

NOTE

Application of Fluorescence Probe Technique for Determination of Glass-Transition Temperature of Polymers: Studies in Polyacrylonitrile (PAN)

A solvent cast film of polyacrylonitrile (PAN) incorporating the fluorescence probe *p-N,N*-dialkylaminobenzilidienemalononitrile (DABN) was studied for its fluorescence over the temperature range 30–180°C. It was observed that the thermal effects on the fluorescence of the dye molecule are dependent on the polymer matrix surrounding it. The rate of decrease in fluorescence of DABN shows a remarkable change after 110°C. This temperature corresponds to the glass-transition temperature (T_g) of the polymer PAN. The observed phenomenon is explained in terms of the change in free volume of the polymer when the polymer changes from a glassy state to a rubbery state at its T_g . Thus the fluorescence probe technique finds useful application for conducting thermodynamic studies of polymers.

INTRODUCTION

In recent years, among the various physical techniques the fluorescence probe technique to study various phenomena occurring in synthetic and natural polymers has become important.^{1–3} The binding of various fluorescence probe molecules to the polymer system is often accompanied by the changes in the decay times and emission characteristics of the probe. These changes have been used to provide useful information about the environment of the fluorescence probe and to follow the changes in conformation of the macromolecules. Because of the relatively short lifetime of fluorescence, usually on the order of 0.01–10 ns, this emission can be used to probe a variety of interesting characteristics of both large and small molecules. Several reviews have been published^{3–6} giving details of experimental procedures and types of information that can be obtained in polymers and micellar systems.

By the appropriate choice of luminescent probes, one can easily study the sequence of distribution in copolymers,⁷ subgroup motion,⁸ intermolecular reaction rates,⁹ ordering and orientation of polymer chains,¹⁰ rotational relaxation of chains, viscosity of macro- or microenvironment,¹¹ glass-transition temperature,^{2,6,7,12} and polymer compatibility,¹³ etc.

In the present work, an attempt has been made to study the effect of temperature on the fluorescence of probe molecules incorporated into a polyacrylonitrile (PAN) polymer matrix in film form using a dye belonging to the *p-N,N*-dialkylaminobenzilidienemalononitrile (DABN) series as fluorescent probe.

The photochemistry and photophysics of the DABN series of donor-acceptor dyes have been recently studied in detail by Loutfy et al.^{14,15} According to those studies these dyes act as excellent fluorescent probes for measuring the torsional rigidity of the surrounding polymer media and for studying the dynamic structural changes occurring over a wide temperature range.

EXPERIMENTAL

DABN was synthesized using a previous method^{13,14} and supplied in the pure form by Seshadri and coworkers of the Dyes Research Laboratory (Univ. Dept. of Chem. Technol., Matunga, Bombay). PAN was synthesized¹⁶ by the method of slurry polymerization. Solutions of PAN, DABN, and their mixture were prepared in dimethylsulfoxide (DMSO) (spectroscopic grade from M/S, S. D. Fine Chemicals, India, used without further purification).

Absorption spectra were recorded using a Bausch and Lomb Spectronic 1201 UV-visible absorption spectrophotometer. Fluorescence spectra were recorded using an Aminco Bowman spectrofluorimeter fitted with a front surface reflection accessory and using an IP28 photomultiplier tube as detector. The fluorescence spectral response was recorded using a Riken Denshi F-3G X-Y/t recorder. Necessary corrections were applied for the spectral responsivities of the grating/monochromator and photomultiplier tube.

Solvent cast films of PAN doped with the fluorescent probe DABN (concentration of the dye optimized for maximum fluorescence of about $1.8 \times 10^{-5} M/L$) were prepared¹⁶ using DMSO as solvent.

Fluorescence probe studies of solvent cast films were conducted by mounting the film on a semicircular, cylindrical brass holder with one face being flat, to which a strip heater was wound for heating the film.¹⁶ A 8085A microprocessor based programmable heater and temperature controller (from E.C.D., Bombay, India) was used.

A constant rate of heating of 3°C/min was maintained throughout the study. Under these conditions, the fluorescence of the dye incorporated into the polymer matrix was studied over a temperature range of 30–180°C.

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of the probe dye, DABN, in DMSO alone and also in PAN (0.2% concentration in DMSO) polymer matrix are shown in Figure 1. The dye exhibits an intense absorption band around 440 nm and a weak fluorescence emission around 514 nm. A noticeable observation is that both the absorption and fluorescence bandwidths of the probe in the polymer matrix in DMSO are identical to those obtained in DMSO alone indicating that the solvating situation of the probe molecule is very similar in both environments. In the present study, the fluorescence intensity of the probe was continuously monitored at 514 nm for a fixed excitation at 440 nm, as the temperature was steadily increased.

Figure 2 shows the effect of the temperature on the fluorescence of the probe molecule incorporated in the PAN film. The fluorescence emission, I_f , of the probe in PAN film decreases exponentially with increasing tem-

perature. This is a regular phenomenon of thermal quenching of a dye in any environment when the temperature of the system is gradually increased.¹⁷⁻¹⁹ An interesting observation is that the fluorescence decay profile shows a break at 110°C. As the temperature is raised above this value, the rate of decrease of the fluorescence intensity changes (i.e., the slope changes) and becomes faster than before. This temperature corresponds to the glass-transition temperature (T_g) of PAN.²⁰ The broken line represents the decay profile that was expected to be followed by the dye.

This behavior of the dye can be explained using the free volume concept. The free volume of the polymeric material increases with increasing temperature. Below the T_g , the polymer is in a glassy state and hence only subgroup motion can occur. Above the T_g , the polymer is in a rubbery state and additional free volume would be available due to the motion of a large polymer chain. The molecular relaxation of the first excited state, S_1 , of the probe molecule being directly dependent on the free volume, the increase in the free volume increases the rotational relaxation rate of the probe and hence decreases the fluorescence intensity. The observed discontinuity in the decay profile at 110°C corresponds to the transformation of PAN from a glassy state to a rubbery state. This suggests that the decrease in fluorescence intensity is not due to the

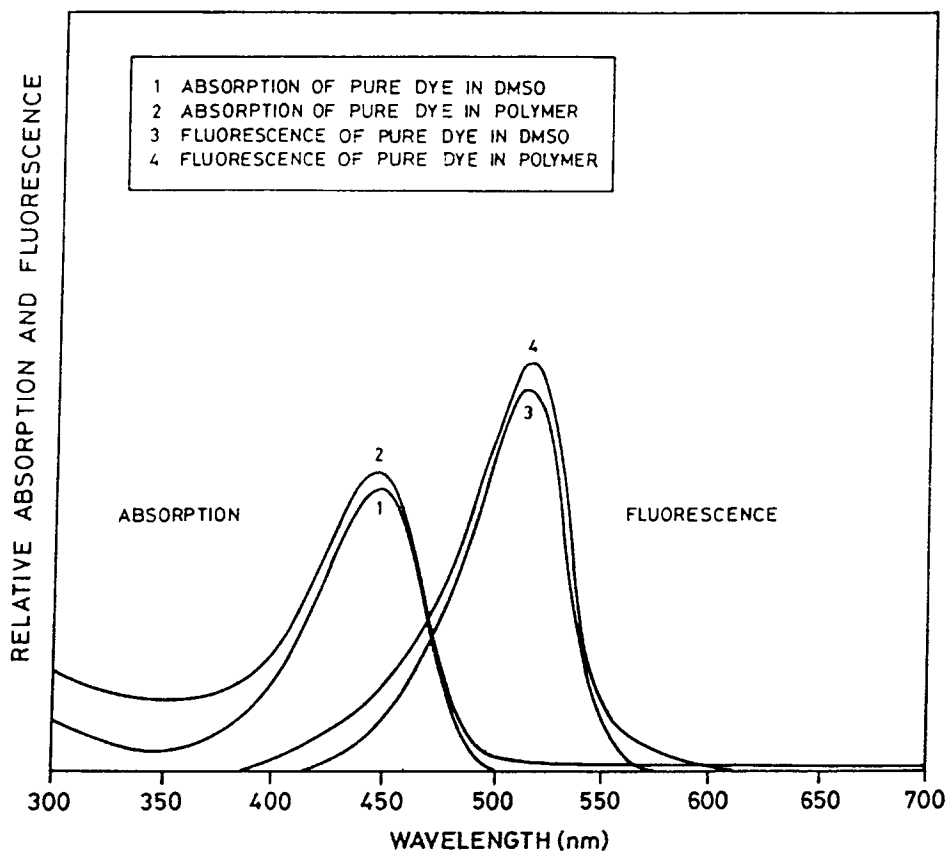


Figure 1 Absorption and fluorescence spectra of the probe in DMSO and in polymer matrix.

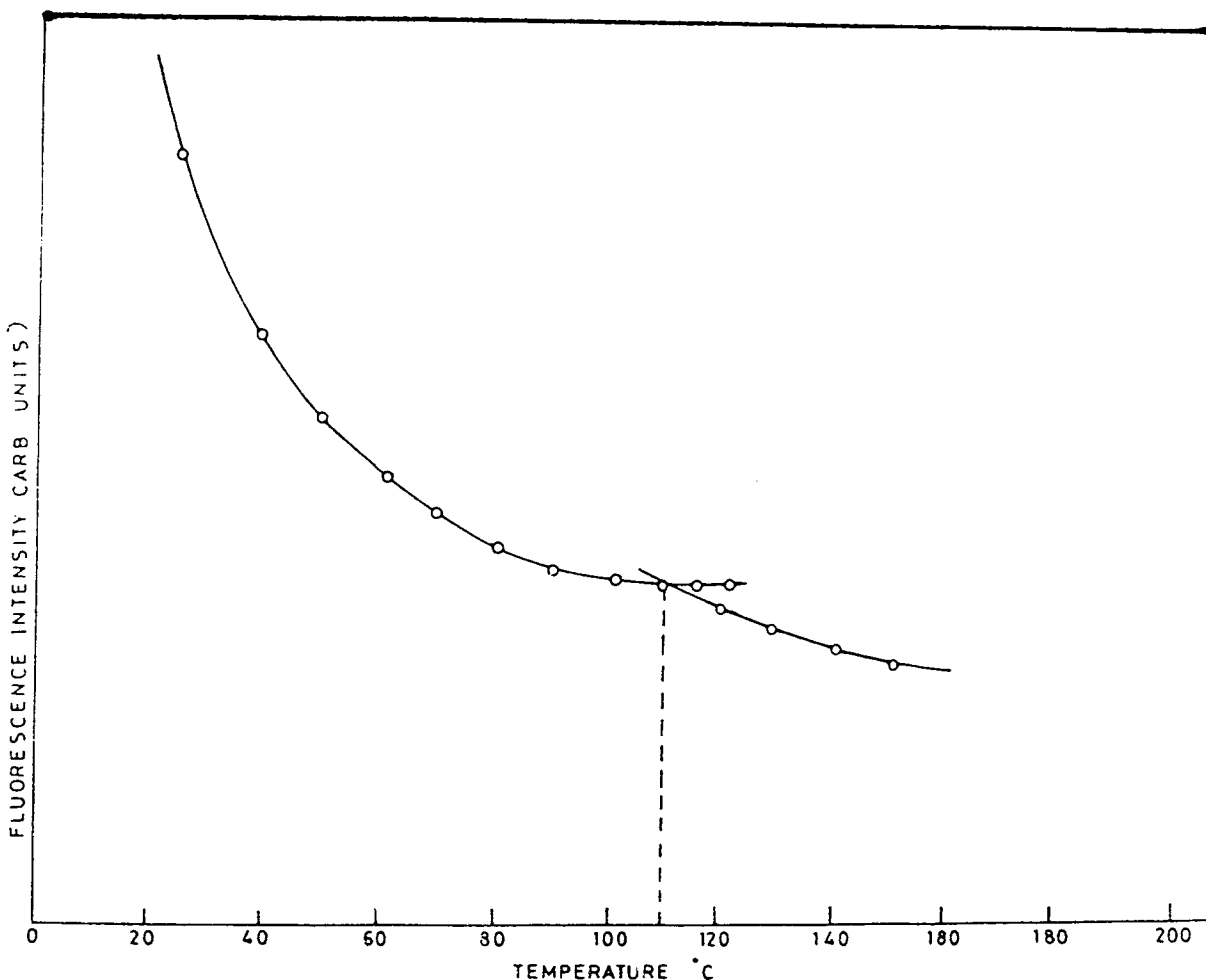


Figure 2 Dependence of fluorescence of probe on temperature in PAN film.

regular temperature dependent intermolecular decay or intermolecular deactivation of the molecule, but due to the structural relaxation of the polymer at its T_g . Similar observations have been made by Somersall and coworkers^{6,7} during their studies on polystyrene and a wide variety of its copolymers such as PS-PVK, PS-MVK, containing both ketone and naphthalene probes. They observed that I_f decreases by up to four orders of magnitude as the temperature of the films was increased from 77 to 300 K. The T_g of PMMA was recently determined by Loutfy¹² using solid films doped with DABN by adopting a similar procedure.

CONCLUSIONS

It can thus be concluded that the temperature dependent fluorescence probe study in polymer matrix is a potential method for determining the glass-transition temperature of several polymers. This technique can also be utilized in determining several other molecular relaxation dependent processes for a variety of polymers and copolymers.

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