Environment effects on the optical properties of some fluorinated poly(oxadiazole ether)s in binary solvent mixtures

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ABSTRACT

The solvatochromic behavior of some fluorinated poly(oxadiazole ether)s was studied using UV–vis absorption and fluorescence spectroscopy in neat solvents and in their solvent mixtures at several ratios of cosolvents. Quantitative investigations of the spectral changes caused by solvent polarity were discussed using the Lippert-Mataga, Bakhshiev and Kawski–Chamma–Viallet polarity functions. Repartitioning of cosolvent between local (solvation shell) and bulk phase was investigated by means of a solvatochromic shift method in chloroform–N,N-dimethylformamide ($CHCl_3$/DMF) and chloroform–dimethyl sulfoxide ($CHCl_3$/DMSO) solvent mixtures. Solvatochromic properties in the binary solvent environments were predominantly influenced by the acidity and basicity of the solvent systems. The fluorescence quenching process by nitrobenzene was characterized by Stern–Volmer plots which display a positive deviation from linearity. This was explained by static and dynamic quenching mechanisms.

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1. Introduction

1,3,4-Oxadiazole derivatives present a specially interest due to their different physicochemical properties and their potential use as electron transporting materials or electroluminescence materials in organic light emitting diodes (OLEDs) [1–5]. Due to their optoelectronic properties [6], high thermal stability [7,8] and mechanical properties [8], fluorinated poly(oxadiazole ether) derivatives have an important role in materials science. Optical properties of solutes in different environments are sensitive to the nature of the solvent, solute–solvent and solvent–solvent interactions. Investigations in mixed solvent media are often used to modify molecular environment in order to gradually change the system properties (dielectric constant, ε, refractive index, n, dipole moment, density and acid–base or acceptor–donor properties). Also, the work in the binary solvent mixtures permits to researchers to choose and to develop systems that are more "environment-friendly" or "green" solvents in composition. The study of local compositions in complex systems (binary liquid mixtures) is useful for understanding the nature and strength of molecular interactions between the component molecules.

The most basic photophysical properties and the solvatochromic behavior of some poly(oxadiazole ether) derivatives in pure solvent solutions and preferential solvation in solvent mixtures have been widely studied by absorption and fluorescence spectroscopy [9,10]. However, solvatochromic behavior and information about local compositions of a dissolved solute in different binary solvent mixtures have been rarely found in the literature. Hence, there is considerable interest in the analysis of effect of solvent environment in binary mixture systems on the optical properties.

In this regard, the effect of solvent environment on the photophysical behavior of some fluorinated poly(oxadiazole ether)s (Fig. 1) in pure solvents and their binary mixtures ($CHCl_3$/DMF and $CHCl_3$/DMSO) was investigated. The solvatochromic data will be then used to estimate the local concentration of the polar component (DMF and DMSO in our cases) that surrounds the solute molecules and correlates with photophysical properties. To evaluate quantitatively the intermolecular interactions, the spectral data were correlated with Catalán parameters of the binary solvent mixtures. Quenching studies of two fluorinated copolymers (Co-6F and Co-9F) excited states by nitrobenzene (NB) have also been performed to obtain information about interactions between solutes and surrounding media.

2. Experimental

4,4′-(Hexafluoroisopropylidene)diphenol, **1a**, and 9,9-bis(4-hydroxyphenyl)fluorene were provided from Sigma Aldrich and used as received. N-methyl-2-pyrrolidone (NMP) was dried over phosphorus pentoxide and distilled under vacuum. 1,1-Bis(4′-hydroxyphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane, **1b**, and 1,1-bis
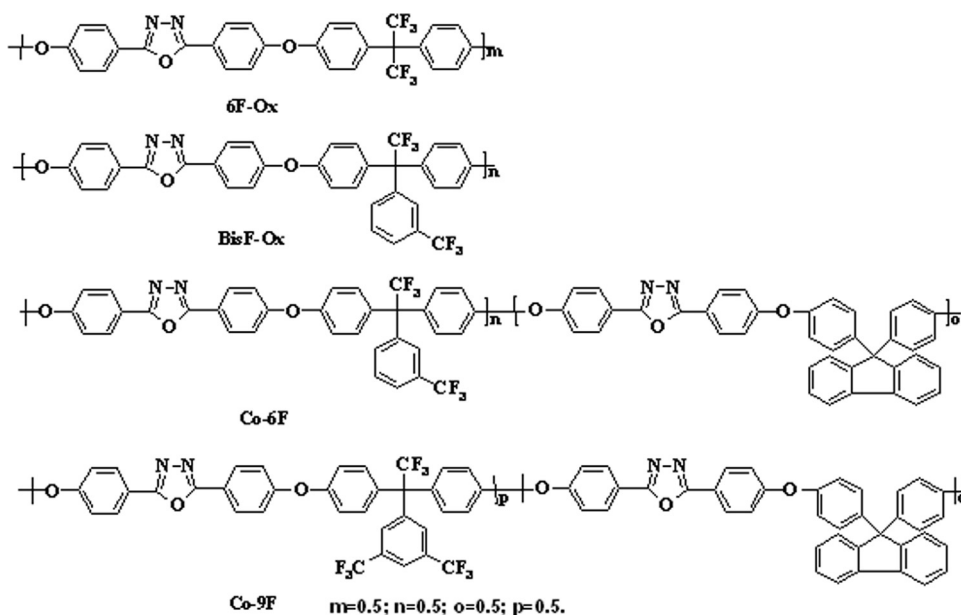
Fig. 1. Chemical structure of fluorinated poly(1,3,4-oxadiazole-ether) derivatives.

(4′-hydroxyphenyl)-1-(3′,5′-ditrifluoromethylphenyl)-2,2,2-trifluoroethane, **1c**, were prepared according to previously published methods [8]. 2,5-Bis(p-fluorophenyl)-1,3,4-oxadiazole was prepared from p-fluorobenzoic acid and hydrazine hydrate, in polyphosphoric acid, according to the literature [11].

Fluorinated poly(1,3,4-oxadiazole-ether)s, 6F-Ox and BisF-Ox were prepared by the conventional aromatic nucleophilic substitution technique of 2,5-bis(p-fluorophenyl)-1,3,4-oxadiazole with fluorinated bisphenols **1a** or **1b**, respectively. Two fluorinated copolymers, Co-6F and Co-9F, were obtained by the same synthetic method, using 2,5-bis(p-fluorophenyl)-1,3,4-oxadiazole and mixtures of equimolar amounts of **1b** or **1c** and 9,9-bis(4-hydroxyphenyl)fluorene, respectively. The polycondensation reactions were carried out at elevated temperature in NMP, in the presence of anhydrous potassium carbonate. The nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to high performance, high temperature poly (aryl-ether)s. The oxadiazole moiety in 2,5-bis(p-fluorophenyl)-1,3,4-oxadiazole acts as an activating group: it can accept a negative charge and lowers the activating energy for the displacement of the p-substituted fluoro group through a Meisenheimer complex, analogous to conventional activating groups such as ketone or sulfone [9,12].

The solvents were of spectroscopic grade. UV–vis absorption spectra were recorded on a Shimadzu 3600 spectrophotometer and fluorescence spectra with a PerkinElmer LS55 fluorospectrometer. The emission spectra were measured by exciting the sample at its absorption maximum. Absorption and emission spectra were recorded in pure solvents and in $CHCl_3$/DMF or $CHCl_3$/DMSO mixtures using different solvent ratios. The binary mixtures were prepared by carefully mixing volumes of each solvent, in the following ratios: 1:5, 2:4, 3:3, 4:2 and 5:1, at room temperature. The multilinear regression was performed with Origin Pro7.5 (Microcal software). For the studies on fluorescence quenching process, 2.5 mL of Co-6F or Co-9F in DMF solution was placed in a quartz cuvette and titrated with different amounts of NB solution ($c = 4.7 \times 10^{-3}$ mol L^{-1}). The concentration of Co-6F and Co-9F in DMF solution, used in the quenching studies was 10^{-5} M.

3. Results and discussion

3.1. Solvent mixtures. Characterization of molecular microenvironments

Effect of binary solvent systems ($CHCl_3$/DMSO and $CHCl_3$/DMF) on the absorption and fluorescence emission of 6F-Ox and BisF-Ox was previously presented [9]. Fluorinated copoly(1,3,4-oxadiazole) ethers (Co6F and Co9F) containing the same number of CF_3 groups like fluorinated poly(1,3,4-oxadiazole) ethers (BisF-Ox and 6F-Ox) [9] showed similar absorption and fluorescence spectral pattern. The wavenumbers of the absorption maxima, $\tilde{\nu}_{abs}^{max}$, emission maxima, $\tilde{\nu}_{em}^{max}$ and calculated Stokes shift values, $SS = \tilde{\nu}_{abs}^{max} - \tilde{\nu}_{em}^{max}$, (cm^{-1}) for studied samples in pure solvents and binary mixtures of $CHCl_3$ and DMF or DMSO are summarized in Table 1.

Using the experimental results obtained for the absorption and emission maxima wavenumbers, the corresponding Stokes shifts (SS) values were calculated (Table 1). The smaller values are found in $CHCl_3$ (nonpolar solvent) comparatively to those obtained in more polar solvents (DMF, and DMSO). Stokes shift values become larger together with the increase of solvent polarity of binary mixtures (Table 1) and indicate that the excited-state geometry can be different from that of the ground state.

The spectral data (Table 1) permits to study the local environments of these compounds in binary solvent mixtures. From values of the Stokes shifts (SS) in pure solvent and their mixtures (Table 1), the local mole% of the polar cosolvent (%LMPC) around a solute in binary solvent mixture [13] as estimated by the following equation:

$$\%LMPC = \frac{(SS_{polar} - SS_{mixture})}{(SS_{polar} - SS_{mixture}) + (SS_{mixture} - SS_{nonpolar})} \quad (1)$$

where the subscripts "nonpolar", "polar", and "mixture" denote the Stokes shift (in cm^{-1}) in the pure nonpolar, polar and binary solvent mixture, respectively.

In mixed solvent systems preferential solvation occurs when the solute microenvironment has more of one solvent than the other, in comparison to the bulk composition (Fig. 2). The ideal