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Photoinitiation Mechanism of a Novel Monomer – Dimethyl-Aminobenzyl-Methacrylate

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Summary

The photophysical behavior of a novel monomer, p-dimethylaminobenzylmethacrylate (DMABMA), which can self-initiate, polymerize and copolymerize was investigated. Results demonstrated that the exciplex which was formed between amino group and double bond in the same molecule was present during photoinitiation.

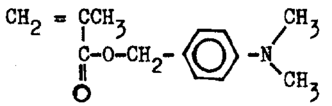
Introduction

A class of good electron donor aromatic tertiary amine has successfully been applied to initiate the photopolymerization of quite a lot of vinyl monomers (YOKATA, 1972, CAO AND FENG, 1980). Some work has been done on the kinetics and mechanism of this kind of polymerization (BARTON et al, 1980). The formation of an exciplex between the excited amine and the vinyl monomer such as methyl acrylate has been demonstrated for the first time (WEI, 1981). Through photodissociation and hydrogen abstraction, some radical species able to initiate the polymerization are formed. Recently, experimental evidence of the formation of ionic radical in the initiation step has been obtained in our laboratory (WU et al, 1982). In some systems, the exciplex fluorescence and the phenomenon of photoconductance have also been studied.

In this study, the photophysical behavior of a novel monomer which can self-initiate, polymerize and copolymerize is investigated. From the results of this study, the initiation mechanism is further clarified.

Experimental

Materials: Synthesis, purification as well as the polymerization kinetics of p-dimethylaminobenzylmethacrylate (DMABMA) was studied in the Department of Chemistry, Peking University (LI, 1982). The results will be published elsewhere.



Polymerization of DMABMA: 0.1 – 0.3% AIBN was added to the solution of DMABMA in benzene. The solution was warmed to 60°C for 24 hrs. Polymer was precipitated by diethyl ether. The product was purified by precipitation from benzene-diethyl ether mixture several times.

Copolymerization of DMABMA with methyl methacrylate: The procedue of copolymerization was identical to that of polymerization. The ratio of

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the two monomers in one of the samples measured by absorption spectroscopy was DMABMA : MMA = 1 : 50 .
All solvents and chemicals used in this work, dichloroethane, cyclohexane, propionitrile, methyl propionate were analytical grade. The monomers, MMA and AN, were purified according to the common methods before use. Fluorescence emission spectra were measured on a Hitachi MPF-4 fluorescence spectrophotometer. Slit width of the first monochromator was 10 nm, and the second one was 6 nm. Measurement was done at room temperature. All the fluorescence spectra reported were corrected.

Results and discussion

The fluorescence emission spectra of DMABMA, its polymer and copolymer with MMA measured with excitation at 329 nm in the solution of 1,2,-dichloroethane are shown in fig. 1 it is obvious that the emission intensities of different species at 354 nm are very different. In the same molar concentration (2.2×10^{-2}M) of DMABMA and P(DMABMA), the emission intensity of the latter is much higher than that of the former. Since molar concentration of dimethylaminobenzyl group in the copolymer is measured to be about 1.4×10^{-2} M, so the quantity of dimethylaminobenzyl group in the copolymer is much less than that in DMABMA, but the emission intensity of the copolymer is much higher. We attributed this difference of the emission intensity to the double bond of vinyl group in the monomer molecule. In the presence of such double bond which can accept an electron from the excited amino group, the fluorescence emission of the aromatic amine moiety is quenched by the exciplex formation. Therefore the fluorescence emission of DMABMA is low because the DMABMA monomer can form exciplex by itself and it will polymerize easily upon irradiation.
From fig.2 it is evident that in the process of photopolymerization, the emission intensity of the DMABMA solution increases gradually at different irradiation intervals. This indicates that during polymerization the amount of carbon-carbon double bond decreases, so the quenching effect also decreases simultaneously. In order to examine whether this double bond can quench the fluorescence emission of the amino group or not, a small amount of MMA monomer was added to the solution of P(DMABMA) (fig.3). Evidently, the fluorescence emission of the dimethylaminobenzyl group was quenched dramatically. However, addition of compounds without double bond such as methyl propionate will not impose similar quenching effect. It is obvious that the fluorescence emission of aromatic amine is quenched by the double bond, not by the ester group.

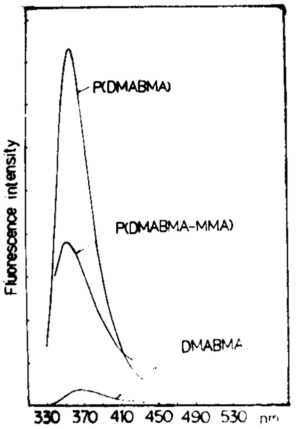


Fig.1 Fluorescence emission spectra of DMABMA, P(DMABMA) and P(DMABMA-MMA) in dichloroethane. $\lambda_{Ex.} = 329$ nm

The fluorescence emission of the aromatic amino group is quenched by the olefinic monomer, but it is well known that the energy of the excited singlet state of olefinic monomer is higher than that of the excited amino group. Therefore, quenching of the fluorescence emission by energy transfer is impossible. In this case, the fluorescence quenching is obviously related to the formation of exciplex (NAKASHIMA et al 1978,

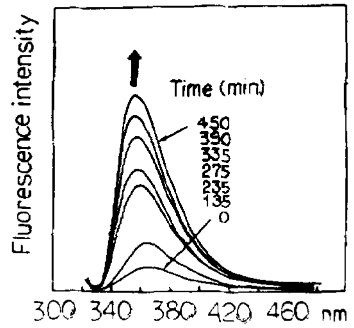


Fig.2 Change of fluorescence intensity of DMABMA solution at different irradiation intervals during photopolymerization

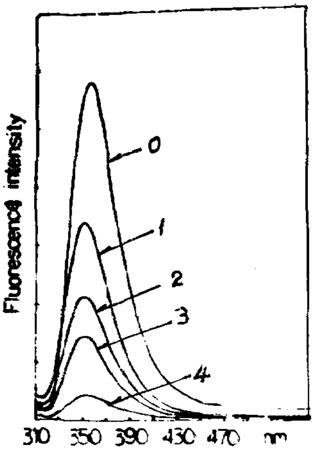


Fig.3 Fluorescence quenching of P(DMABMA) solution in 1,2-dichloroethane by different amounts of MMA. Conc. of polymer: 9.2×10^{-4}M. Conc. of quencher: 0) without quencher 1) 2×10^{-1}M 2) 3×10^{-1}M 3) 6×10^{-1} M 4) 1.2 M

MATAGA, 1979). However. we could not observe the fluorescence emission of the exciplex, although we have tried several techniques, such as changing the solvent and changing the concentration of the solution. In this experiment we have observed that, as the concentration of DMABMA solution in cyclohexane increased to a certain degree, the fluorescence emission intensity at 354 nm decreased gradually. In order to eliminate the influence of self-quenceing due to high concentration, parallelly we measured the fluorescence spectra of dimethyltoluidine which does not contain a double bond, in different concentration for comparison. It has been observed that, at similar conditions, the fluorescence intensity of DMT was about 20 times higher than the fluorescence intensity of DMABMA. As the concentration of both solutions increased from 5×10^{-5} to 1×10^{-2} M gradually, the fluorescence intensity underwent an enhancing and then a quenching stage. Fig.4 shows that at low concentration, the rate of the enhancement of DMT fluorescence is obviously higher than that of DMABMA. However, as the concentration increases to a certain degree, the fluorescence turns to a quenching stage. The trend of fluorescence quenching of DMABMA is faster than the other one. Although the fluorescence of the exciplex was not found in the spectra, the phenomena of the fluorescence quenching described above may demonstrate the existence of intermolecular exciplex formation.

In order to determine whether the charge transfer complex of DMABMA is present in the ground state, we have measured the absorption spectra of dimethyltoluidine and methyl methacrylate in dichloroethane solution. The absorption spectrum was observed to be the sum of the spectra of DMT and MMA taken separately.

The experimental results of the fluorescence quenching of copolymer P(DMABMA-MMA) by MMA and AN are shown in fig. 5 and 6.

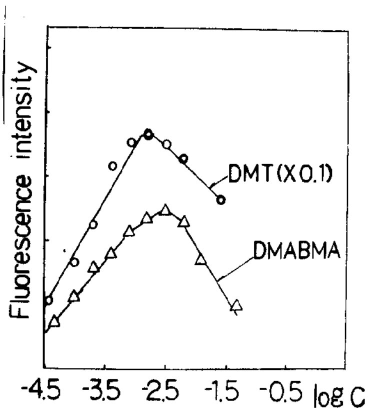


Fig.4 Change of fluorescence intensity of DMT and DMABMA solution in cyclohexane at different concentration

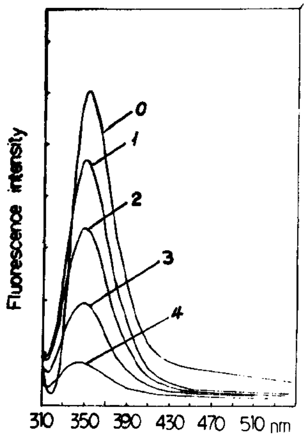


Fig.5 Fluorescence quenching of P(DMABMA-MMA) solution by different quantities of MMA. Conc. of copolymer: 1.4 x 10^{-3}M (DMABMA). Conc. of quencher: 0) without quencher 1) 1 x 10^{-1} 2) 2 x 10^{-1} 3) 4 x 10^{-1} 4) 8 x 10^{-1}M

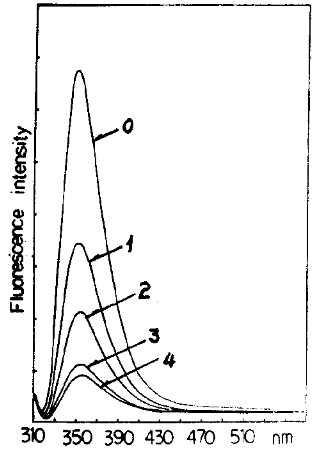


Fig.6 Fluorescence quencring of P(DMABMA-MMA) solution by different quantities of AN. Conc. of copolymer: 1.4 x 10^{-3} M(DMABMA). Conc. of quencher: 0) without quencher 1) 1.9 x 10^{-1} 2) 3.8 x 10^{-1} 3) 7.6 x 10^{-1} 4) 9.5 x 10^{-1}M

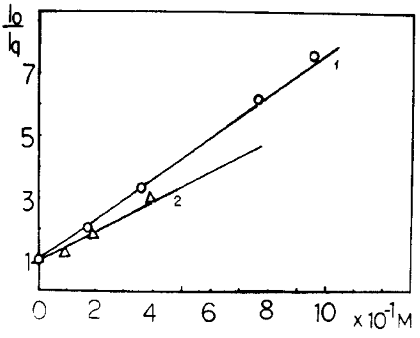
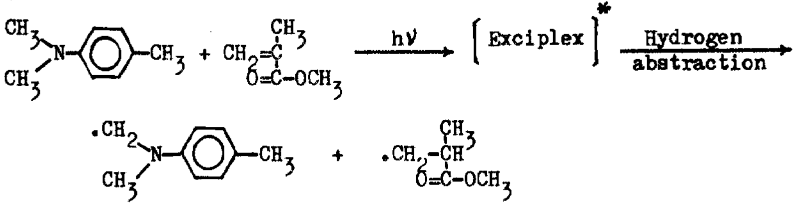
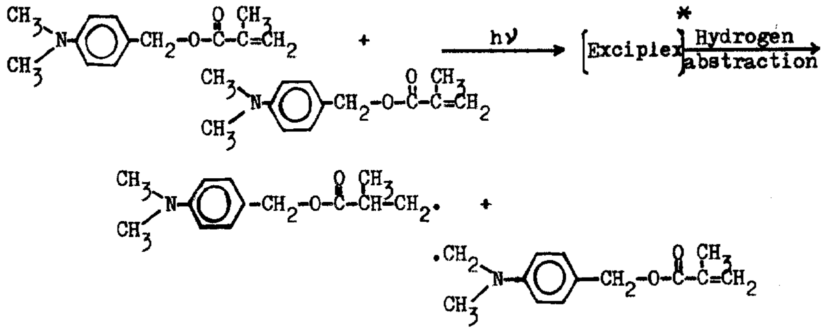


Fig.7 Stern-Volmer plots of fluorescence quenching of P(DMABMA-MMA)
1) by AN 2) by MMA

The results indicate that the copolymer P(DMABMA-MMA) behaves similarly, the fluorescence emission of which is quenched efficiently by the monomer. However, if methyl propionate and propionitrile were used to substitute the methyl methacrylate and acrylonitrile, respectively, a similar quenching effect was not observed. These results further illustrate that the fluorescence quenching is not effected by the ester or cyano group but by the double bond. According to the results from fig.5 and 6, the Stern-Volmer plots of fluorescence quenching were given in fig. 7. By comparison of the slopes, the higher quenching efficiency of acrylonitrile is ascribed to the more electron negative cyano- group, so it is easier to form exciplex and thus to quench the fluorescence more efficiently. According to the recent results of Cao (CAO and FENG,1980), aromatic amine absorption existed on the end group of poly(acrylonitrile) and PMMA macromolecules which were synthesized by using dimethyltoluidine as as initiator on photopolymerization. It is the evidence for initiation of AN and MMA polymerization by the aromatic amine radical photogenerated by hydrogen abstraction as follows:



Based on this interpretation, a possible mechanism of photoinitiation of DMABMA was proposed in similar type:



Further work is in progress in our laboratory.

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