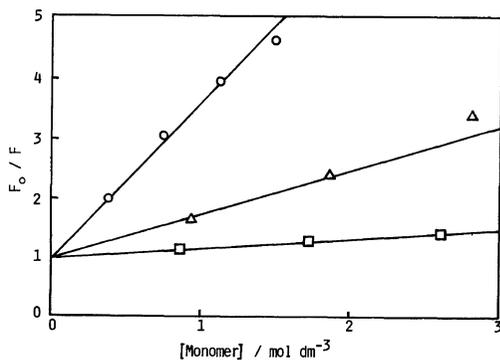
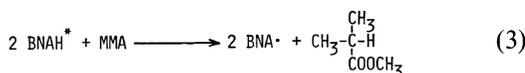
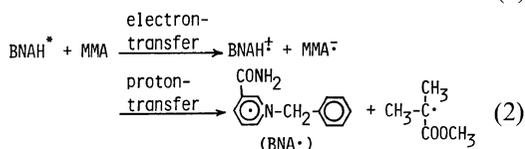


Figure 5. Stern-Volmer plots for the fluorescence of BNAH (ex. 350 nm, em. 420 nm) in CH_2Cl_2 in the presence of MMA (\triangle), St (\square) and AN (\circ).

this order is related to the electron-accessibility of the monomers.

The results for the both photopolymerization and fluorescence measurement suggest the following initiation mechanism.



BNAH is excited by UV-irradiation and reacts with MMA to produce 1-benzyl-3-carbamoylpyridinyl radical (BNA \cdot) and methyl isobutyrate radical through the electron- and proton-transfers. The unstable methyl isobutyrate radical initiates the polymerization of MMA, and the stable BNA \cdot terminates the polymerization. Dimethyl maleate and fumarate are known to be reduced to dimethyl succinate under the photoactivation of BNAH,⁸ and thus, at a higher concentration of BNAH, MMA may react with two moles of BNAH* to give two moles of BNA \cdot and one mole of methyl isobutyrate through electron- and proton-transfers. To confirm the presence of reduced products in the polymerization mass, MMA and AN were polymerized respectively in dichloromethane in the reaction vessel described in the previous paper,¹³ and irradiated at 303 K under bubbling nitrogen, using a Fuji Glass High Pressure Mercury Lamp HL-100 (100 W). The molar ratio of BNAH to monomer was one to ten. After irradiation for 6 h, the contents were evaporated *in vacuo* to dryness. The molecular weight distribution of the residual matter was measured by gel permeation chromatography. In the case of AN, THF-insoluble polyacrylonitrile was separated to some extent from the residual matter. The results are shown in Figure 6, in which peaks 1 and 2 coincide with the elution volumes of

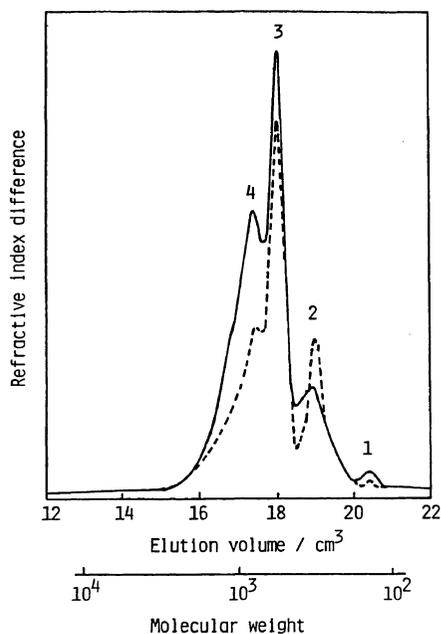


Figure 6. Gel permeation chromatogram of solid products for the photopolymerization of MMA and AN with BNAH in CH_2Cl_2 : MMA (—) and AN (---), 1 mol dm^{-3} ; BNAH, 0.1 mol dm^{-3} ; temp, 303 K; time, 6 h. GPC measurement: column, Shodex KF802-KF803; eluent, THF. Peaks 1 and 2 coincide with the elution volumes of authentic BNAH and DDTBP, respectively.

authentic BNAH and 1,1'-dibenzyl-3,3'-dicarbamoyl-1,1',4,4'-tetrahydro-4,4'-bispyridine (DDTBP), respectively. Peaks 3 and 4 probably correspond to the oligomers of MMA and AN, on the basis of a comparison with standard polystyrenes. However, the results of gas chromatography for the distillate from the reaction mass under reduced pressure did not show the existence of reduced products such as methyl isobutyrate and propionitrile. The involvement of eq 3 in this polymerization system, therefore, it still doubtful.

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