Cinnamates. 5. Light-Sensitive Polycinnamates with Internal Charge Transfer. The Study of the Local Dielectric Constant and Viscosity

Jerzy Pączkowski

Department of Chemistry and Chemical Engineering, Technical and Agricultural University, Seminaryjna 3, 85-326 Bydgoszcz, Poland

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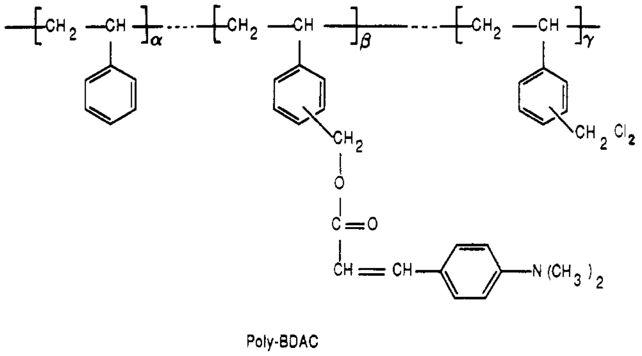
ABSTRACT: In this paper the spectroscopic properties of a light-sensitive polymer containing a pendant 4-(dimethylamino)cinnamate ester group are described. This specific cinnamate displays typical charge-transfer character in the absorption and emission spectra. On the basis of the Lippert theory and the Stokes shifts, the dipole moments for the ground and excited states have been calculated for the low molecular weight analogue of the tested polymer. Irradiation of polyBDAC in DMF solution showed that during irradiation the local dielectric constant and local viscosity are changing. With use of the Lippert theory and the relation between quantum yields for fluorescence and temperature, the local dielectric constant and the local viscosity of fluorescing molecules have been calculated.

Introduction

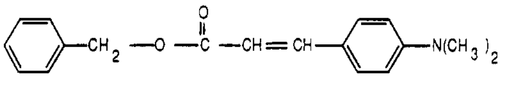
Luminescence spectroscopy provides a powerful technique for the study of polymer structure and mobility. The electronically excited states of molecules are sensitive to the molecular environment. Fluorescence methods have been used in the investigation of the macroscopic environment of a chromophore. A number of studies have been reported on the use of excimer or exciplex formation in polymeric systems to examine the local segment mobility and conformation,[1-7] phase separation and polymer compatibility,[8-13] or the study of polymerization.[14,15] All these applications of luminescence spectroscopy have been the subject of several reviews.[16,17]

Aromatic systems with strong donor and acceptor substituents often exhibit in polar solvents anomalous emission properties, e.g., large Stokes shift or dual luminescence. This type of emission is related to an internal charge-transfer process (ICT). The ICT process has important consequences for the photophysical properties of molecules. In rigid molecules, generally only configuration changes in the solvent cage are involved due to the dipole moment changes in the excited state. In this case an unusually large Stokes shift is observed, without major changes in the shape of the emission spectra. Verification came by the measurement of the excited-state dipole moment, via the theory of solvent shifts.[18-23] In the flexible molecules it was found that the following applied: (1) Dual fluorescence of numerous compounds is due to large structural changes in an adiabatic process involving the twist to perpendicular conformation with full separation of charge between donor (D) and acceptor (A). This class of excited species is called the twisted intramolecular charge-transfer (TICT) state[24-26] and is a very useful tool for the testing of polymeric systems.[27,28] (2) One fluorescence band is due to possible internal relaxation channels, involving many kinds of rotations around molecule bonds.[29] This system is also useful for the testing of polymeric systems,[7,8,30] because of its high sensitivity to viscosity and polarity of the surrounding solvent molecules.[18-23] Tazuke et al. emphasized[27,28] that the intramolecular donor–acceptor system is expected to be utilized as a fluorescence probe in the light-sensitive polymer studies.

Chart I



Poly-BDAC



BDAC

The light-sensitive polymer containing a 4-(dimethylamino)cinnamic acid ester moiety[31] is an example of a photopolymer-containing chromophore, which serves a dual function; e.g., it is able to photo-cross-link a polymeric system and exhibit typical spectroscopic charge-transfer properties.

This paper reports the changes that occur during continuous irradiation of the photophysical properties of the light-sensitive polymer containing a 4-(dimethylamino)cinnamic acid ester moiety.

Results and Discussion

The structure of the light-sensitive polymer studied is presented in Chart I. For the study, the monomeric equivalent of the light-sensitive group benzyl 4-(dimethylamino)cinnamate was also prepared.[31]

The absorption spectra of BDAC in the region 25 000–35 000 cm^{-1} are shown in Figure 1. The first strong transition ($\epsilon \approx 25\,000$) overlaps the weaker second band at about 32 000 cm^{-1} ($\epsilon \approx 10\,000$). The polarity of the solvent does not cause better resolution. This indicates that both bands are of the $\pi \rightarrow \pi^*$ type. Only one single fluorescence band is observed at room temperature for BDAC in all solvents (see Figure 2), nonpolar as well as

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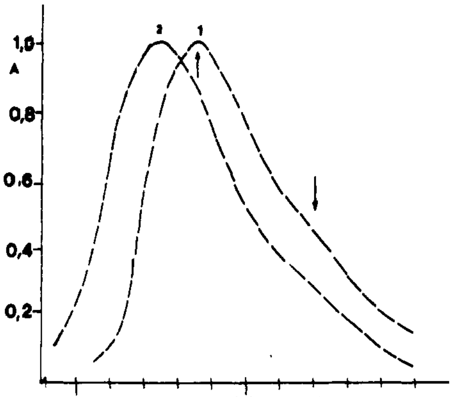

Figure 1. Absorption spectra of BDAC: (1) absorption spectra in isooctane; (2) absorption spectra in DMF.

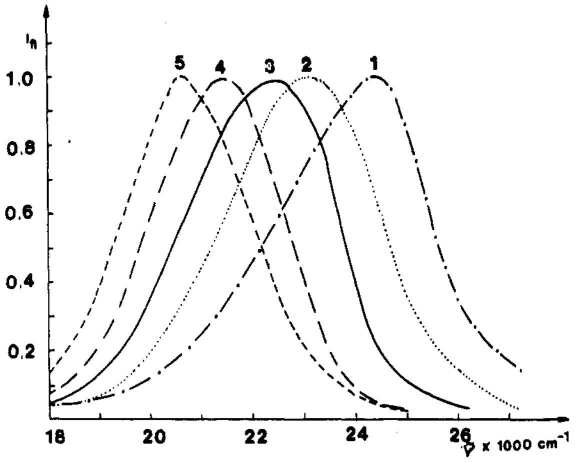

Figure 2. Steady-state fluorescence spectra for BDAC recorded in various solvents at λ_{ex} = 365 nm; (1) n-hexane, (2) toluene, (3) $CHCl_3$, (4) CH_3CN, (5) MeOH.

polar ones. The position of the fluorescence is strongly solvent dependent. This allowed us to establish the basic photophysical properties for BDAC.

The change of the dipole moment on excitation may be estimated according to Lippert[18] on the basis of Stokes shifts

$$\tilde{\nu}_A \pm \tilde{\nu}_{fl} = \pm m_{1,2}\left[\frac{\epsilon - 1}{2\epsilon + 1} \pm \frac{n^2 - 1}{2n^2 + 1}\right] + [\tilde{\nu}_A{}^0 \pm \tilde{\nu}_{fl}{}^0] \quad (1)$$

where $\tilde{\nu}_A{}^0$ and $\tilde{\nu}_{fl}{}^0$ represent the wavenumbers of unperturbed transitions and

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{\alpha^3 hc} \quad (2)$$

$$m_2 = \frac{2(\mu_e{}^2 - \mu_g{}^2)}{\alpha^3 hc} \quad (3)$$

where μ_g is the dipole moment of the ground state, μ_e is the excited-state dipole moment, and α is the Onsager cavity radius. Figure 3 shows the plots of $\tilde{\nu}_A \pm \tilde{\nu}_{fl}$ versus the proper solvent function. The data from Figure 3 and the ground-state dipole measurement results allowed us to calculate the excited-state dipole moment and the Onsager cavity radius. The results are presented in Table I.

In our earlier paper[31] we suggested that the polymeric chain forms a specific microenvironment for BDAC molecules. This supposition for the other kind of molecule indicating charge-transfer properties has been proven earlier by Tazuke et al.[27,28] In order to confirm this idea experimentally, the quantum yields of fluorescence emission for both BDAC and polyDBAC in various solvents were measured. The results obtained suggest that the polymeric chain strongly influences the photophysical properties of the BDAC molecule. Figure 4 shows, for the sake of comparison, the correlation between the quantum yields of fluorescence for BDAC and polyBDAC and the Reichardt and Dimroth intramolecular solvent polarity function E_T.[30,33,34] The results allow us to conclude that the state responsible for the fluorescence emission is surrounded by a less polar environment for the polymeric system compared to the free BDAC molecules. For the illustration of the photophysical behavior of the BDAC molecules, the quantum yield of fluorescence and the position of the fluorescence center gravity wavenumber (meant as a center of fluorescence band half-width) as a function of the dielectric constant of various DMF–toluene mixtures have been established. Results are shown in Figures 5 and 6. It can be seen from Figure 5 that the fluorescence quantum yield of BDAC decreases slowly at small concentrations of toluene (ϵ = 2.38) in DMF and rapidly at low concentrations of DMF (ϵ = 36.5) in toluene.

Continuous irradiation of polyBDAC in DMF solution causes changes in the electronic absorption spectra (Figure 7) and fluorescence emission spectra (Figure 8). The changes in the electronic absorption spectra for polyBDAC upon irradiation are typical for this type of light-sensitive polymer. More interesting are the effects in the fluorescence emission spectra. As Figure 8 shows, irradiation of polyBDAC in DMF solution causes an extension of the fluorescence band to the short-wavelength area. This is interpreted as a result of decreasing microenvironment polarity (see curve 3 in Figure 8) for BDAC molecules.

Figure 10 summarizes all observed changes in the fluorescence spectra for polyBDAC in DMF upon irradiation at 313 nm. There are two important features of the observed changes. The first is related to the shape and position of the fluorescence curve and the second to the increase of the fluorescence quantum yield. On the basis of the schematic presentation of the solvent microenvironment for BDAC molecules (see Figure 9) and results shown in Figure 10, one can conclude that, during irradiation of polyBDAC, the microenvironment polarity for BDAC is decreasing.

The Lippert equation was used to calculate the local polarity for BDAC. To calculate the position of the fluorescence gravity center, wavenumber has been used. The unperturbed $\tilde{\nu}_A{}^0 - \tilde{\nu}_{fl}{}^0$ value for this type of analysis was established to be equal to 310 cm^{-1}. The results are summarized in Table II.

The θ value is understood as an average degree of filling by the polar solvent molecule of the solvent sphere around the BDAC molecule.

$$\theta_2 \equiv \theta = Z_2/(Z_1 + Z_2) \quad (4)$$

Z_1 and Z_2 represent the average number of nonpolar and polar solvent molecules. The local dielectric constant is described by the following equation:

$$\epsilon_L \approx \epsilon_1\theta_1 + \epsilon_2\theta_2 \quad (5)$$

Combination of eqs 4 and 5 gives

$$\theta = (\epsilon_L - \epsilon_1)/(\epsilon_2 - \epsilon_1) \quad (6)$$

As shown in Table II, there is very good agreement on the values for local polarity (calculated and experimental ones from Figure 6) obtained for nonirradiated polyBDAC. Dissimilarities become apparent after irradiation.

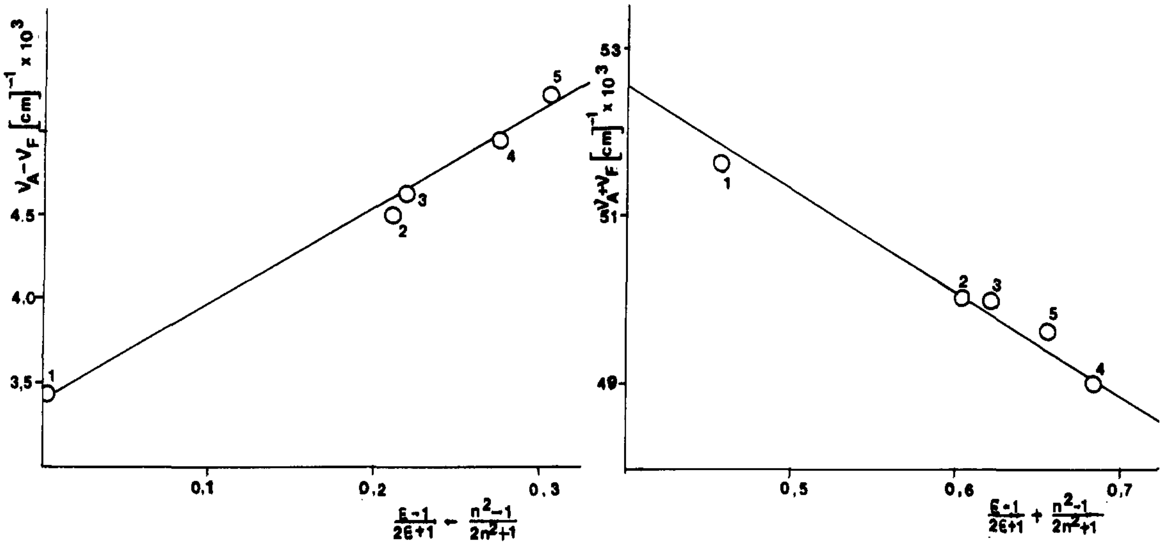

Figure 3. Plots of $\tilde{\nu}_A - \tilde{\nu}_{fl}$ and $\tilde{\nu}_A + \tilde{\nu}_{fl}$ versus solvent functions for BDAC: (1) benzene, (2) THF, (3) CH_2Cl_2, (4) DMF, (5) MeCN.

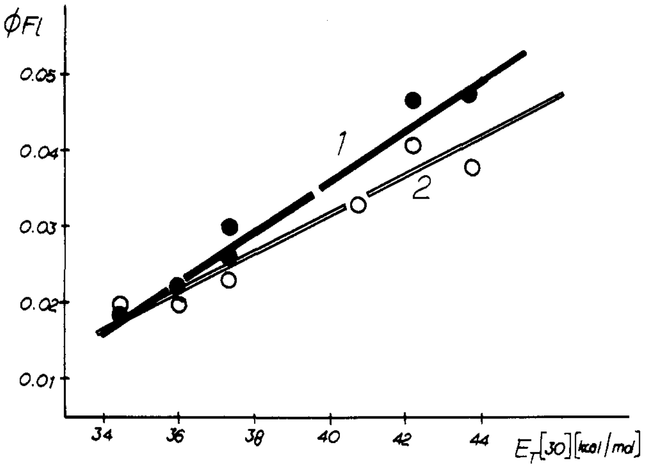

Figure 4. Fluorescence spectra quantum yield as a function of the empirical solvent parameter E_T:[30] (1) BDAC, (2) polyBDAC.

Table I
Basic Photophysical Properties of Benzyl 4-(*N*,*N*-Dimethylamino)cinnamate (BDAC)

μ_g, D	m_1, cm^{-1}	m_2, cm^{-1}	μ_e, D	α^3, Å^3
6.3	5.6 × 10	1.07 × 10	22.4	156

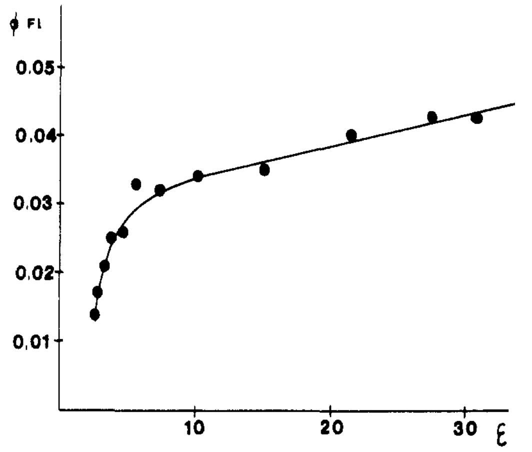

Figure 5. Fluorescence quantum yield as a function of the polarity of a DMF-toluene mixture.

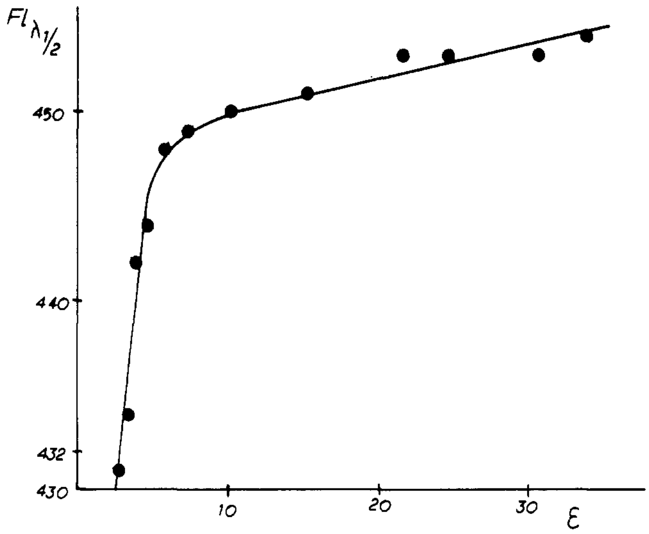

Figure 6. Dependence of the fluorescence center of gravity vs the solvent polarity.

However, the calculated results are more reasonable, because the $\epsilon = 4$ (from Figure 6) indicates a nearly nonpolar environment.

The second significant change recorded in Figure 10 is the change in the fluorescence quantum yield for an irradiated polyBDAC solution. Analysis of the data from Figure 5 and 6 and Table II indicates that the quantum yield for BDAC molecules should decrease instead of increase. For the explanation of this phenomenon, the increase of local viscosity is assumed to be the reason for the luminescence intensity increase. For illustration the quantum yield measurement results for BDAC in various solvents are presented in Table III.

One noticeable feature is obvious in Table III. For the essentially similar toluene ($\epsilon = 2.55$) solution and polystyrene ($\epsilon = 2.38$) film, the quantum yield of fluorescence in polystyrene is 3 times higher than that in toluene solution.

From the Lim, Laposa, and Yu[35] study, it is known that the fluorescence yields are related to the temperature by the following equation:

$$1/\phi - 1 = ke^{-E_1/RT} \quad (7)$$

A similar relation was observed for BDAC in various DMF-toluene solutions (various ϵ). This is shown in Figure 11. For the flexible molecule the value of E_1 varied consid-

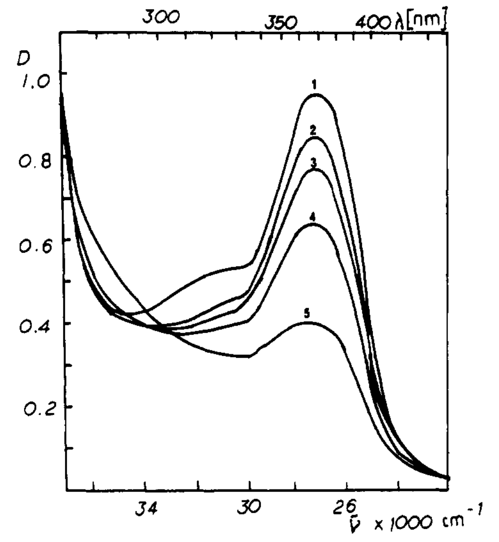

Figure 7. Changes of the absorption spectra of polyBDAC in DMF solution upon continuous irradiation at 313 nm: (1) before irradiation, (2) 24 min of irradiation, (3) 48 min, (4) 96 min, (5) 200 min of irradiation.

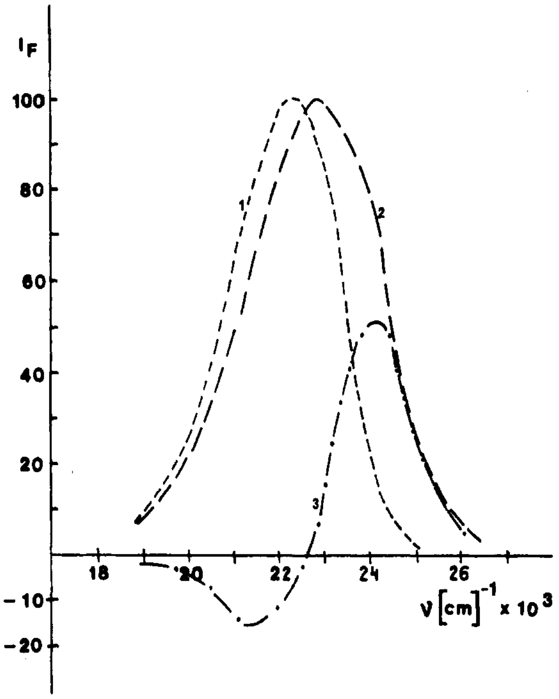

Figure 8. Changes of the fluorescence spectra of polyBDAC in DMF solution upon continuous irradiation at 313 nm: (1) before irradiation, (2) after 60 min of irradiation, (3) subtraction of the curve before irradiation from the curve after irradiation.

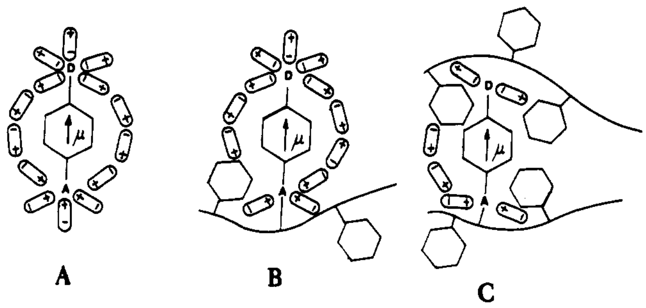

Figure 9. Conceptual comparison of the Onsager solute–solvent interaction: (A) free BDAC molecule, (B) BDAC molecule covalently bound to the polymeric chain, (C) BDAC molecule covalently bound to the photo-cross-linked polymeric chain.

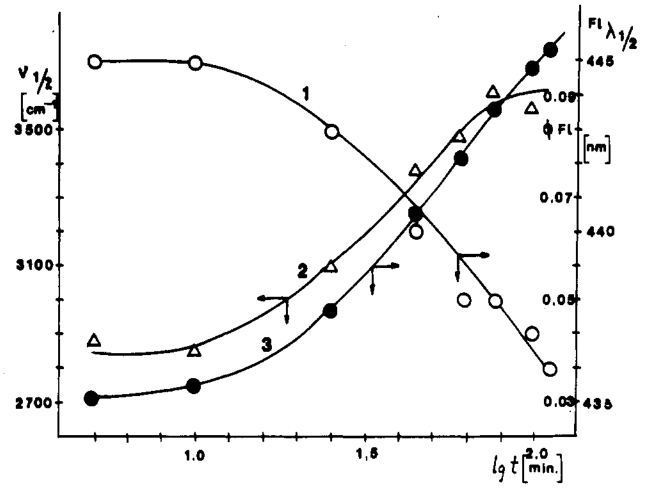

Figure 10. Changes of the photophysical properties of polyBDAC upon continuous irradiation at 313 nm: (1) position of fluorescence gravity center, (2) the fluorescence band half-width, (3) fluorescence quantum yield.

Table II
Local Dielectric Constants of Irradiated PolyBDAC in DMF Solution

t, min	$\lambda_{\bar{\nu}_{1/2}}$,[a] nm	ϵ(calc)	ϵ(exptl)	θ
0.0	452	19.1	20.5	0.42
25	448	14.6	6.0	0.36
45	442	11.5	4.5	0.26
60	438	9.8	4.0	0.21

[a] $\lambda_{\bar{\nu}_{1/2}}$ is the wavelength of the fluorescence gravity center.

Table III
Influence of Solvent Parameters on Fluorescence Quantum Yield for BDAC

solvent	ϵ	ϕ_{fl}
toluene	2.38	0.014
polystyrene film	2.55	0.040
DMF	36.7	0.048

erably and is in fact close to the value of ΔE characterizing variation of solvent fluidity with temperature[36]

$$\frac{1}{\eta} = \frac{1}{A} e^{-\Delta E/RT} \tag{8}$$

where η is viscosity. If $E_1 \approx \Delta E$, then

$$\eta = K \frac{\phi}{1 - \phi} \tag{9}$$

where $K = kA$.

The calculation of microscopic viscosity is based on the following simplifications: (1) The macroscopic viscosity does not influence the microscopic viscosity, at least at low concentrations of polymer. (2) The fluorescence emission efficiency is limited by the local viscosity. (3) The fluorescence intensity is governed by the local dielectric constant.

It is necessary to distinguish the microscopic (local) and macroscopic (solution) viscosities. The differences between these two viscosities are well-known.[17,38] The microviscosity is the viscosity measured by some suitable probe rather than the macroscopic viscosity, which is observed by a conventional method. The local viscosity is a combination of the effects due to solvent and its interaction with segments of the polymer chain adjacent to the relaxing chromophore. The differences between the local and macroscopic viscosities are illustrated by Nishijima and co-workers[39,40] by applying the depolarization of fluorescence measurements of the local viscosity

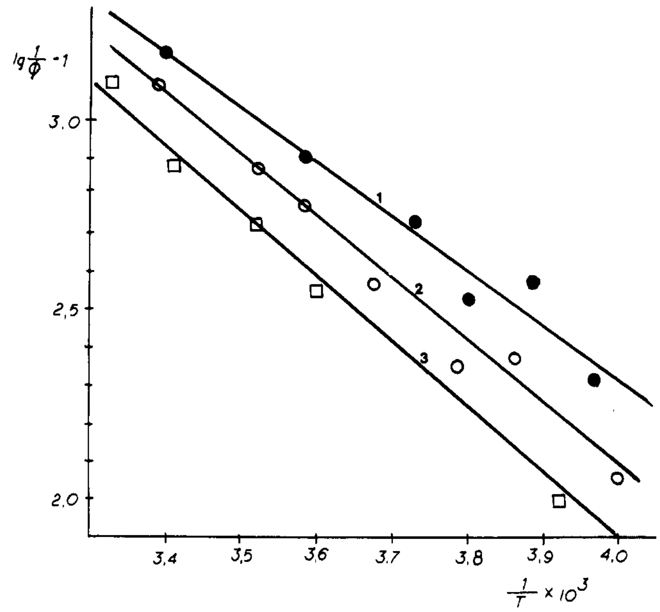

Figure 11. Correlation between the fluorescence quantum yield for BDAC and the temperature in various DMF–toluene mixtures: (1) ϵ of the solvent of about 12, (2) ϵ of about 15, (3) ϵ of about 10.

and the melt viscosity. In particular, it is deduced that the local viscosity is related to the movement of segments of the polymer molecule of about molecular weight 2000, e.g., about 60 ethylene units. It was also shown that the local viscosity changes linearly up to a certain degree of polymerization and beyond a certain degree of polymerization is independent of molecular weight, while the melt viscosity is dependent upon the degree of polymerization.

For a polymeric solution the more recent work[27,28,40,41] illustrates the difference between the local and macroscopic viscosity. It has been known for some time[24,42,43] that 4-(dimethylamino)benzoate (DB) exhibits double fluorescence. The short wavelength (b^*) band is believed to be due to a coplanar molecule while the long wavelength (a^*) band originates from a molecule with a perpendicular conformation, which causes a full charge separation. It has been shown that the following occur: (i) the relative intensities of the a^* and b^* bands are different for the free BD molecule and for the DB attached to the polymeric chain; (ii) below room temperature for the polymeric system the ratio of the emission intensities of the a^* and b^* bands is kinetically controlled while, in the monomeric analogue, an equilibrium has been reached. Therefore, it was concluded that the twisting of the dimethylamino group is strongly impeded when it is attached to the polymer; (iii) it was found that the activation energy for the formation of the twisted form remains constant up to polymer concentration 75 wt %; (v) polymer side chains control the ground-state conformational distribution of the DB chromophore as demonstrated by the red edge effect (REE) and by the broadening of the absorption spectra.

All these above-mentioned properties are easy to explain by applying the local viscosity concept.

On the basis of the previously mentioned approximations, the A values were measured for proper toluene–DMF mixtures, and k values were calculated from results presented in Figure 11. The final results of the local viscosity calculations are summarized in Table IV.

As can be seen from Table IV, irradiation of polyBDAC in DMF solution causes an increase of the local viscosity. Assuming the initial microviscosity as a viscosity of pure DMF (η = 0.92 cP at 20 °C), one can conclude that after irradiation the local viscosity is increased up to 18.2 cP (close to the viscosity of ethylene glycol at 20 °C).

Table IV
Local Viscosities of Irradiated PolyBDAC in DMF Solution

t, min	ϵ_1	ϕ_{fl}	K	η, cP
25	15	0.048	0.85 × 10	4.3
45	12	0.067	1.50 × 10	10.8
60	10	0.090	1.84 × 10	18.2

Experimental Section

PolyBDAC and BDAC were prepared by using a procedure described earlier.[31]

All solvents were spectroscopic grade (POCh Poland, Merck) and used without further purification. Toluene was shaken with 5% of its volume of concentrated sulfuric acid for 10 min, allowed to stand for 5 min, and separated. The operation was repeated three times. The toluene was then shaken with water and diluted with sodium hydroxide until fresh portions were no longer colored. Finally the solvent was distilled.

The electronic absorption spectra were recorded with a UV–vis M40 Carl–Zeiss Jena spectrometer. The steady-state luminescence measurements were carried out by using a multifunctional modular Cobrabid MSF 102 spectrofluorimeter. Relative quantum yields were measured by using quinine sulfite as a standard.

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