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A striking observation on the fluorescence of a twisted intramolecular charge transfer (TICT) molecule used to probe polymer dynamics in the bulk state

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Abstract

An anomalous effect on the twisted intramolecular charge transfer (TICT) phenomenon of 4-(N,N-dimethylamino) benzonitrile (DMABN) dissolved in elastomers such as poly(propylene oxide), poly(ethylene oxide) has been observed. Under irradiation, the normal fluorescence of DMABN in these matrices has been found to increase strongly while the emission arising from the TICT state decreases slightly.

Introduction

Fluorescence probe techniques are increasingly used in polymer science in order to get useful insights into the dynamic behaviour of the macromolecular media. Bulk polymer dynamics are a novel topic relevant to the basic understanding of the polymer motions at a molecular level.

In previous studies (1), the excimer fluorescence technique has been successfully applied to investigate the local molecular dynamics of polymer chains in the solid state. This method is based on the analysis of the fluorescence emission arising from small intramolecular excimer-forming probes dissolved in elastomeric matrices. The rotational process involved in excimer formation requiring large scale motion, these probes undergo their conformational change via a free-volume-dependent molecular relaxation process related to the glass-transition phenomenon of the matrix .

Derivatives of 4-(N,N-dimethylamino) benzonitrile (DMABN) or ethyl 4-(N,N-dimethylamino) benzoate, giving rise to a "twisted intramolecular charge transfer" state (TICT), are expected to act as molecular probes sensing polymer segment mobility. These molecules emit two emission bands, one corresponds to the non-charge- transfer state (b* band), the lower energy one (a* band) is ascribed to the TICT state in which the donor and acceptor moieties are perpendicular to each other.

The volume swept out during that particular mode of molecular motion is smaller than that involved in intramolecular excimer formation. Thus the TICT molecules could be good candidates for probing secondary relaxations of polymers in the bulk state since they require a small amount of free volume to reach the twisted state.

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A number of studies have been reported on the use of TICT formation in polymeric systems to examine local segmental mobility. Tazuke (2) used ethyl 4-(N,N-dimethylamino) benzoate as a TICT fluorescence probe and linked this probe to poly(methylmethacrylate) and various poly(alkylmethacrylates) via alkyl chains of variable length. These studies performed in dilute solutions, provide useful information on the effect of a neighboring side chain on the twisting motion of the TICT chromophore. K.A. Al-Hassan and W. Rettig (3) have shown in an analysis of the fluorescence of dimethylaminobenzonitrile and related molecules in polymethylmethacrylate in the glassy state that TICT compounds can act as microprobes for the free volume in polymers in the solid state.

This paper reports an analysis of the emission behaviour of DMABN dissolved in elastomers such as poly(propylene oxide), poly(ethylene oxide) as well as poly(dimethylsiloxane). The experiments have also been carried out in 1,2-propanediol which can be considered as the monomer of the poly(propylene oxide) and in 2-methoxy-ethyl ether (diglyme), a molecule which is free of terminal OH groups. For the purpose of comparison, 1-methyl-5-cyanoindoline, where the dimethylamino group is held in the planar position was dispersed in the same polymers.

Experimental part

DMABN (Aldrich) was purified by vacuum sublimation.

1-methyl-5- cyanoindoline (MCI) was prepared as described (4).

The poly(propylene oxide) with molecular weight 425 (PPO 425) $HO-[CH_2-CH(CH_3)-O-]_nH$, the 1,2-propanediol (PD) $CH_3-CH(OH)-CH_2OH$, the 2-methoxyethyl ether (diglyme) $(CH_3OCH_2CH_2)_2O$ were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and the poy(ethylene oxide) with molecular weight 400 (PEO 400) $HO-[CH_2-CH_2-O-]_nH$ was purchased from Aldrich-Chemie (Steinheim).

The poly(dimethylsiloxane) with molecular weight 5000 $[Si(CH_3)_2-O-]_n$ was kindly supplied by Rhône-Poulenc Industries. The fluorescence spectra were recorded on a Fica Model 55 MK II spectrofluorimeter equipped with a 450W xenon lamp and a R 212 photomultiplier tube and on a Jobin-Yvon JY3CS spectrofluorimeter with a 150W xenon lamp.

The fluorescent molecules ($10^{-5} < c < 10^{-4}$ M) were dissolved in the polymers which are all in the liquid state at ambient conditions. The solutions were stirred to assure that the probes were homogeneously dispersed in the polymeric media.

Results and discussion

The emission spectrum of DMABN in PPO 425 (Fig.1) exhibits two emission bands (dual fluorescence). The higher-energy emission band around 350 nm and the lower-energy one around 450 nm are assigned to the planar non-charge transfer state (b* band) and the TICT state (a* band), respectively.

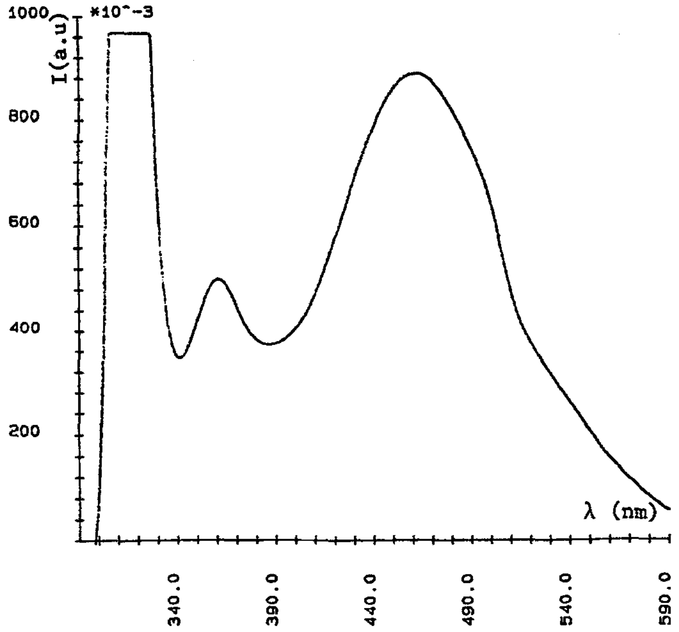


Fig.1: Emission spectrum of DMABN in polypropylene oxyde (PPO) 425, at room temperature - c ≈ 10^{-5} .M

Our initial purpose in this study is to determine whether the rotational motion of the amino substituent required for the TICT formation is affected by free volume effects induced by changing either the temperature or the pressure of the sample.

Surprisingly, under UV irradiation (λ = 310 nm) at room temperature, the normal fluorescence (I_{Fb}) of DMABN in PPO 425 exhibits a pronounced increase in intensity while that arising from the TICT state decreases slightly . I_{Fb} increases by as much as twice or three times within about one hour. In the dark, both intensities tend to recover the initial value in about 24 h or more. The reversible changes in intensity reveal the photophysical nature of the phenomenon. A similar behaviour has been observed for DMABN in PD, in diglyme as well as in PEO 400.

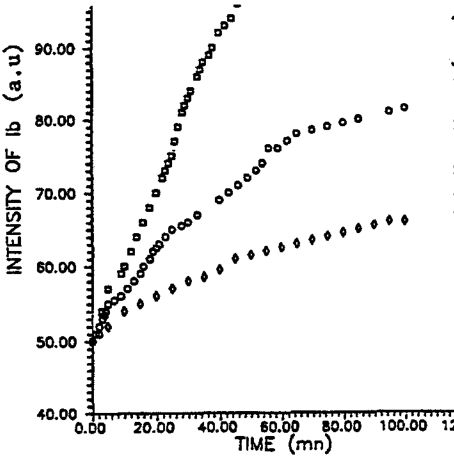


Fig.2: Effect of traces of water on time dependence of normal fluorescence intensity of deoxygenated solutions of DMABN in PPO (c≈10^{-5}M) :

OOO nontreated solutions

◊◊◊solution treated on molecular sieves

□□□ with addition of water(1M).

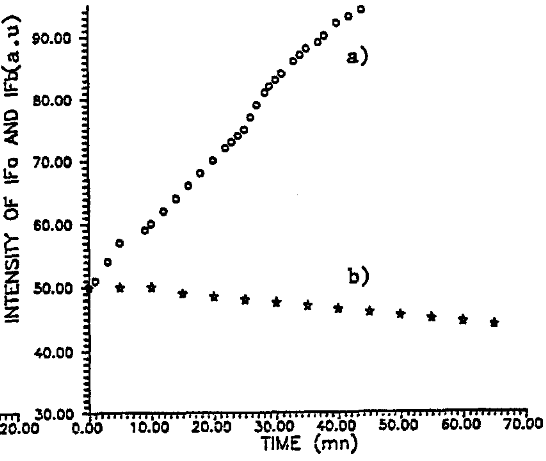


Fig.3: Time dependence of fluorescence intensities of DMABN in PPO under irradiation at 310nm -c ≈ 10^{-5}M :

a) normal fluorescence I_{Fb} analyzed at 350nm.

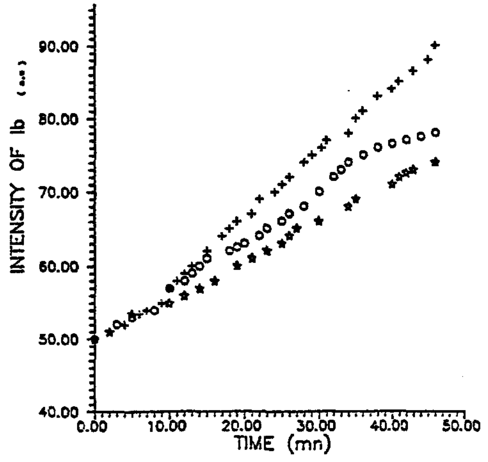
b)anormal fluorescence I_{Fa} analyzed at 450nm.

In order to get an insight into this new phenomenon, we have tried to investigate the influence of some parameters expected to affect the TICT formation.

Among these parameters, the role of water present as impurities in the medium seem to play a crucial importance in the appearance of the dual fluorescence. In previous papers (5), some of us draw evidence that flexible TICT molecules such as para-substituted N,N-dialkylanilines which are flat in the free state give rise to the anomalous fluorescence (fluorescence arising from the TICT state) when they acquire a twisted conformation in the ground state. This twisted conformation may be induced through hydrogen bonding either in hydroxylic media or by complexation with traces of water present in the solvent. By drying PPO 425 by means of molecular sieves, the normal emission of DMABN still increases under irradiation but the time-dependent evolution is less pronounced than in the nontreated polymer (Fig.2).In the same conditions, I_{Fa} only shows a slight intensity evolution (Fig.3).

Quenching of fluorescence by dissolved oxygen has also been suspected to play a role on the observed phenomenon. The investigations have been carried out on argonated solutions or on samples degassed by a repetitive freeze-pump-thaw cycle. Deoxygenated solutions behave under irradiation in a quite similar way than oxygenated ones.

Finally we have changed the number of photons reaching the sample by varying either the entrance slit of the excitation monochromator or the operating intensity of the xenon lamp. In both cases, I_{Fb} displays as depicted in Fig.4 a similar variation in the first part of the curve but levels in the long times of exposure to a different value than that obtained in the standard conditions.



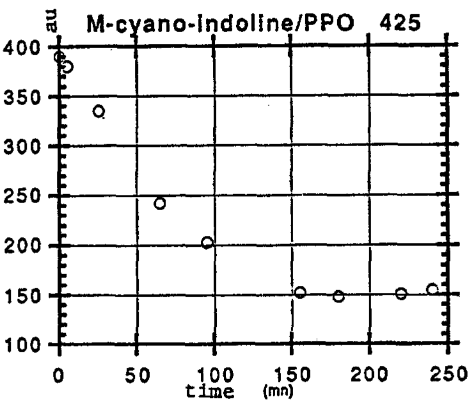


Fig.4:
Excitation density effect on the time dependence of the normal fluorescence I_{Fb}
of DMABN in PPO treated on molecular
sieves and deoxygenated, $c=10^{-5}$M.
***slits on excitation beam :4-10nm
ooo " " " 10-10 nm
+++ " " 20-20nm

Fig.5:
Relative time dependence on UV irradiation (310nm) of the fluorescence of 1-methyl-5-cyanoindoline in PPO ($c=10^{-5}$M).

Let us now examine the time-dependent emission behaviour of 1-methyl-5-cyanoindoline (MCI) which only gives rise to the normal fluorescence. Contrary to the case of DMABN, the fluorescence intensity of MCI in PPO

425 decreases under photoirradiation (Fig.5) and returns to its original value after several hours in the dark. A same behaviour is obtained for DMABN dispersed in PDMS. As previously mentioned (5), in this hydrophobic medium, the TICT formation does not occur and thus the fluorescence arising from the non-charge-transfer state (I_{Fb}) is only observed. Let us note that these time-dependent fluorescence intensities are accompanied in all the investigated matrices by a decrease of the optical densities of the absorption spectra. This change of the absorption could suggest an increase of the sample volume induced by ultraviolet irradiation. Effectively an increase of the volume would lead to an artificial decrease of the probe concentration explaining then the change of the optical density and consequently the decrease of the normal fluorescence of MCI in PPO 425 and of DMABN in PDMS.

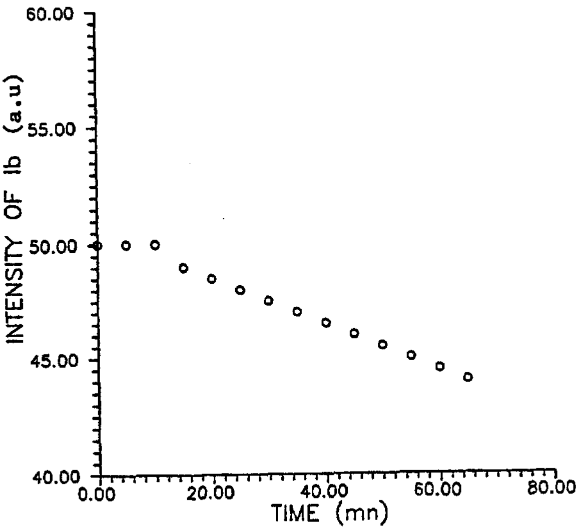


Fig.6 : Time dependence under UV irradiation (310 nm) of the fluorescence of DMABN in polydimethylsiloxane (PDMS) = 10^{-5}M.

Before giving tentative explanations for the phenomena occurring in the other media investigated in this present study, let us first recall that in the case of DMABN, the TICT formation only occurs when probe molecules are complexed through hydrogen bonding with the OH groups of the various matrices or with traces of water present as impurities in the media (5). But the normal fluorescence I_{Fb} arises not only from the above species but also from the noncomplexed DMABN molecules. As it was shown above, the presence of water enhances under irradiation the time-dependent evolution of the normal fluorescence intensity. A photoinduced volume change may lead to a rearrangement of water molecules around the TICT probe. This rearrangement could displace the equilibrium between noncomplexed DMABN and complexed DMABN molecules with water so as to increase the noncomplexed ones thus increasing the emission arising from these states- i.e., the normal fluorescence I_{Fb}. This possibility is only speculative and needs further investigations concerning especially the microviscosity change of the surrounding environment ofthe probe. Let us note that photoinduced changes in physical and chemical properties of polymer solutions have already been reported. Irie (6) has incorporated photosensitive chromophores into polymer systems in order to induce conformational transformation of the polymer chains leading to photostimulated changes in volume or viscosity of the medium.

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