# A Polymerizable Photoredox Initiation System for Vinyl Photopolymerization

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## SYNOPSIS

A polymerizable photoredox system consisting of 4-methacryl oxybenzophenone (MABP) and N,N-dimethylaminoethyl methacrylate (DMAEMA) used for the photopolymerization of acrylonitrile (AN) was studied. It was found that the polymerization rate is proportional to the 0.93th power for the AN concentration, the 0.28th power for the MABP concentration, and the 0.25th power for the DMAEMA concentration. The overall activation energy of the polymerization obtained is 30.43 kJ/mol. The recorded ESR spectrum indicates that the excited-state MABP abstracts hydrogen mainly from the methyl group of the dimethylamino moiety. The comparison of the initiation ability of polymeric MABP or polymeric DMAEMA with their monomeric forms has also been done and the results indicate that in good solvents P(MABP) has a much higher initiation ability than that of monomeric MABP, but monomeric DMAEMA and P(DMAEMA) display almost the same initiation ability. In poor solvents, the initiation ability of P(MABP) is not so obviously higher than that in good solvents. The result of UV analysis of P(AN) initiated by the MABP–DMAEMA system indicates that both MABP and DMAEMA not only initiate the photopolymerization of AN, but also enter into P(AN) polymer chains. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

There are many reports concerning the photopolymerization of vinyl monomers initiated by benzophenone–aliphatic tertiary amines such as the benzophenone–triethylamine photoredox system, and the initiation mechanism has been revealed exhaustively.[1-4] The advantage of this system is that oxygen does not inhibit but, rather, accelerates the photopolymerization at a suitable concentration of amines.[5]

Recently, the photopolymerization of vinyl monomers initiated by benzophenone and the polymerizable tertiary amine N,N-dimethylaminoethyl methacrylate (DMAEMA) has been reported by Shirota et al.[6] We have also studied the fluorenone–DMAEMA system for the photopolymerization of acrylonitrile (AN),[7] but the photoredox initiation system consisting of polymerizable benzophenone and the polymerizable aliphatic tertiary amine system has not been reported. The benefit of polymerizable initiators is that the initiation components not only initiate the photopolymerization, but also participate in the polymerization and enter into polymer chains. Thus, the remains of low molecular initiator species in polymers, especially amines, can be reduced or avoided. This is significantly favorable for in situ curing of biomedical materials. In this article, the photoinitiation behavior of polymerizable photoredox systems consisting of 4-methacryl oxybenzophenone (MABP)–DMAEMA, P(MABP)–DMAEMA, or MABP–P(DMAEMA) for AN polymerization are reported.

## EXPERIMENTAL

### Materials

DMAEMA was purchased from Polyscience Corp. and freshly distilled under reduced pressure before use. 4-Hydroxybenzophenone was purchased from

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Aldrich Corp. and used without further treatment. 2-Methyl-2-nitritopropane (MNP) was prepared as described in the literature.[8] DMF was dried with $CaH_2$ and distilled under reduced pressure. AN was redistilled before use.

## Preparation of MABP

MABP was prepared by reaction of 4-hydroxyben-zophenone and methacryloyl chloride in $CHCl_3$ in the presence of pyridine at 40–45°C. The crude product was recrystallized from ethanol. It is a white needle crystal with mp 66–67.5°C.

ANAL: Calcd: C, 76.65%; H, 5.31%. Found: C, 76.50%; H, 5.30%.

$^1H$-NMR ($\delta$, ppm, in $CDCl_3$ 80 KHz): 2.07 (3H, s), 5.77 (1H, t), 6.40 (1H, t), 7.20–7.90 (9H, m). IR (KBr, $cm^{-1}$): 1733 (ester group), 1652 (alkene $C{=}C$ stretch), 1596, 1433, 1446, 3050 (aromatic ring).

## Polymerization

The photopolymerization of AN was carried out in a glass dilatometer with approximately 6 mL volume in DMF at 25°C. The light source was a 300 W high-pressure mercury lamp, filtered with a potassium chromate solution. The polymerization system was purged with nitrogen for 20 min.

P(MABP) was prepared by polymerization of MABP in benzene initiated by AIBN and purified by precipitation from methanol. P(DMAEMA) was prepared by polymerization of DMAEMA in benzene initiated by AIBN and purified by precipitation from ice-cooled THF.

## UV and ESR Spectral Analysis

The UV spectrum was recorded on a Shimadzu UV-250 model spectrophotometer at room temperature. The ESR spectrum was recorded on a Bruker ER-200D SRC ESR spectrometer.

## RESULTS AND DISCUSSION

### Photopolymerization of AN Initiated by the MABP–DMAEMA System

The MABP–DMAEMA system can initiate the photopolymerization of AN as easily as can the ben-zophenone–triethylamine system. By varying the concentration of one of the three components, i.e.,

AN, MABP, or DMAEMA, and keeping that of the other two constant, the relationships between the polymerization rate ($Rp$) and [AN], [MABP], or [DMAEMA] can be obtained. The plots of lg $Rp$ − lg [AN], lg $Rp$ − lg [MABP], and lg $Rp$ − lg[DMAEMA] are linear, as shown in Figure 1. From the slopes of the straight lines, we found that the polymerization rate is proportional to $[AN]^{0.93}$, $[MABP]^{0.28}$ and $[DMAEMA]^{0.25}$, respectively. Hence, the relationship between $Rp$ and the concentration of AN, MABP, and DMAEMA can be written as

$$Rp \propto [AN]^{0.93}[MABP]^{0.28}[DMAEMA]^{0.25}$$

It is close to that of the photopolymerization of MMA initiated by the benzophenone–triethylamine system.[5] From the lg $Rp$ − $1/T$ plot shown in Figure 2, the overall activation energy for the photopolymerization has been calculated to be 30.43 kJ/mol, which is close to that of the conventional photoinitiated polymerization.

The intrinsic viscosity [$\eta$] of P(AN) initiated by the MABP–DMAEMA photoredox system in DMF was measured. Shown in Figure 3 is the relationship between [$\eta$] and DMAEMA concentration. It can be seen that the molecular weight of P(AN) de-
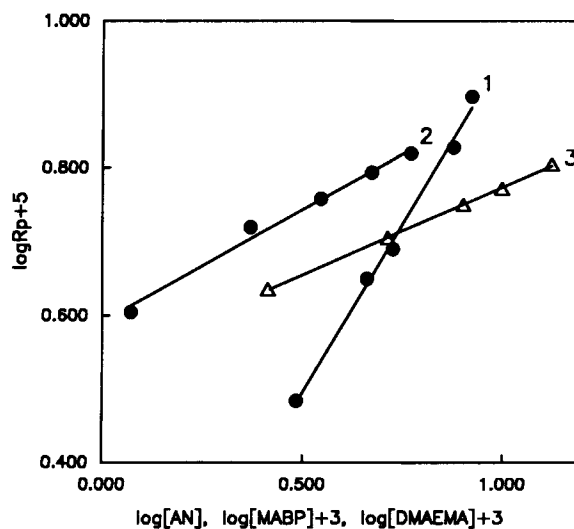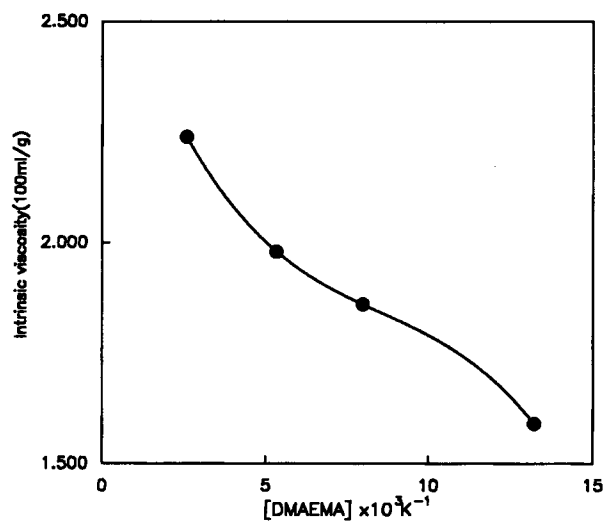


**Figure 1** Relationship between $Rp$ and concentration of AN, MABP, or DMAEMA: (1) log $Rp$ − log [AN] plot, [MABP] = 2.28 × $10^{-3}$ mol/L, [DMAEMA] = 4.45 × $10^{-3}$ mol/L; (2) log $Rp$ − log [MABP] plot, [AN] = 5.34 mol/L, [DMAEMA] = 4.53 × $10^{-3}$ mol/L; (3) log $Rp$ − log [DMAEMA] plot, [AN] = 5.34 mol/L, [MABP] = 2.32 × $10^{-3}$ mol/L.
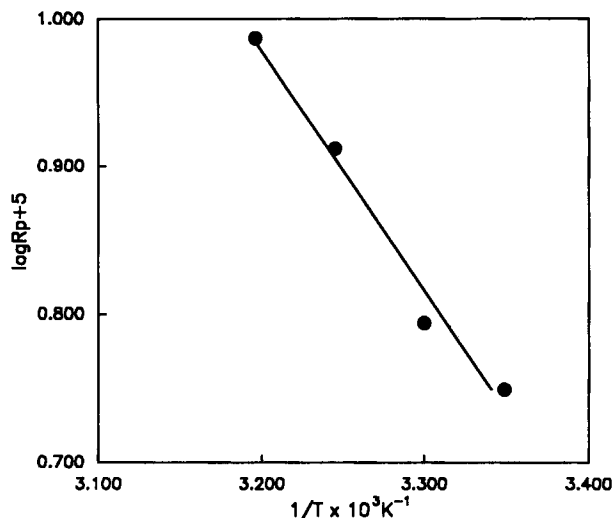
**Figure 2**  log $Rp$ − 1/$T$ plot for AN photopolymerization initiated by the MABP-DMAEMA system: [AN] = 5.34 mol/L, [MABP] = 2.38 × $10^{-3}$ mol/L, [DMAEMA] = 4.62 × $10^{-3}$ mol/L.

creases with the increase of concentration of DMAEMA. This obviously indicates that DMAEMA affects the photoinitiation reaction as does triethylamine (TEA) in the benzophenone–TEA photoredox system.

To reveal the photoinitiation mechanism of this polymerizable photoredox system, the ESR spectrum of MABP-DMAEMA in benzene using 2-



**Figure 3**  Relationship between intrinsic viscosity of P(AN) and concentration of DMAEMA in the MABP-DMAEMA system.
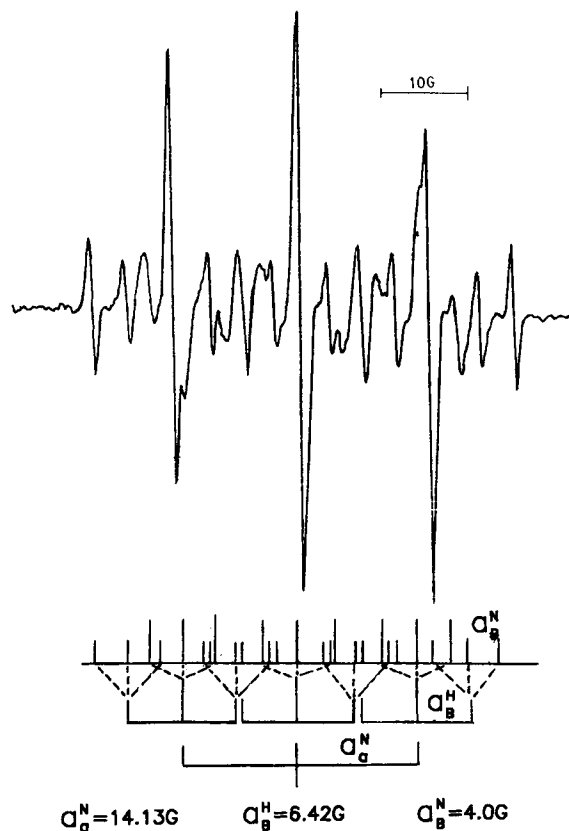


**Figure 4**  ESR spectrum of MABP-DMAEMA-MNP in benzene, irradiated for 7 min: [MABP] = [DMAEMA] = 0.01 mol/L, [MNP] = 5.0 × $10^{-3}$ mol/L.

methyl-2-nitritopropane (MNP) as radical trapper was recorded as shown in Figure 4. From the spectrum, according to the nuclear–electron spin coupling principle, it can be concluded that the final steady radical is the radical (III) (Scheme 1) formed probably by the radical (II) with trapper MNP. In the molecular radical (III), the N—O radical exhibits 27 peaks due to the interaction of the N—O radical with two $\alpha$-H atoms and an $\alpha$-N atom and some of the peaks duplicate each other. This indicates that the spectrum is much more complicated than that of the radical formed by the triethylamino radical with MNP.[9] The three higher peaks are probably due to the steady radical (V) formed by the trapping of radical (IV) from the C=C double bond with trapper MNP. According to the results of kinetics and the ESR spectrum, it is proposed that the initiation mechanism of this photoredox system is quite similar to that of the benzophenone-triethylamine system and can be shown as the following:
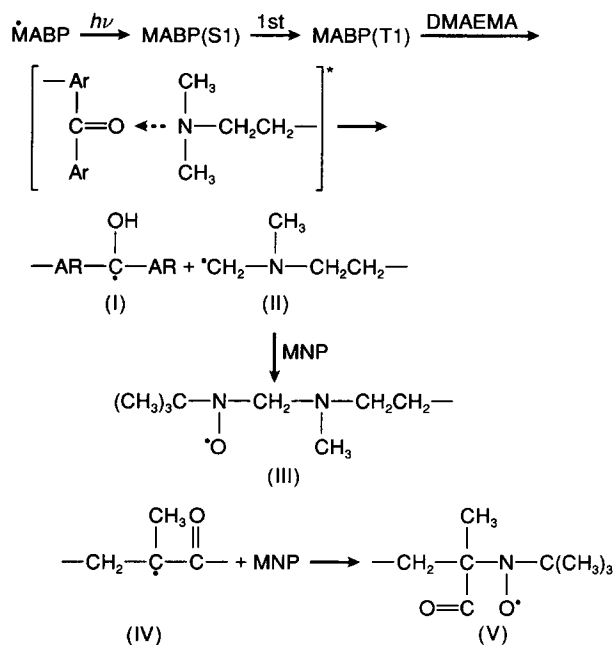
It should be noticed that in this initiation system the excited triplet MABP abstracts hydrogen mainly from the methyl groups of dimethylamino groups but not from the methylene groups. This may be due to the steric hindrance of the methacryloxy groups.
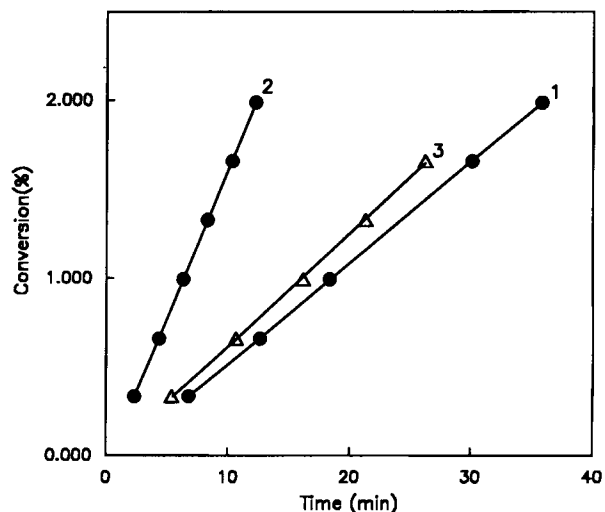
## Photopolymerization of AN Initiated by Polymeric Photoinitiators

There are several reports on polymers containing photosensitive chromophore moieties such as benzophenone in the side chain.[10-12] As compared with the low molecular benzophenone photoinitiator, the polymeric initiator P(MABP) exhibits higher initiation efficiency. In this study, both components of the MABP–DMAEMA photoredox initiation system are polymerizable. They can be easily polymerized

**Table I   Photopolymerization Rate of AN**

| | $R_p$ ($\times 10^5$ mol/L s$^{-1}$) | |
| --- | --- | --- |
| Initiators | DMF (25°C) | DMF–MeOH[a] (30°C) |
| MABP–DMAEMA | 4.4 | 2.1 |
| P(MABP)–DMAEMA | 12.7 | 3.0 |
| MABP–P (DMAEMA) | 4.9 | — |

[a] DMF–methanol (5 : 1 in volume). [AN] = 4.57 mol/L. [MABP] = [P(MABP)] = 2.28 $\times$ 10$^{-3}$ mol/L. [DMAEMA] = [P(DMAEMA)] = 4.46 $\times$ 10$^{-3}$ mol/L.



**Figure 5**   Time–conversion plot of the photopolymerization of AN in DMF initiated by the (1) MABP–DMAEMA system, (2) P(MABP)–DMAEMA system, and (3) MABP-P(DMAEMA) system. [AN] = 4.57 mol/L, [MABP] = [P(MABP)] = 2.28 $\times$ 10$^{-3}$ mol/L, [DMAEMA] = [P(DMAEMA)] = 4.46 $\times$ 10$^{-3}$ mol/L.
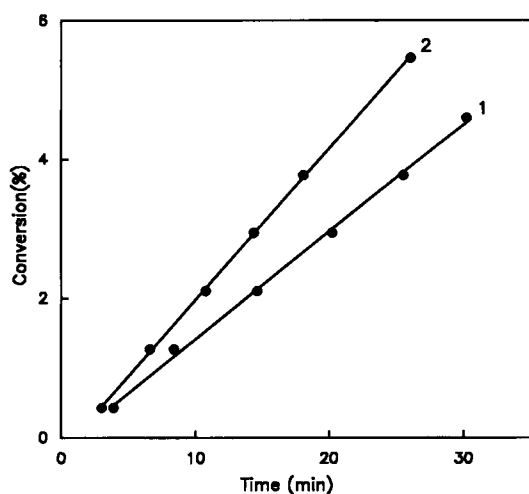
by initiation of AIBN or by UV irradiation. Their polymers should also display the ability to photoinitiate or photosensitize polymerization of vinyl monomers.

To reveal the effect of P(MABP) or P(DMAEMA) on the photopolymerization rate of AN, the combination of P(MABP) with DMAEMA or that of MABP with P(DMAEMA) was used. From Table I and Figure 5, it can be seen that the P(MABP)–DMAEMA system demonstrates a higher initiation ability than that of the MABP–DMAEMA system. In DMF, the polymerization rate of AN initiated by the former is almost three times higher than that initiated by the latter. Polymeric DMAEMA does not display such obvious enhancement of the polymerization rate of AN in comparison with monomeric DMAEMA in the MABP–DMAEMA system. This may be assigned to that benzophenone, as the chromophore moiety on the P(MABP) chains, is excited by UV irradiation and, then, the energy migration occurs along the P(MABP) chains. Thus, the collision probability of excited triplet benzophenone moieties with dimethylaminoethyl groups of DMAEMAs would be increased and it would be leading the hydrogen abstraction reaction between the excited benzophenone and DMAEMA. The polymer effect by energy migration has been previously reported by Kamachi et al.,[10] Carlini et al.,[11] Kwang et al.,[12] and Li et al.[13] Gen-
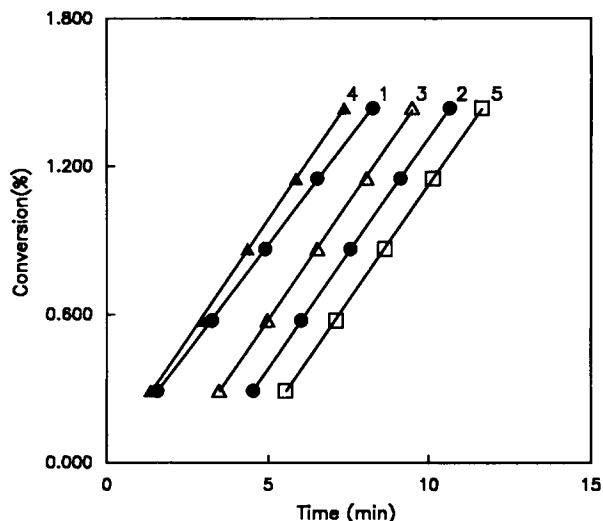
erally, tertiary amine coinitiators produce highly reactive carbon-centered radicals that are efficient initiating species for vinyl monomers.[14,15] Thus, the resulting DMAEMA radicals or P(DMAEMA) radicals (II) might be the dominating active species that initiate the photopolymerization of AN.

From Table I and Figure 6, it can be also seen that in the DMF–MeOH mixture, a poor dissolving system for P(MABP), the photopolymerization rate of AN initiated by both the MABP–DMAEMA and P(MABP)–DMAEMA systems decreases. However, the P(MABP)–DMAEMA system displays still higher initiation ability than that of the MABP–DMAEMA system, but the polymerization rate of AN initiated by P(MABP)–DMAEMA was only 1.5 times of that initiated by MABP–DMAEMA. In other words, the promoting effect of energy migration on photopolymerization in a poor solvent is not so obvious as in a good solvent. The above results show that the suitable conformation of P(MABP) in solution is an important factor affecting the photoinitiation efficiency of the system. The more compact conformation of P(MABP) chains promotes the recombination of ketyl radicals and limits the collision of DMAEMA molecules with excited triplet benzophenone moieties, thus reducing their initiation efficiency.

The influence of the molecular weight of P(MABP) on the polymerization rate has been investigated. Shown in Figure 7 is the time–conversion



Figure 7 Time–conversion plot of the photopolymerization of AN initiated by the P(MABP)–DMAEMA system with different molecular weights of P(MABP) at 30°C. [AN] = 5.34 mol/L, [P(MABP)] = 2.48 × 10⁻³ mol/L, [DMAEMA] = 4.40 × 10⁻³ mol/L. Molecular weight of P(MABP) (× 10⁻³): (1) 6.8, (2) 7.7, (3) 12.5, (4) 27.8, (5) 35.0.

plot for the photopolymerization of AN in DMF initiated by the P(MABP)–DMAEMA system with different molecular weights of P(MABP). The results of Figure 7 and Table II show that the molecular weight of P(MABP) does not affect the polymerization rate at all in the range of molecular weight of P(MABP) from 6800 to 35,000. It can be interpreted that the maximal transfer distance for energy migration along P(MABP) chains is satisfied.

## UV Spectral Analysis of P(AN) Initiated by MABP–DMAEMA

In the case of the polymerizable photoredox system consisting of MABP and DMAEMA as an initiator



Figure 6 Time–conversion plot of the photopolymerization of AN in DMF–methanol (5 : 1 in volume) initiated by the (1) MABP–DMAEMA system and (2) P(MABP)–DMAEMA system. [AN] = 4.57 mol/L, [DMAEMA] = 4.46 × 10⁻³ mol/L, [MABP] = [P(MABP)] = 2.28 × 10⁻³ mol/L.

Table II The Influence of Molecular Weight of P (MABP) on the Photopolymerization Rate of AN

| | Molecular Weight of P(MABP) (×10⁻⁴) | | | | |
| --- | --- | --- | --- | --- | --- |
| | 0.68 | 0.77 | 1.25 | 2.80 | 3.50 |
| Polymerization rate (conversion %/min) (×10³) | 1.76 | 1.91 | 1.97 | 1.89 | 1.92 |
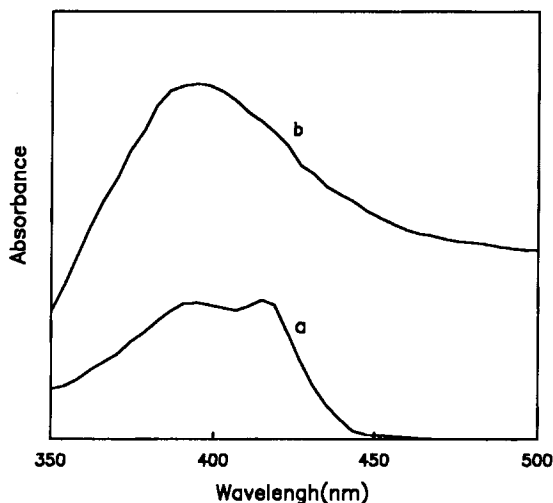
**Figure 8** UV absorption spectra of P(AN) initiated by the MABP–DMAEMA system: (a) P(AN) treated with TCNE; (b) P(AN) treated with DNPH.

of vinyl polymerization, it is expected that under the UV light irradiation both components will polymerize alone or act as comonomers entering into the P(AN) polymer chains. To verify whether MABP and DMAEMA take part in the polymerization and enter into P(AN) chains, tetracyanoethylene (TCNE) and 2,4-dinitrophenylhydrazine (DNPH) were used for the identification. It is well known that tertiary amines can form a charge transfer complex (CTC) with TCNE that shows a characteristic UV absorption at 415 nm. The carbonyl group of benzophenone can react with DNPH to form hydrozone with an absorption peak at 395 nm. These could be used for the identification of tertiary amino groups of DMAEMA or carbonyl groups of MABP in polymer chains. Figure 8 shows the UV absorption spectra of P(AN) initiated by the MABP–DMAEMA system treated with TCNE and DNPH, respectively. From this figure, it is clearly indicated that both MABP and DMAEMA not only act as initiators, but also participate in polymerization—polymerization by themselves or copolymerization with AN.

## CONCLUSION

A polymerizable photoredox system consisting of 4-methacryloxy benzophenone (MABP) and dimeth-

ylaminoethyl methacrylate (DMAEMA) used for the photopolymerization of AN was investigated kinetically. MABP and DMAEMA could not only form the photoredox system to initiate the vinyl polymerization but could also participate in the polymerization.

From the resulting ESR spectrum, it was revealed that in this polymerizable photoredox system the DMAEMA radical acted as an active species, initiating the polymerization of vinyl monomers as did triethylamine. For AN photopolymerization, the P(MABP)–DMAEMA system displayed a higher initiation ability than that of MABP–DMAEMA and MABP–P(DMAEMA).

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