Synthesis, Photochemical and Photophysical Behavior of Vinyl Monomers with Donor/Acceptor Architectures and Their Polymers

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Introduction

In recent years, a wide range of vinyl monomers and their polymers bearing various photo- or electroactive chromophores have been studied and applied in the fields of advanced composites, optical materials and devices.[1] Generally, the C=C bond of vinyl monomers was used as a useful tool to attach various photo- or electroactive groups to a polymer backbone. However, little attention was paid to the effect of the polymerizable C=C bond on the photochemical or photophysical behavior of these vinyl monomers and their polymers. We have had long-standing interest in the synthesis and photochemical behavior, including fluorescence and photosensitization behavior, of acrylic monomers and their polymers with electron-donating chromophore moieties.[2-12] It was found that the fluorescence emission intensities of these monomers are always dramatically lower than those of their corresponding polymers at the same chromophore concentration. Accordingly, we termed such a phenomenon as fluorescence structural self-quenching effect (SSQE) in order to distinguish from the well-known fluorescence concentration self-quenching effect. Recently, Cumpston et al. [13] and Warman et al.[14] separately described a similar phenomenon. The interpretation of their fluorescence data was consistent with the concept of SSQE. In this talk, we summarized our results on the design, synthesis, fluorescent properties as well as the application of these monomers and their polymers.

A(=)-D(*) and D(=)-A(*) monomers

Table 1 illustrates the structures of these monomers. For the A(=)-D(*) monomers, the electron-donating nature of the chromophores is mainly contributed by nitrogen, oxygen and sulfur

Table 1   Structures of the A(=)-D(*) acrylic monomers and D(=)-A(*) monomers

atoms in the forms of N,N-dimethylaminophenyl groups and heterocyclics, and the C = C bonds act as electron acceptors. These monomers display little fluorescence in solution while their saturated counterparts and the polymers show strong fluorescence at the same

chromophore concentrations. The fluorescence of their polymers can be quenched by the electron-deficient unsaturated compounds such as acrylonitrile (AN), methyl acrylate (MA), etc., but not by the saturated analogues such as propionitrile and methyl propionate. This indicates that the acrylic carbon-carbon double bonds do play an important role on the SSQE. These acrylic monomers, exhibiting SSQE, can be photopolymerized and act as polymerizable sensitizers to initiate the photo-polymerization of other acrylic monomers which do not have chromophore moieties.

In order to explore whether SSQE occurs for the vinyl monomers having an opposite state in electronic nature compared with the above acrylic monomers, we have synthesized vinyloxy monomers which have electron-accepting chromophore moieties (Table 1). The structures of these monomers can be represented as D(=)-A(*). Similar fluorescence properties have been found. Thus, it is concluded that SSQE is not an accidental phenomenon but a commonly observed one for the monomers whose carbon-carbon double bonds are electron-accepting and the fluorophores are electron-donating, and reversibly. Further study shows that the SSQE occurs mainly via an intra-molecular charge transfer interaction between the donor and acceptor in the same molecule.

A(=)-D(*)-A(=)monomers

Our studies concerned with the SSQE of A(=)-D(*) acrylic monomers have been extended to A(=)-D(*)-A(=) monomers having two electron-accepting moieties attached to a chromophore moiety, such as bismaleimides with electron-donating chromophore moieties. This was motivated by the fact that bismaleimide resins show excellent processing characteristics without the formation of volatile byproducts, and outstanding thermomechanical and flammability behaviors in the finally cured state. [15] The structures of these monomers are summarized in Table 2. [16]

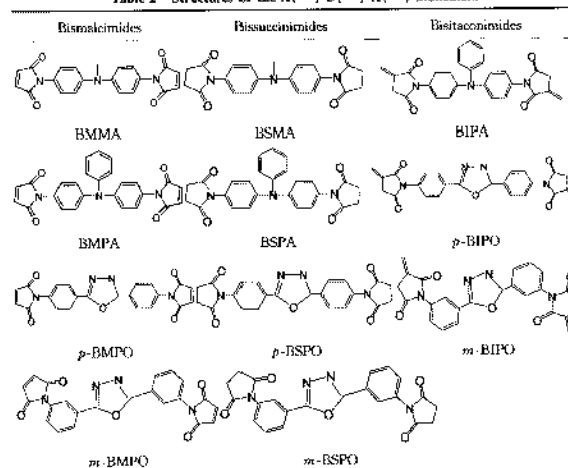Table 2   Structures of the A(=)-D(*)-A(=) monomers

Fig. 1 shows the fluorescence spectra of the bismaleimide monomer BMMA and its saturated model compound BSMA. It can be seen that the intensity of BSMA is drastically higher than that of the monomer BMMA at the same chromophore concentration. In fact, there is almost no fluorescence emission detected for monomer BMMA. The result of fluorescence quenching of BMMA by maleic
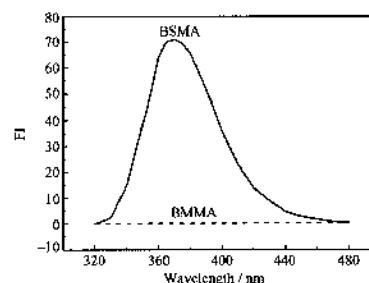

Fig. 1 Fluorescence spectra of bismaleimide BMMA and bissuccunimide BSMA in 1,2-dichloroethane

anhydride implies that the SSQE of BMMA is mainly caused by the intramolecular charge transfer interaction between the electron-donating N,N-diphenyl-N-methylamine chromophore and the electron-accepting C-C double bond of the maleimide group. Since the C=C bond of the maleimido residue plays a significant role in the fluorescence SSQE of A(=)-D(*)-A(=) bismaleimides, their fluorescence intensities can be expected to increase as the C=C bond is consumed in the reaction of these bismaleimides.To understand whether the change in fluorescence intensity is capable of reflecting the consumption of the C=C bond, a model reaction of BMMA with isobutylamine in solution was carried out as shown in Scheme 1.
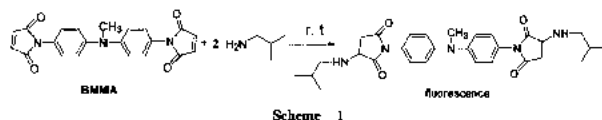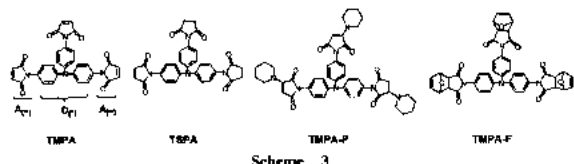
Scheme 1

Furthermore, the above reaction was extended to the cure reaction of bismaleimide/diamine resins. An aliphatic diamine, 1,6-diaminohexane (DAH), was chosen as a comonomer for the cure reaction in order to avoid the interfering fluorescence of aromatic diamines as shown in Scheme 2. Monitoring the cure reaction is thus possible by means of this new fluorescence approach based on the SSQE. The advantage of the new fluorescence approach is that it provides information on the chemical structure of C=C bond, which is unavailable from the currently applied environment-sensitive fluorescence probe technique.
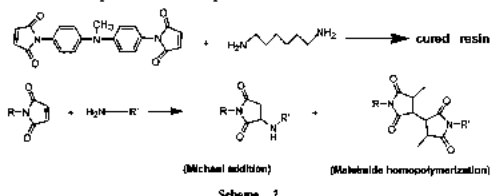
Scheme 2

(A (=)-D (*)(-A (=))-A (=)) Monomers

As an extension of our previous work, we synthesized a kind of trismaleimide (TMPA) bearing electron-donating chromophore (A(=)-D(*)(-A(=))-A (=)) and its corresponding model compound, TSPA. For comparison, two other compounds, Michael adduct (TMPA-P) of TMPA and piperidine, Diels-Alder adduct (TMPA-F) of TMPA and furan, were also prepared (Scheme 3).[17] The reaction of TMPA and piperidine was carried out at room temperature in acetone and the fluorescence of the solution was monitored with time. It was found

Scheme 3

that the fluorescence intensity increased gradually as the electron-poor C=C bond was consumed during reaction. Therefore, it is suggested that the fluorescence intensity of TMPA can directly reflect its C=C bond consumption during reaction. As described above, for TMPA, an intramolecular multiple charge transfer (CT) pathway leads to its fluorescence quenching. Therefore, it is assumed that the fluorescence is switched off because the CT pathway is open. For the Michael adduct TMPA-P, the electron poor C=C bond (A (=)) was consumed, thus, the fluorescence was switched on because the CT pathway was close. However, the fluorescence switch is irreversible. A retro-Michael addition is difficult, which can only occur to a certain extent at a high temperature of 180(C. Interestingly, the Diels-Alder adduct TMPA-F also displays a strong fluorescence. The Diels-Alder addition reaction is reversible. The Diels-Alder adduct TMPA-F can give out furan at 60°C in solution via a retro-Dial-Alder addition, where the electron poor C=C bond (A (=)) is formed again. In this case, the intramolecular charge transfer (CT) pathway is open again to cause the intramolecular fluorescence quenching. Due to a reversible Dial-Alder addition leading to a reversible intramolecular CT pathway (open and close), the fluorescence is reversibly switched on and off. Therefore, a new fluorescence method can be developed. (Fig. 2)
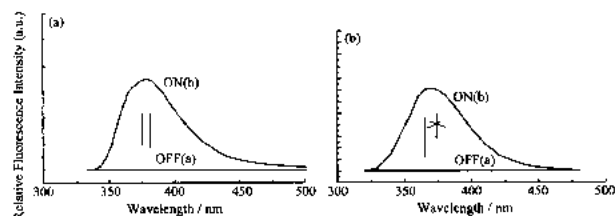

Fig. 2. Reversible fluorescence behavior for Diels-Alder addition (a) and irreversible fluorescence behavior for Michael addition (b).

Conclusions

We can summarize our results and findings as follows: (1) Fluorescence structural self-quenching effect (SSQE) can be observed as a general phenomenon for vinyl monomers containing chromophores of opposite electronic nature. The mechanism of this phenomenon can be attributed to the intra-molecular charge transfer. (2) This fluorescence properties can be used to detect the polymerization and curing process, which directly reflect the consumption of C=C bonds; and it may also be used as reversible fluorescence detectors for reaction and self-assembly in solution.

Acknowledgments

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