The effect of high pressure and controlled stretching on the intramolecular twist of p-N-N-dimethylaminobenzylidenemalononitrile in polyvinylacetate and polyvinylchloride

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The effect of high pressure and controlled stretching on the intramolecular twist of *p*-N-N-dimethylaminobenzylidenemalononitrile in polyvinylacetate and polyvinylchloride

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Abstract

The effect of pressure and controlled stretching has been measured on both the steady-state and time-dependent emission from *p*-N-N-dimethylaminobenzylidenemalononitrile (DMABMN) in polyvinylacetate (PVA) and polyvinylchloride (PVCl). Using a model involving the radiative and non-radiative rates of dissipation of the excited state energy as well as the transfer rates between the planar and twisted excited states, one can predict the changes in steady-state emission from the time-dependent data for both the effect of pressure and controlled stretching. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

There exists a large class of molecules, frequently benzene derivatives, with donor and acceptor side groups with an essentially planar ground and excited state but which, in the excited state, can isomerize by twisting of one or more side groups with an accompanying charge transfer. These so-called TICT molecules have been extensively studied at atmospheric pressure (e.g., [1–12]) because of their potential technological and scientific applications. In particular, they have been used in polymeric matrices to probe the 'free volume' and other characteristics of

polymers. They may emit from one or both excited states. In the latter case, there is a large Stokes' shift for the twisted state emission.

A number of pressure studies have been made utilizing the steady-state emission [13–16]. In a recent Letter [17], we presented both steady-state and time-dependent emission data for julolidinemalononitrile (JDMN) and (DMABMN) in polymethylmethacrylate (PMMA). In both cases, only emission from the planar excited state is observed. We showed that the large change in steady-state emission intensity could be predicted from the time-dependent data.

In this study, we show that for DMABMN (Fig. 1) in polyvinylacetate (PVA) and polyvinylchloride (PVCl) there are significantly different effects of pressure on the steady-state emission in-

tensity which can be predicted from time-dependent data using the model presented in Fig. 2.

Recently we have developed a tool which permits us to apply a controlled linear stretch to a polymer at 1 atm. pressure making absorption and emission measurements at each degree of stretch [18]. We present results for both polymers and show that there is an effect of stretch on the barrier between the two excited states and that the steady-state results can be predicted from the time-dependent data.

2. Experiment

DMABMN, PVCl (58 000 MWt) and PVA (55 000 MWt) were purchased from Aldrich Chemical. The DMABMN was recrystallized. The polymers were used as purchased since they showed no emission at the exciting wavelength. The polymers and the DMABMN were dissolved in chloroform, evaporated slowly, and then were dried in a vacuum oven for two days at 40°C. For PVA which has a $T_g = 35$–40°C a layer of teflon was used in the evaporating dish to make it easier to cut samples. The concentrations used were 10^{-3} mol/mol of monomer for PVA and 2×10^{-4} mol/mol of monomer for PVCl.

The high pressure and stretching techniques and the optical system have been described in detail elsewhere [18–23]. We need only mention that the excitation for steady-state measurements is obtained via the 441.6 nm line of a He–Cd laser and that for the time-dependent decay the samples are excited by 100 fs pulses from a 76 MHz mode-locked Ti:Sapphire laser after frequency doubling to 405 nm with a BBO crystal. The detection system involves a Spex 0.27 m monochromator, a Tennelec 863 TAC, an Ortec 582 discriminator and Hamamatsu R1564
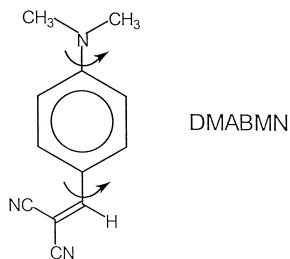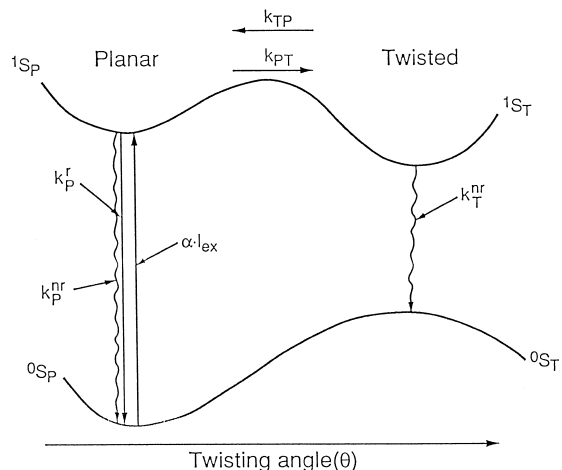

Fig. 1. Structure of DMABMN.

Fig. 2. Model for the processes involved in the ground and planar and twisted excited states.

MCP–PMT. The system has a basic exponential decay with a time constant of ~ 15 ps. However at an intensity of about one hundredth of the initial value there is a further complex component of about 100 ps lifetime.

3. Model

The model used to describe the process involved is shown in Fig. 2. Since there is only a single emission peak with a modest Stokes' shift, it is assumed that only non-radiative decay occurs from the twisted excited state. Information can be extracted from the time-dependent data from the following relationships:

$$\frac{I(t)}{I(o)} = \gamma(\exp - \beta_1 t) + (1 - \gamma)(\exp - \beta_2 t).$$

$$(1)$$

Then, by straightforward algebra [17], one can obtain:

$$k_P^r + k_P^{nr} + k_{PT} = k_P + k_{PT}$$
$$= \gamma \beta_1 + (1 - \gamma) \beta_2, \qquad (2)$$

$$k_T + k_{TP} = (1 - \gamma)\beta_1 + \gamma \beta_2, \qquad (3)$$

$$k_{PT} k_{TP} = \gamma \left[(1 - \gamma)(\beta_1 - \beta_2)^2 \right]. \qquad (4)$$
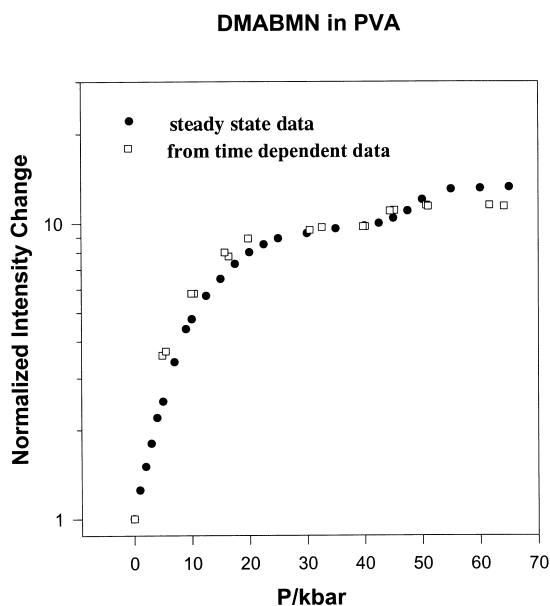
DMABMN in PVA

Fig. 3. The effect of pressure on the emission efficiency of DMABMN in PVA (●) from steady-state measurements and (□) predicted from time-dependent data.

The steady-state dependence can be predicted in terms of the above combinations of rate constants, for the pressure effect by:

$$\frac{I(p)}{I(o)} = \frac{\alpha(p)k_r(p)}{\alpha(o)k_r(o)}$$

$$\times \left[\frac{(k_{PT}k_{PT})(o) - \left(\frac{k_{PT}k_{TP}}{k_T + k_{TP}}\right)(o)}{(k_P + k_{PT})(p) - \left(\frac{k_{PT}k_{TP}}{k_T + k_{TP}}\right)(p)} \right]. \tag{5}$$

A corresponding equation can be written for the effect of controlled stretching. There are considerable data (e.g., Ref. [24]) to show that radiative rates over this pressure range in polymeric media are not significantly pressure dependent. Also the absorption peak does not change shape with pressure. The absorption at 441.6 nm shows very little pressure dependence. Thus, for the pressure experiments, the square-bracketed expression should relate the steady-state and time-dependent data.

For the stretching experiment, the fraction of the sample exposed either to the laser beam for excitation or the light from the monochromator in absorption varies with the stretch. The ratio of the area under the emission peak to that under the absorption peak I/A normalized to 1 atm. should be compared with the bracketed expression in Eq. (5), with L/L_o replacing (o) and $L/L_o = n$ (> 1) replacing (p).

4. Results and discussion

4.1. Pressure dependence

The pressure dependence of the steady-state emission intensity is given by the solid circles in Fig. 3 (in PVA) and Fig. 4 (in PVCl). In each case, it is the average of five loads with very small deviation $(< \pm 5\%)$. In PVA there is an increase by a factor of ~ 11 by 20 kbar, a tendency to level and a reproducible rise of ~ 10–15% between 45 and 50 kbar. In PVCl the increase is by a factor of ~ 30 with a leveling above ~ 25 kbar. The glass transition tem-
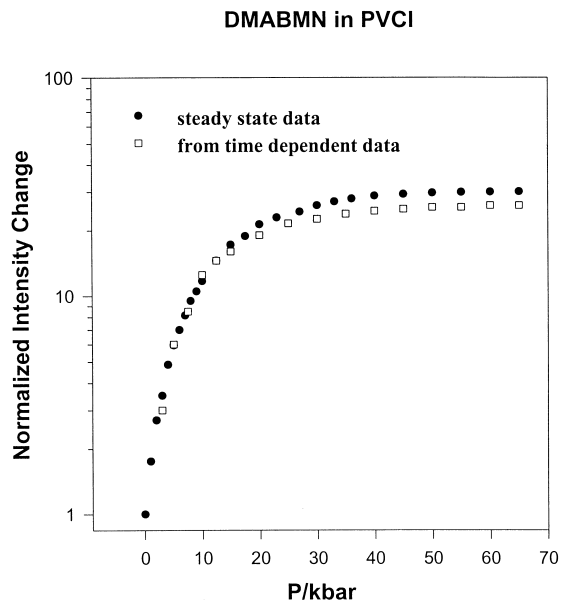
DMABMN in PVCl

Fig. 4. The effect of pressure on the emission efficiency of DMABMN in PVCl (●) from steady-state measurements and (□) predicted from time-dependent data.

perature T_g is ∼ 35–40°C in PVA and ∼ 100–110° in PVCl, for the materials used here. The PVA is relatively soft at room temperature and 1 atm. so that, even though T_g increases with pressure, it presents less resistance to the twist. The source of the small but definite rise at 45–50 kbar is not at present known.

The pressure results were reversible on release of pressure. The stretching results were not, although after several days they were restored ∼ 50% to the original value.

The changes in efficiency predicted from the time-dependent data (average of three loads) and Eq. (5) are given by the open squares. Note that for PVA the time-dependent data predict the small second rise, but in the range 40–50 kbar.

For PVCl at 1 atm., we could not get a satisfactory deconvolution of the instrumental constants which, as indicated under Section 2, was complex. At 3 kbar and above the data were treatable. The predicted data are normalized at 5 kbar. The agreement is quite satisfactory.

5. Controlled stretch

In Fig. 5 we present the ratio of the emission to the absorption intensity for PVCl (solid triangles) and PVA (solid circles) as a function of stretch using the square-bracketed expression in Eq. (5) with the notation $L/L_o = 1$ replacing $p = o$ and $L/L_o = n \, (n > 1)$ replacing p, one can predict the steady-state results from time-dependent measurements. The correspondence is shown by the open triangles for PVCl and the open squares for PVA. For PVCl at $L/L_o = 1$ we could not satisfactorily deconvolute the instrumental response but at $L/L_o = 2$ higher we could do so. (Both the steady-state and time-dependent data shown are the average of three loads.)

There are several points to be made:

1. There is a definite effect of controlled stretching on the barrier between the planar and twisted excited states. It is smaller than the effect of compression but not insignificant.
2. The effect in PVA is smaller than in PVCl for the reasons discussed above for the pressure data.
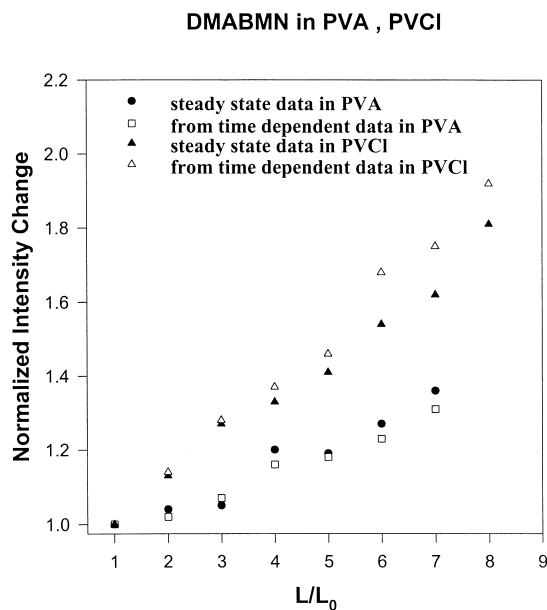
DMABMN in PVA , PVCl

Fig. 5. The effect of controlled stretch on the emission efficiency of DMABMN in PVA (●) from steady-state measurements and (□) predicted from time-dependent data; DMABMN in PVCl (▲) from steady-state measurements and (△) predicted from time-dependent measurements.

3. The time-dependent data predict quite quantitatively the steady-state results.

6. Conclusions

Compression of DMABMN in polymeric media (PVA and PVCl) increases the luminescence efficiency by increasing the barrier to the non-emitting twisted excited state. The increase in efficiency is greater in PVCl than in PVA since the latter is more pliable. One can predict the steady-state results from times-dependent measurements.

Controlled linear stretch of the polymers provides a smaller, but quite measurable, increase in steady-state emission which can be predicted from the time-dependent results. Again, the effect is larger in PVCl than in PVA and is predictable from the time-dependent measurements.

Acknowledgements

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