

VINYL MONOMERS BEARING CHROMOPHORE
MOIETIES AND THEIR POLYMERS
X. INITIATION AND PHOTOCHEMICAL PROPERTIES OF
p-(*N,N*-DIMETHYLAMINO)STYRENE AND ITS POLYMERS*

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Abstract A vinyl monomer having an electron-donating moiety, *p*-(*N,N*-dimethylamino)styrene (DMAS), was synthesized. It was combined with benzoyl peroxide (BPO) to form a redox initiation system to initiate the polymerization of methyl methacrylate (MMA). UV spectra measurements show that DMAS enters the PMMA chain as well. Both DMAS and its polymer P(DMAS) display strong fluorescence, and the fluorescence can be quenched by electron-deficient compounds such as methacrylonitrile, fumaronitrile and methyl methacrylate etc. Moreover, DMAS can also form charge transfer complex (CTC) with strong electron acceptors such as tetracyanoethylene (TCNE). The difference between the photochemical properties of DMAS and P(DMAS) were explained in terms of molecular structure change and polymer conformation effect in solution. In addition, the CTC and exciplex formation of DMAS or P(DMAS) with C_{60} were also studied.

Keywords *p*-(*N,N*-dimethylamino)styrene, CTCs, Exciplex, C_{60} , Polymerizable initiator

INTRODUCTION

The research of charge transfer complex (CTC) in polymer system can be traced back to the 1960's. It was found at that time that *N*-vinylcarbazole (VCZ) could initiate its own polymerization by forming a CTC with an electron acceptor^[1,2]. Later, the study was extended to other monomers and sensitizers, for example, methyl methacrylate (MMA) or acrylonitrile (AN) with aromatic amino compounds^[3], and other polymerization methods such as photopolymerization^[4]. However, most of the previous works were limited in the field where the complexes were formed between two different molecules. We have long been interested in the investigation of photochemical properties of vinyl monomers having chromophore moieties and their polymers. A series of vinyl monomers have been synthesized and polymerized in our lab^[5-12]. A common characteristic between these monomers is that both electron donor and electron acceptor coexist within the same molecule. Depending on the electronic nature of the chromophores, these monomers can be classified into two catalogues, that is, molecules with an electron donating chromophore and an accepting double bond, and those with a electron accepting chromophore and a donating double bond. Two of the representatives are shown in the Scheme 1.

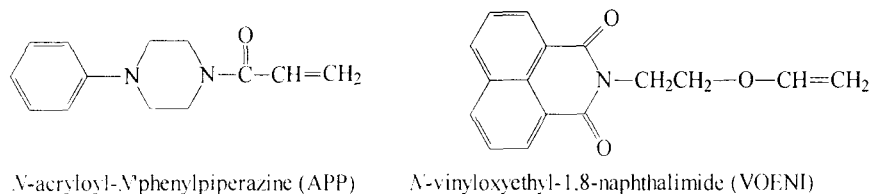
It has been found that all of these monomers display a phenomenon which we termed as fluorescence "Structural Self-Quenching Effect" (SSQE): the fluorescence intensity of the monomer is always dramatically lower than that of its corresponding polymer of the same

* This project was supported by the National Natural Science Foundation of China.

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Received December 11, 1998

chromophore concentration. This phenomenon was explained in terms of intra- and/or intermolecular exciplex formation between the double bonds and chromophores. This explanation was further confirmed by quenching the fluorescence of the polymers with certain quenchers having electron-deficient or electron-rich double bonds. Furthermore, these monomers have also been used alone or together with organic or inorganic peroxide to sensitize the photo- or thermal polymerization of typical vinyl monomers, and they have been found to enter the resulting polymer chains simultaneously.



Scheme 1

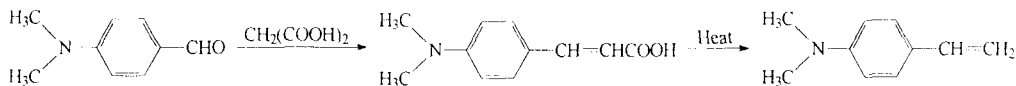
In order to get a better understanding of how the nature of double bonds affects SSQE, another kind of monomer with an electron donating chromophore and a nearly electron-neutral vinyl group, i.e. *p*-(*N,N*-dimethylamino)styrene (DMAS), was synthesized and studied photochemically. It was also expected that DMAS, similar in structure with *N,N*-dimethylaniline (DMA), can form a redox initiation system with benzoyl peroxide (BPO) to initiate the polymerization of vinyl monomers. Since DMAS will enter the polymer chains as strong electron donating chromophores, the resulting homo- and copolymers, when doped with a strong electron acceptor, may possess some intriguing properties, such as the improvement of the electron conductivity^[13].

EXPERIMENTAL

Materials and Methods

N,N-dimethylaminobenzaldehyde, malonic acid, piperidine and other reagents were commercial products of Beijing Chemical Plant and used as received. All solvents used for UV and fluorescence spectra measurement were carefully purified according to conventional procedures, and control experiments were conducted to assure the purity of the solvents. Infrared spectra were recorded on a Nicolet 750 FT-IR Spectrometer. ¹H-NMR spectra were recorded on a Bruke ARX-400 instrument. Chemical shifts are expressed in ppm downfield from TMS.

Synthesis of DMAS



4-*N,N*-dimethylaminocinnamic acid was synthesized from the reaction of *N,N*-dimethylaminobenzaldehyde with malonic acid in pyridine and in the presence of a small amount of piperidine^[14], the yield was 60%. DMAS was prepared via a modified Knoevenagel method and the whole procedure was carried out as follows.

28 g of 4-*N,N*-dimethylaminocinnamic acid, 2 g of anhydrous copper sulfate and 0.1 g of 4-hydroquinone were placed in a 100 mL round bottom flask and 60 mL of diphenyl ether was added. The flask was connected with a set of distillation equipment and was heated to 270°C in a sand-bath under nitrogen. The collected distillate was neutralized with dilute hydrochloric acid to transfer the product from diphenyl ether to aqueous phase. Then sodium carbonate was added to

the separated aqueous phase to recover the crude DMAS. The oil phase was separated out and the aqueous phase was extracted with ethyl ether. The combined organic phase was dried over sodium carbonate. After removing the solvent, a small amount of zinc powder was added. Vacuum distillation was then performed to produce a colorless liquid at 82–84°C/66.5 Pa. Yield 27%. $^1\text{H-NMR}$ (δ , CDCl_3): 2.91 (6H, *s*), 5.01 (1H, *d*), 5.51 (1H, *d*), 6.66 (3H, *m*) and 7.29 (2H, *m*); IR(KBr): 3083, 3040, 990 and 887 cm^{-1} ($\text{C}=\text{C}$), 2887, 1444 and 1353 cm^{-1} ($-\text{N}(\text{CH}_3)_2$), 1522 and 820 cm^{-1} ($\text{Ar}-$); elemental analysis: calculate, C 81.59%, H 8.90%, N 9.52%; found, C 81.49%, H 8.65%, N 9.25%.

Synthesis of P(DMAS)

P(DMAS) was obtained by radical polymerization of DMAS at 70°C in toluene using AIBN as the initiator. The polymer obtained was purified by reprecipitation from toluene into petroleum ether (60–90°C), and dried under vacuum. The molecular weight of P(DMAS) was measured by GPC using THF as an eluent and calibrated with polystyrene standards. $^1\text{H-NMR}$ (δ , CDCl_3): 1.38 (2H, *m*), 1.93 (1H, *m*), 2.87 (6H, *m*), and 6.52 (4H, *m*); IR (KBr): 2882, 1443 and 1340 cm^{-1} ($-\text{N}(\text{CH}_3)_2$), 1518 and 814 cm^{-1} ($\text{Ar}-$).

Kinetic Study of MMA Polymerization

The kinetics of the polymerization of MMA initiated by DMAS/BPO system was pursued by the dilatometric method. A 3 mL dilatometer made of Pyrex glass was used and placed in a thermostat. The polymerization system was purged with nitrogen for 15 min just before heating.

Absorption and Fluorescence Spectra

The absorption spectra of DMAS and P(DMAS) were recorded on a Shimadzu UV-250 Spectrophotometer. The fluorescence spectra were recorded on a Hitachi M-850 Fluorescence Spectrophotometer at room temperature. The slit widths of the monochromators were both 5nm.

Redox Potential

The redox potentials were measured by a Solartron 1250 frequency response analyzer with three electrodes, the working electrode and the counter electrode are made of platinum, the reference electrode is Ag/AgCl. Slipping range is ± 1.5 V (versus Ag/AgCl), and the scanning rate is 50 mV/s. A supporting electrolyte is composed of saturated solution of tetraethylammonium perchlorate in dichloromethane.

RESULTS AND DISCUSSION

Redox Initiation System by Combining DMAS with BPO

It is difficult to polymerize DMAS by initiation with peroxides such as BPO, LPO, etc. due to the conjugation of carbon-carbon double bond with the electron-donating dimethylamino group. Though DMAS can be thermally polymerized by initiation of AIBN, the rate is very slow^[15]. However, DMAS can be used together with BPO to form a redox initiation system to initiate the polymerization of MMA. By varying the concentration of one of the three components individually, i.e. MMA, BPO, or DMAS, while keeping that of the other two unchanged, the relationship between the polymerization rate (R_p) and [MMA], [BPO], or [DMAS] can be obtained as follows:

$$R_p \propto [\text{MMA}]^{1.0} [\text{BPO}]^{0.5} [\text{DMAS}]^{0.5}$$

By varying the polymerization temperature, the overall activation energy (E_a) was obtained to be 30.93 kJ/mol. Both the rate equation and the E_a value are in good agreement with the general kinetics of a polymerization initiated by a redox initiator^[16], indicating that DMAS forms a redox system with BPO.

PMMA obtained above displayed a distinct absorption peak at 305 nm in dichloroethane

solution, while the PMMA obtained by initiation of AIBN did not show such a peak. Even after reprecipitating PMMA from benzene into methanol for several times, the absorption peak intensity at 305 nm of the purified PMMA remained unchanged as described in Fig. 1. Since the characteristic absorption peak of P(DMAS) is at 305 nm, the result proves that DMAS enters the PMMA chain. A potential application of this property is to use it in the *in situ* curing of biomedical materials to avoid or reduce the release of harmful amines.

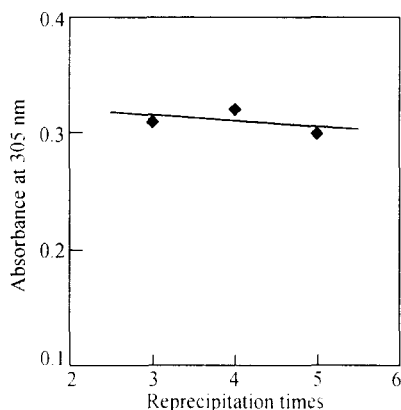


Fig. 1 UV-absorbance of PMMA initiated by DMAS-BPO after different reprecipitation times

Fluorescence Behavior of DMAS and its Polymer

As mentioned in the introduction section, one of the purposes of this work is to further study the influence of the nature of the double bond on the fluorescence structural self-quenching effect (SSQE). Shown in Fig. 2 are the fluorescence emission spectra of DMAS and P(DMAS) in dichloroethane (DCE). It can be seen that DMAS shows much stronger fluorescence than P(DMAS) at the same concentration of the chromophore, that is to say, SSQE does not occur for DMAS. This result is contrary to our previous observations, but it is reasonable. In DMAS, the electronic state of the carbon-carbon double bond is nearly neutral, or may even display some electron-donating nature due to the conjugated structure. This conjugated molecule can exhibit strong fluorescence upon UV irradiation. After the carbon-carbon double bond is polymerized, however, the resonance energy of the conjugation system of the chromophore (dimethylamino phenyl group) is smaller than that of DMAS. Thus, the fluorescence peak of DMAS red shifts in comparison with that of P(DMAS) (see Table 1). It can thus be concluded that the electronic-complementary structure is a prerequisite for the SSQE. The fact that the overall fluorescence intensity of P(DMAS) is rather weak as compared with that of the monomer was considered to be due to the random coil conformation of the polymer in solution. In polymer solution, the chromophores cannot be uniformly distributed, the chromophore moieties are closer to each other than in the case of solutions of small molecules. The local chromophore concentration in polymer solution may be much higher than the expected one, as a result, the polymer exhibits a much weaker fluorescence than it should be due to the concentration self-quenching effect.

If this interpretation is valid, the fluorescence of P(DMAS) should be affected by solvents. We thus measured the relative intensities of emission fluorescence of both DMAS and P(DMAS) in different solvents. The results are summarized in Table 1. It can be seen that the fluorescence intensity of DMAS does not change much in various solvents, however, for P(DMAS), a drastic increase in fluorescence intensity was observed by changing the solvent from DCE to DMF. In good solvents, such as DMF, the interaction between the solvent and P(DMAS) causes the chromophores to separate, and the concentration self-quenching effect is reduced, and hence

strong fluorescence intensity can be observed.

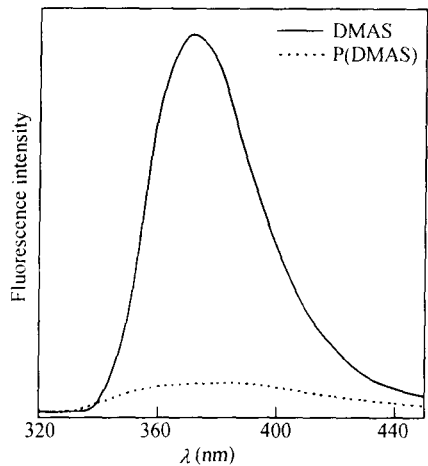


Fig. 2 Fluorescence spectra of DMAS and P(DMAS) in dichloroethane
Concentration of chromophore: 5×10^{-4} mol/L

Table 1. The relative fluorescence intensity and emission wavelength of DMAS and P(DMAS) in various solvents*

Solvent	$\epsilon^a)$	DMAS		P(DMAS)	
		$\lambda_{em}(nm)$	Intensity	$\lambda_{em}(nm)$	intensity
Benzene	2.3	365	71 ^{b)}	353	72
THF	7.6	367	141	353	46
DCE	10.4	371	123	363	13
DMF	36.7	377	136	361	87

* λ_{ex} : DMAS: 267nm, P(DMAS): 298nm; a) ϵ : dielectric constant, b) λ_{ex} = 283 nm

CTCs and Exciplexes Formation of DMAS and P(DMAS) with Electron-Deficient Compounds

Having a strong electron donating dimethylamino group, both DMAS and P(DMAS) can form exciplexes with electron acceptors, such as methacrylonitrile (MAN), acrylonitrile (AN), methyl methacrylate (MMA), methyl acrylate (MA), fumaronitrile (FN) and tetracyanoethylene (TCNE) under UV irradiation. The exciplex formation can be demonstrated by the regular quenching of the fluorescence of DMAS or P(DMAS) by adding the above electron-deficient compounds. For example, the quenching of the fluorescence of DMAS by MMA is shown in Fig. 3. The Stern-Volmer constants for various quenchers were obtained and listed in Table 2. Apparently, with the increase of “e” value of the quencher, its quenching efficiency increases as well. In addition, it was also observed that for the same quencher, the fluorescence of DMAS was quenched more efficiently than that of P(DMAS). That is to say, DMAS forms exciplex with electron acceptor more easily than P(DMAS). These results may be caused by two factors: firstly, DMAS may be a stronger electron donor than P(DMAS); secondly, it might be difficult for the quenchers to interact with the electron-donating chromophores on the polymer chain.

Table 2. The correlation between the Stern-Volmer constants and “e” values of various quenchers in dichloroethane

Quencher		MMA	MA	MAN	AN	FN	TCNE
e (eV)		0.4	0.64	0.68	1.23	2.73	-
$k_q \tau (mol^{-1}L)$	DMAS	55	56	21.4	19.6	128	12000
	P(DMAS)	6.25	16.4	6.89	8.29	23.2	7400

In order to clarify whether DMAS and P(DMAS) exhibit different electron donating abilities,

we measured the redox potentials of DMAS and P(DMAS) by cyclic voltammetry. It was found that both compounds showed only one oxidation peak at +0.75 V, indicating that they display almost the same electron donating abilities in the irreversible electron donating process. This result supports the conclusion that it is the polymer conformation that affects the exciplex formation between P(DMAS) and small quencher molecules.

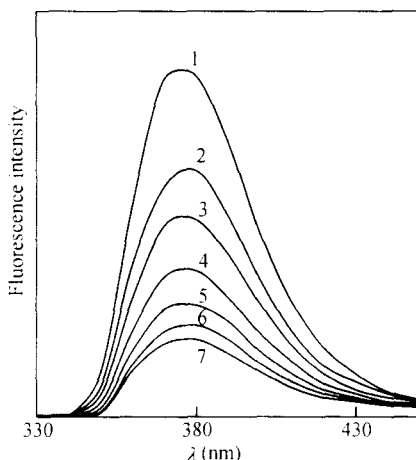


Fig. 3 Fluorescence quenching of DMAS by MMA in dichloroethane
Concentration of MMA (mmol/L): 1) 0, 2) 9.3, 3) 18.7, 4) 28.1, 5) 37.4, 6) 46.8, 7) 56.1

Another observation that needs to be mentioned during the fluorescence study is that DMAS forms CTC in the ground state with very strong electron acceptor such as TCNE. This was proved by the presence of a CTC absorption peak at 565 nm as shown in Fig. 4 and the upward curvature in the Stern-Volmer plot as well (Fig. 5)^[17].

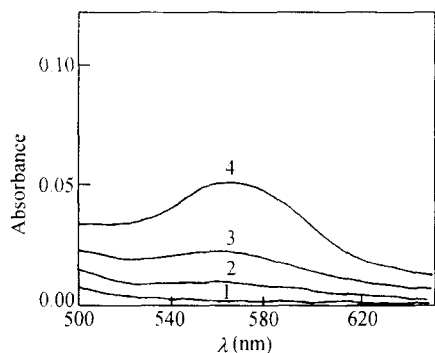


Fig. 4 UV absorption spectra of charge transfer complex of DMAS with TCNE in dichloroethane
[DMAS] = 5×10^{-4} mol/L, [TCNE]: 1) 0, 2) 2.0×10^{-3} mol/L, 3) 1.0×10^{-2} , 4) 5.0×10^{-2} mol/L

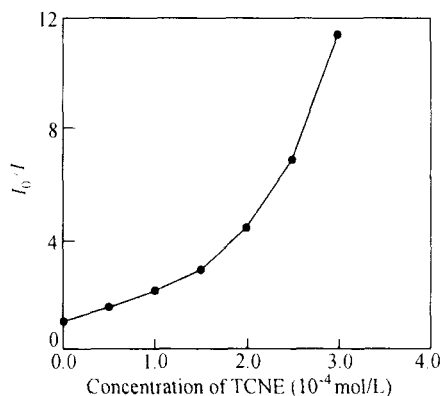


Fig. 5 Stern-volmer plot of DMAS quenched by TCNE in dichloroethane

Charge Transfer Phenomena of C_{60} with DMAS and P(DMAS)

The discovery of fullerenes is perhaps the most arresting event in science in the 1980's^[18]. Huge amount of research works has been reported on the structure and properties of fullerenes in the field of chemistry, physics, material science, etc. since then. C_{60} can act both as an electron acceptor and an electron donor. We have found in previous studies that C_{60} can form CTCs or

exciplexes with several electron donors, such as 4,4'-azobis(*N,N*-dimethyl)aniline (ABDMA), *N,N,N',N'*-tetramethylbenzidine (TMB), *N'*-(4-*N'',N''*-dimethylaminophenylmethylene)-*N,N*-dimethyl-*p*-phenylenediamine (DPDB) as well as polymers having electron-donating chromophores. The complexes formed show stronger third order NLO properties than C_{60}/C_{70} itself^[19]. Inspired by these results, we investigated the charge transfer phenomenon between C_{60} and DMAS or P(DMAS). It was found that C_{60} can quench the fluorescence of DMAS and P(DMAS) regularly, the Stern-Volmer plots are shown in Fig. 6. The upward curvature from linearity for P(DMAS) clearly indicates a combination of static quenching and dynamic quenching, which means that charge transfer occurs at both the ground state and the excited state. As for DMAS, a straight Stern-Volmer plot is obtained, but the Stern-Volmer constant is very large ($6 \times 10^4 \text{ mol}^{-1}\text{L}$). This result implies that a pure static quenching occurred in the mixture of DMAS and C_{60} . Further fluorescence lifetime measurement confirmed this conclusion. Figure 7 shows that the lifetime of P(DMAS) fluorescence gradually decreases when more and more C_{60} was added while the lifetime of DMAS was almost unaffected. This again confirms that the excited state of DMAS is not disturbed at all, the charge transfer only takes place in the ground state.

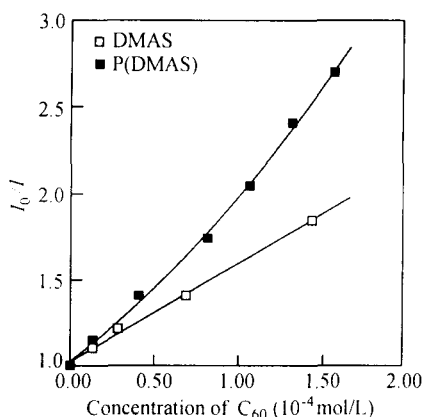


Fig. 6 Stern-volmer plot of DMAS and P(DMAS) quenched by C_{60} in dichloroethane

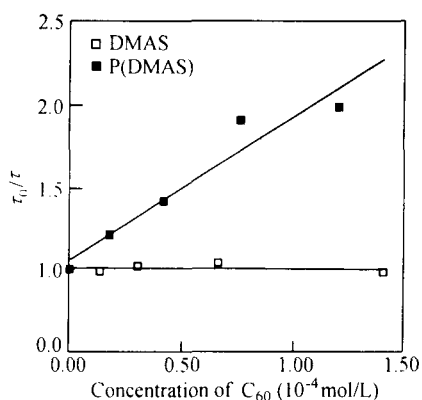


Fig. 7 Changes in fluorescence lifetime of DMAS and P(DMAS) at different concentration of C_{60} in dichloroethane

The influence of polymer conformation on the fluorescence of P(DMAS) was also confirmed by fluorescence lifetime measurement. For DMAS, only one fluorescence lifetime was observed at 3.2 ns, however, two lifetimes were detected for P(DMAS) at 15.3 ns and 1.3 ns, respectively. This may be attributed to the restricted rotation of chromophore moieties on the polymer chain and the different micro-environment of the chromophores inside and outside the polymer coil.

CONCLUSIONS

As a polymerizable electron donor, DMAS not only forms a redox system with BPO to initiate the polymerization of MMA, but also enters the polymer chain. Both DMAS and P(DMAS) exhibit strong fluorescence, but SSQE was not observed because the electronic-complementary structure necessary for SSQE does not exist in DMAS. Charge transfer phenomena were observed for DMAS and P(DMAS) with electron-deficient compounds. In the presence of very powerful electron acceptors, such as TCNE and C_{60} , charge transfer occurs in both the excited state and the ground state. The difference between the photochemical properties of DMAS and P(DMAS) was explained in terms of molecular structure change and polymer conformation effect in solution.

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