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PHOTOPHYSICS OF LASER DYES IN AQUEOUS POLYMER MEDIA

by

G. Jones, II, M. A. Rahman, and M. S. Farahat

Department of Chemistry
Boston University
Boston, Massachusetts 02215

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INTRODUCTION

The present research program encompassed the 12-month period, April 1, 1989 - March 31, 1990, and is related to earlier work at Boston University concerning the photophysical and photochemical properties of laser dyes, funded by ONR during 1978-82. Experimental work related to the program has continued during the past year with funding through a grant from the Army Research Office (DAAL03-89-K-0162).

Objectives of the program included the study of the effects of unusual medium on the fluorescence properties of a series of coumarin laser dyes. Special attention was given to the solubilization of the commonly available dyes in water with the aid of the polyelectrolyte, poly(methacrylic acid) (PMAA). An important strategy was the isolation of dye species in the "hypercoils" associated with the polyelectrolyte for moderately acidic pH. Under these conditions in which the acidic carboxyl side chains are not ionized, the microenvironment of bound dye species is relatively "dry" and viscous. These environments for solubilized dye are important in terms of the accompanying increases in dye emission yield, lifetime, and polarization. Dye materials are also less susceptible to photodegradation since they are sequestered in polymer interiors away from adventitious quenchers. Comparison was made in the study of coumarin dye bound to PMAA through the attraction to the hydrophobic interior sites or, alternatively, through covalent attachment to the polyelectrolyte. In the latter case, dye remains bound in the polymer domain through the conformational transition in which of globular, compact polymer is changed to a charged rod-like structure.

The present results are also important in terms of the ability of dye fluorophores to "report" (through changes in photophysical properties) on the progress of folding of the polymer and the nature of hypercoil interiors for the fully folded state. The results provide not only some direction in terms of the development of new resilient aqueous media for dye laser action, but also in the use of absorption and emission properties of organic chromophores in polymeric hosts in applications in microelectronics or photonics.

ACHIEVEMENTS OF THE PROGRAM: A SUMMARY

The photophysical properties of a series of coumarin laser dyes in an aqueous polyelectrolyte medium have been measured. The binding of the dyes to poly(methacrylic acid) (PMAA) in water has been demonstrated through the observation of dramatic blue-shifts of fluorescence bands and increases in emission quantum yield and lifetime and polarization. The systematic changes in fluorescence properties reveal that the hydrophobic dyes reside in relatively non-polar (dry) and highly viscous microdomains at lower pH values for aqueous PMAA solutions in which a highly compact conformation of the uncharged polyelectrolyte is important. The transition from the hypercoiled conformation (pH 4-8) can be followed readily by reference to coumarin fluorescence wavelength, quantum yield and polarization data. Photophysical measurements are also reported for a coumarin moiety that has been covalently attached to the PMAA backbone. For the covalently bound dye, more subtle alteration of fluorescence properties are found over the entire range of pH examined, reflecting the close association with both compact and elongated (charged) forms of PMAA.

The results of the work have been reported in one published conference proceedings and two oral presentations. An additional paper is now in preparation. During the funding period, the Principal Investigator completed a review concerned with the photochemistry of laser dyes that appeared in "Dye Laser Principles: With Applications."

PERSONNEL

Principal Investigator: G. Jones, II, Professor of Chemistry and Department Chairman, Boston University

Research Assistants - Graduate Students:

M. A. Rahman (B. Sc., M. Sc., University of Dhaka), thesis defense, September, 1991

M. S. Farahat (B. S. Renssalear Polytechnic Institute, M. S. Worchester Polytechnic Institute), continuing in Ph. D. program

PAPERS AND CONFERENCE REPORTS

1. G. Jones II and M. A. Rahman, “Novel Environments for Laser Dyes”, Proceedings of the International Conference, LASERS- 89, D. G. Harris and T. M. Shay, Eds., STS press, McLean VA, 1990, p.476

2. G. Jones, II, "Photochemistry of Laser Dyes," in "Dye Laser Principles: with Applications," F. J. Duarte and L. W. Hillman, Eds., Academic Press, New York, 1990.

3. G. Jones II and M. A. Rahman, “Photophysical properties of coumarin dyes in aqueous solutions of poly(methacrylic acid)”, ACS meeting abstract, 199th National meeting, American Chemical Society, Boston, Massachusetts, April, 1990. Abstract No. 386

4. G. Jones, II and M. A. Rahman, "Fluorescence Properties of Coumarin Laser Dyes in Aqueous Polymer Media. Chromophore Isolation in Poly(methacrylic acid) Hypercoils," J. Org. Chem., to be submitted.

BACKGROUND

In a series of earlier reports from this laboratory the effects of medium on the emission properties of the coumarin dyes that are important for lasing in the blue-green have been reported.[1] Changes in solvent polarity bring about alteration in the fluorescence wavelength, quantum yield and lifetime, emission polarization properties,[2] self quenching and photodegradation characteristics,[3] and the encounter with electron transfer quenchers.[4] Aqueous media have also been of interest due to the anticipated benefits of reduced thermal gradients for water vs typical organic solvents under lasing conditions (less problematic influences of transient refractive index effects).[1,5] To this end the solubilization of normally insoluble coumarins in water with the aid of surfactant[6] or cyclodextrin[7,8] reagents has also been studied. The generally important result of these studies is that the rapid non-radiative decay that mitigates fluorescence for many coumarin dyes (especially for a medium of pure water) is suppressed when dye is sequestered in the domain of an amphiphilic reagent.

In our study of solubilizing agents for the coumarins we discovered the effectiveness of polyelectrolytes that are based on acrylate monomers, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA).[9] Especially effective was the latter polymer (PMAA), a polyelectrolyte that has been the object of numerous investigations. The intriguing feature of this class of water soluble polymers is the dramatic change in microscopic and bulk properties that occur on charging of the polymer chain that accompanies a rise in bulk medium pH in the range of 4-8 as carboxylic acid moieties are deprotonated. The conformational transition has been investigated using a wide array of physical techniques including potentiometric titration[10] and fluorescent probing.[11] Particularly pertinent to the present work are the recent reports of the behavior of fluorescence probes of the microenvironment of PMAA coils.[11] In these studies organic fluorophores have been incorporated into polyelectrolyte domains through electrostatic or covalent attachment. The common result is the observation of some change in emission properties on alteration of the polymer shape and charge as PMAA is opened from a compact or globular form into an elongated rod-like conformation at higher pH's at which charged carboxylate units engage in electrostatic repulsion. In several investigations of PMAA, the feature of hypercoiling at low pH has been exploited to alter the rates of bimolecular reaction, either through the partitioning of reagents between polymer and aqueous domains, or through the co-binding of potential reactants.[12]

We report here the results of a study in which coumarin dyes have been solubilized in water through binding to PMAA. Dye fluorescence is remarkably enhanced in many instances, in certain cases to a degree not observed for other amphiphilic sequestering media. The coumarin dyes in turn provide sensitive probes of *micropolarity and microviscosity*, parameters that provide valuable insight to polyelectrolyte structure and the conformational transition in water.

EXPERIMENTAL SECTION

Materials. Coumarins 102, 153, 120, and 339 (Scheme 1) were Kodak laser grade dyes and were used as received after checking for purity by chromatographic (tlc, silica gel, $MeOH:CH_2Cl_2 = 1:3$) and spectroscopic techniques. Coumarin 1 purchased from Aldrich was purified by recrystallization from methanol-water. Coumarin 35 was synthesized and purified according to a published procedure.[13] Poly(methacrylic acid) (PMAA) was prepared by AIBN (2,2'-azobisisobutyronitrile) initiated polymerization of methacrylic acid (freshly distilled under reduced pressure) in DMF with continuous nitrogen purging (60^0C, 12 hours), and purified by multiple precipitation from methanol on addition of ethyl ether. The polymer was fractionated by the procedure described by Flory[14] except that each polymer solution was homogenized by cooling, and the second fraction obtained with number averaged molecular weight of 25,000 (determined by glass viscometry) was used. Viscosity measurements were carried out for 1-2 g/dl of polymer solution in water (0.002 N in HCl) with an Ubbelohde viscometer having an outflow time for water of 338.5 seconds at 25^0 C. The molecular weight of the polymer conjugate was determined from the intrinsic viscosity by the equation[15]

$$[\eta] = 6.6 \times 10^{-4} M^{0.5}$$

Synthesis of coumarin derivatives and PMAA-coumarin conjugate. The synthesis of different coumarin derivatives and the PMAA-coumarin conjugate is outlined in scheme 2 and 3. The individual steps are described below:

3-Nitro-7-diethylamino-4-methylcoumarin (II). 3-Nitro-7-diethylamino-4-methylcoumarin was prepared by nitration of 7-diethylamino-4-methylcoumarin according to the method of Machida, et al.,[16] with slight modifications.

3-Amino-7-diethylamino-4-methylcoumarin (III). The nitrocoumarin (II) (3 g, 0.01 mol) was dissolved in 200 ml ethyl acetate in a 500 ml hydrogenation vessel, 500 mg palladium (10%, on activated charcoal) was added to it, and the reaction mixture was subjected to hydrogenation at 50 psi. Aliquots were withdrawn at intervals of two hours and tested by tlc (silica gel, methylene chloride) for progress of reaction. When all the nitrocompound had disappeared, the reaction mixture was filtered and the filtrate was evaporated under vacuum to yield 2.5 g of a pale yellow solid material, which was recrystallized from ethanol. The pale-yellow solid (2.2 g, 80% yield) with m.p. 103^0 C was identified as compound

III from NMR ($CDCl_3$): 7.4, d, 1H, C(5) - H, 6.7, dd, 1H, C(6)-H, 6.5, d, 1H, C(8)-H, 3.8, s, 2H, C(3)-NH_2, 3.4, q, 4H, N-CH_2-, 2.2, s, 3H, C(4)-CH_3, 1.2, t, 6H, N-C-CH_3.

3-(7-diethylamino-4-methylcoumarin) isothiocyanate (IV). Compound (III) (2 g , 0.008 mol) was dissolved in 200 ml acetone and 2.5 g calcium carbonate was added to it. The suspension was heated to boiling and 1 ml thiophosgene was added. The reaction mixture was heated to reflux and the progress of the reaction was followed by tlc which showed that the reaction was over in about ten minutes. The reaction mixture was refluxed for an additional twenty minutes and filtered to remove calcium carbonate and excess thiophosgene was distilled off. In order to remove the thiophosgene completely, several portions of a small amount of acetone were added and the evaporation was repeated. The reaction mixture was dried under vacuum to yield 1.5 g of yellow solid which was recrystallized from hot acetonitrile and needle shaped crystals (1.2 g, 50% yield) (m.p. 157^0 C) were obtained. The solid was identified to be compound (IV) from NMR ($CDCl_3$): 7.6, d, 1H, C(5) - H, 6.8, dd, 1H, C(6)-H, 6.5, d, 1H, C(8)-H, 3.6, q, 4H, N-CH_2-, 2.4, s, 3H, C(4)-CH_3, 1.2, t, 6H, N-C-CH_3.

1-(4-Methylphenyl)-3-(3-(7-diethylamino-4-methylcoumarinyl)) thiourea (V). Compound (IV) (57.6 mg, 0.20 mmol) was dissolved in in 20 ml methanol with the aid of 5 ml chloroform and p-toluidine (2.14 g, 0.02 mol) was added to this solution. The reaction mixture was stirred at room temperature, and the progress of reaction was followed by tlc (silica gel, $CHCl_3$). After about 12 hours complete conversion of the isothiocyanate was observed. The reaction mixture was dried under vacuum and the residual solid was dissolved in 20 ml $CHCl_3$. The unreacted p-toluidine was removed by extraction with 1N aqueous HCl. After evaporating the dried $CHCl_3$ extract under vacuum the solid was recrystallized from benzene-cyclohexane. The solid (47 mg, 60% yield) (m.p. 183^0 C) was identified as compound V from NMR in $CDCl_3$: 7.7, 5H, C(5) - H and 4H of other benzene ring, 6.6, dd, 6.55, dd, 1H, C(6)-H, 6.4, d, 1H, C(8)-H, 3.3, q, 4H, N-CH_2-, 2.3, s, 3H, C(4)-CH_3, 2.1, s, 3H, C(4')-CH_3, 1.1, t, 6H, N-C-CH_3.

1-(4-Vinylphenyl)-3-(3-(7-diethylamino-4-methylcoumarinyl)) thiourea (VI). Compound (IV) (57.6 mg, 0.20 mmol) was dissolved in 10 ml MeOH with the aid of 5 ml chloroform and p-aminostyrene (238 mg, 2.0 mmol) was added to this solution. The reaction mixture was stirred at room temperature and the progress of reaction was followed by tlc (silica gel, $CHCl_3$). After about 24 hours complete conversion of the isothiocyanate was observed. After removing the solvent under vacuum the residual materials were dissolved in 2 ml CH_2Cl_2 and applied to a silica gel column and eluted with chloroform when compound (V) was separated from excess p-aminostyrene and any by-product. A slightly sticky crystalline solid was obtained by evaporation of the column eluent for compound (V). After recrystallization from benzene-cyclohexane 27 mg (35% yield) yellow solid, m.p. 197^0 C, was obtained. The solid was identified as compound (V) from NMR in $CDCl_3$: 7.7, 5H, C(5) - H and 4H of other benzene ring, 6.6, dd, C(4')-C(H), 6.55, dd, 1H, C(6)-H, 6.4, d, 1H, C(8)-H, 5.65, d, 1H, and 5.2, d, 1H, C(4')-C-CH_2, 3.3, q, 4H, N-CH_2-, 2.3, s, 3H, C(4)-CH_3, 1.1, t, 6H, N-C-CH_3.

Synthesis and characterization of the conjugate of PMAA and coumarin derivative (IV). Freshly distilled methacrylic acid (2 ml, 25 mmol) was dissolved in DMF (20 ml) and compound VI (0.02 g, 0.05 mmol) was added to the solution. The solution was deoxygenated by bubbling nitrogen for about 30 minutes and heated to about 60^0C after which 0.2 g AIBN was added. The polymerization reaction was allowed to proceed for about 24 hours during which the temperature was kept at ~ 60^0 and nitrogen was continuously bubbled through. After 24 hours the reaction mixture was poured in to excess (ca. 150 ml) $CHCl_3$ and the precipitated polymer was collected and washed with diethyl ether. The polymer was purified by repeated precipitation from methanol by adding ethyl ether. The purified polymer (1.2 g) was dried under vacuum and its molecular weight (45,000) was determined by glass viscometry. The concentration of polymer residue was calculated from the measured weight of polymer, neglecting the very small contribution from the dye moiety. In this way, a P/D ([polymer residue]/[dye]) ratio of 1600 was obtained for the conjugate.

Instrumentation. Absorption spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Emission spectra were measured on Perkin-Elmer MPF-44A and SLM 48000 fluorimeters. Fluorescence quantum yield and lifetime values were measured on the SLM 48000 phase-shift fluorimeter.

General techniques. Stock solutions (2.0 mM) of different coumarin dyes were prepared in ethanol by dissolving measured amounts of solid materials. A decimolar stock solution of PMAA was prepared in deionized water. Dye-polymer solutions of desired P/D (ratio of concentration of polymer residue and dye) were prepared by mixing specific amounts of dye and polymer stock solutions in deionized water. The pH of the aqueous solutions was recorded on a Fisher-Accumet pH meter. Dilute NaOH and HCl aqueous solutions were used to control pH.

All experiments were performed at room temperature with air-saturated solutions unless otherwise mentioned. For measurements of absorption spectra 1-10 μM dye solutions was employed in 1 cm path length quartz cells. For measurement of corrected fluorescence spectra, fluorescence quantum yield and lifetime with the SLM 48000 fluorimeter, dye concentrations were kept low so that O.D. at excitation wavelength was less than 0.2.

Solubility of coumarin dyes in aqueous polymer solution. For measurement of the solubility of coumarin dyes in aqueous polymer solution excess dye was stirred overnight in the polymer solution at pH 3. The resulting solution (filtered) was measured for optical density at the absorption maximum of a solution of the dye in ethanol-water (1:4). The concentration of the polymer solubilized dye was calculated from comparison of optical density of the solution with the molar extinction co-efficient of the dye in ethanol-water (1:4). Effect of polymer conformation on its dye solubilizing power was examined by ionizing the polymer by adding alkali (NaOH) solution.

Fluorescence polarization. Fluorescence polarization values of the coumarin dyes in different media were measured in the L-format on both Perkin-Elmer MPF-44A and SLM 48000 fluorimeters. Excitation at the maximum of long-wavelength absorption band led to fluorescence monitored at the maximum of the emission band. Concentrations of dye solutions were 10 μM (O.D. values ~0.2 at λ_{ex}). Reproducibility of measured values of P was within ± 5 %. Measured polarization values were converted in to anisotropy values (r) using the relation, $r = (2P)/(3-P)$.

Fluorescence quantum yield measurements. Known values of the quantum yield of the dyes in ethanol[2a] were taken as standard. Excitation was done towards the blue side of the visible absorption band. Dye concentration was 10 μM so that optical density at the excitation wavelength was less than 0.2.

Fluorescence lifetime measurements. For the measurement of fluorescence lifetime the excitation wavelength was set towards the blue side of the visible absorption band and the total emission was detected without an emission monochromator. Cut-off filters (420 nm, 475 nm, and 515 nm) were used to prevent Raman scattered light from entering the detection chamber. An aqueous solution of glycogen (scatterer) was used as standard. Modulation frequencies were used in the range of 10 to 250 MHz.

RESULTS AND DISCUSSION

Enhancement of solubility of coumarin dyes in water by addition of poly(methacrylic acid). Some coumarin dyes, especially the fluorinated ones, are almost insoluble in water. Enhancement of water solubility was observed in aqueous micellar[6] and cyclodextrin[7] solutions. Poly(methacrylic acid) in its hypercoiled conformation ($pH < 4$) was examined for its potential of solubilizing water insoluble coumarin dyes in the hydrophobic microdomain. Significant enhancement of solubility of the dyes in water was observed in presence of PMAA (Table 1). About a hundred and two hundred fold increase in solubility was observed for the most water insoluble dyes, C153 and C35, respectively.

The dye solubilizing power of the polymer was found to be strongly dependent on its conformation. When a saturated solution of C153 in 0.1% aqueous PMAA was titrated with NaOH, a gradual decrease of optical density was observed at pH values above 4.5. At pH's above 7, O.D. values were identical with those in water in absence of the polymer. This experiment demonstrates that the dye solubilizing power of compact hypercoiled form the polymer is lost upon expansion of the polymer chain.

Poly(acrylic acid), on the other hand, does not demonstrate any enhancement of coumarin solubilities in water even at low pH (~3), a saturated solution of coumarin 1 in 1.0% aq. PAA is ~ 10^{-4} M, which is of almost same concentration as saturated aqueous solution. Hence, the solubilizing power of PMAA merits from the hydrophobic force originating from the pendant methyl groups.

Alteration of photophysical parameters of coumarin 1 subsequent to solubilization in aqueous poly(methacrylic Acid): The effect of solubilization in aqueous PMAA on the photophysical parameters of coumarin dyes has been examined. In this study coumarin 1 (C1) has been taken as representative of the family. In ethanol solution C1 absorbs at 373 nm (ε = 2.24 x 10^4 M^{-1} cm^{-1}) and emits strongly at 443 nm (Figure 1). A 10 nm red-shift in the absorption spectrum, and a 20 nm red-shift in emission spectrum of the dye, are observed for aqueous solution. The photophysical parameters of the dye in the aqueous PMAA hypercoil (pH ~ 3) are accumulated in Table 2. The incorporation of dye molecules in the polymer domain is indicated by the gradual increase of fluorescence polarization (P) value upon addition of the polymer. Binding with the polymer is not found to make any significant change in the absorption spectrum of C1 but large (~ 33 nm) blue-shift of the emission spectrum is observed. Such a large amount of blue-shift indicates a very non-polar environment in the interior of the polymer hypercoil.[11] An emission wavelength of 443 nm for PMAA solutions corresponds to a micropolarity similar to that of benzene by comparison of the solvatochromic data for C1 in different solvents.[3]

The effect of the polymer on the photophysical parameters of the dye attains some saturation at high P/D (> 1000). The phenomenon is demonstrated in the plot for P as a function of P/D in Figure 2. The flourescence polarization value (P) increases sharply with the addition of polymer in the low P/D regime. Above P/D 500 the changes are smaller and somewhat saturation of P value is observed above P/D 1000.

The effect of PMAA conformation on binding of coumarin 1 with the polymer has been examined by emission titration. Figure 3 shows the variation of emission wavelength of the dye in an aqueous solution of PMAA at P/D 1000 as a function of pH. The blue-shifted emission observed for the dye in the PMAA hypercoil prevails up to pH 4, above which a gradual red-shift of the emission is observed. At high pH (>6) the emission spectrum of the dye resembles that in water with very low value (~0.02) of fluorescence polarization. The transitional region for emission wavelength resembles the conformational transition of the polymer. Thus, it is clear that with the unfolding of the polymer the dye is gradually exposed to the aqueous environment and no association of the dye exists with the charged rod-like polymer.

Photophysical parameters of some other coumarin dyes in aqueous poly(methacrylic acid). As it has been observed for coumarin 1 that the effect of PMAA solubilization on the photophysical properties of the dye attains a somewhat optimum effect at P/D 1000 and that the hypercoiled conformation of the polymer is most suitable in dissolving the dye in the polymer domain free from influence of the bulk aqueous medium, further study with other coumarin dyes has been kept limited to conditions of P/D 1000 and pH 3. The dyes selected for this study are shown in Scheme 1. Photophysical properties of the dyes in aqueous polymeric solution along with the values for water and ethanol solutions are accumulated in Table 3.

It is evident from the fluorescence polarization values in Table 3 that only coumarin dyes carrying tertiary nitrogen on the 7-amino position are solubilized in the PMAA hypercoil as reflected by high P values compared to aqueous solution. Dyes containing primary (C120) and secondary (C339) nitrogen on the 7-amino position are not solubilized in the polymer microenvironment, rather remain in the bulk aqueous medium, a result reflected in the similar P values for the dyes in aqueous and aqueous polymeric solution. Subsequently, no significant effect of added polymer is observed on the photophysical properties of C120 and C339. At pH higher than 7 when the polymer attains an elongated rod-like conformation, dye molecules become totally free from polymer environment as indicated by very low values ($P \sim 0.02$) values of fluorescence polarization.

Fluorescence quantum yield and lifetime of PMAA-bound coumarin dyes. Binding with PMAA in water renders a significant influence on the emission intensity of selected coumarin dyes. The fluorescence quantum yields of the PMAA-bound coumarin dyes are presented in Table 4 along with the values in ethanol and water. For the dyes, C1, C35, and C153, whose emission intensity is quenched in water in comparison to the values in ethanol or methanol, binding in the PMAA hypercoil rejuvenates the fluorescence intensity. In some cases the fluorescence quantum yield of the polymer bound dyes are significantly higher than the values in ethanol or methanol. Exceptional is the case with C102 which has a very high value of Φ_F in water. The dye maintains the high value of Φ_F in the PMAA hypercoil.

The fluorescence lifetime values of the dyes in different media are also presented in Table 4. Fluorescence lifetime values of C1, C35 and C153 in water are too low to be measured with reliable accuracy with the present capabilities of the SLM fluorimeter. However, the values (<0.5 ns) presented for these dyes in water are reasonable limits with measurements with low precision. Measurements were done at 10-20 modulation frequencies in the range 10-150 MHz and the fitted result was an average of all these measurements. In every case attempts were made to fit the experimental parameters with single, double or even triple exponential decays and the result with best values of χ_r^2 was taken. In PMAA the three dyes mentioned above have high values of τ_F, the values being even higher than those in ethanol. For C1 and C35 the phase and modulation data fits better with a biexponential decay consisting of a long and a short component for the lifetime. But for the more hydrophobic dye C153 single component lifetime is observed. A single component lifetime is also observed for C102 in PMAA hypercoil. For this dye τ_F value in water is higher than in ethanol.

Rate constants for radiative and nonradiative decays of the singlet excited states of the dyes have been accumulated in Table 5. In calculation for the values of the parameters in water lifetime values for C1, C35 and C153 have been taken as 0.5 ns. It is found from Table 5 that the dyes have comparable rates for radiative decay in all the media measured. Also the nonradiative decay rate constants for the dyes are more or less comparable in ethanol and aqueous PMAA.

Polarity of PMAA hypercoil. Most of the coumarins are solvatochromic dyes; i.e. their emission spectra are strongly influenced by the polarity of the medium. The strong solvatochromic blue-shift of the emission spectra of PMAA hypercoil bound coumarin dyes indicates the highly non-polar nature of the polymer domain. The emission spectrum of coumarin 153 in PMAA hypercoil is shown in Figure 4 along with the emission spectra of the dye in different other solvents. It is evident from Figure 4 that PMAA hypercoil is much more non-polar than ethanol. Actually, it is very close to cyclohexane in terms of polarity.

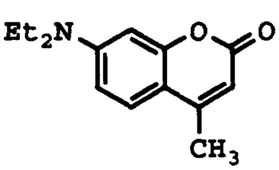
Photophysical properties of the covalent conjugate of coumarin 1 with PMAA. Dye loading of the PMAA-coumarin covalent conjugate was calculated to be equivalent to P/D 1600. The photophysical parameters of the conjugated dye was examined in aqueous solution at two different pH's (3 and 8); the results are presented in Table 6. Also presented in Table 6 are the photophysical parameters of the model compound (V). The model compound has a very low fluorescence quantum yield (0.1) even in ethanol. Incorporation in PMAA hypercoil enhances the fluorescence quantum yield (0.32) by about three times, and unfolding of the polymer to the elongated rod-like structure eliminates the polymer effect as expected. But the effect of conjugation of the dye with the polymer is quite different. A remarkably high value of the fluorescence quantum yield (0.65), about seven times higher than the value for the model compound in ethanol, is observed for the polymer-conjugated coumarin dye at pH 3. The blue-shifted fluorescence with a high value for quantum yield and polarization (0.32) indicates residence of dye chromophore inside the polymer hypercoil. Again, the fluorescence quantum yield value of 0.23 at pH 8 (that means, in water) is a significantly high value for aminocoumarin with mobile diethylamino groups. Under similar conditions Φ_F values for the model compound and other coumarin dyes with mobile diethylamino groups has been found to be less than 0.1. An unusually high value of fluorescence polarization (0.22) for the conjugate at pH 8, as compared to the low values of about 0.02 for the parameter for coumarin dyes under similar conditions indicates considerable restriction to the rotation of the chromophore, even when the dye is attached to the open polymer coil for which considerable exposure to water is expected.

Emission titration of the PMAA-coumarin conjugate in aqueous solution indicates the gradual unfolding of the polymer with ionization as revealed by the red-shift of emission with increasing pH (similar to Figure 3). The conformational transition of the polymer is found to take place in the pH range of 4.5 to 6.5.

Fluorescence lifetime measurements reveal a heterogeneity of binding sites for the conjugated dye in the polymer domain. At pH 3 (hypercoiled PMAA) the phase and modulation data fit to a single component lifetime of 4.2 ns with χ_r^2 value of 3.4. But a far better fit ($\chi_r^2 = 0.7$) is obtained for a biexponential decay with lifetimes of 7.1 ns (17%) and 3.8 ns (83%). Both of the components of lifetime indicate presence of dye chromophore in the polymer domain, the longer component indicating a situation where some chromophore units are more deeply buried in the polymer domain. Biexponential decay of singlet lifetime is also observed for the polymer-dye conjugate system at high pH (8) when the polymer attains the elongated rod-like conformation exposing dye chromophore to the bulk aqueous medium. One of the components is very short (0.5 ns) indicating greater contact of the chromophore with water than the chromophores exhibiting longer lifetime (2.9 ns).

Scheme 1

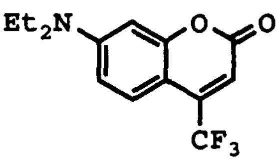
Structure of coumarin dyes



C1(460)

λ_a = 373 nm

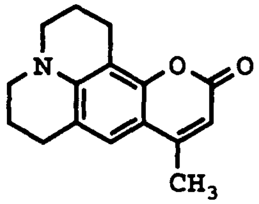
λ_f = 443 nm



C35

λ_a = 402 nm

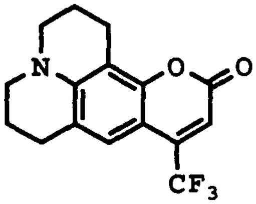
λ_f = 500 nm



C102(480)

λ_a = 389 nm

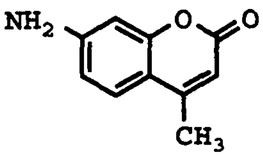
λ_f = 462 nm



C153(540A)

λ_a = 422 nm

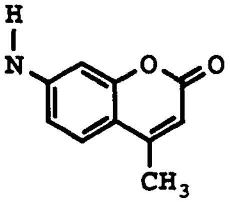
λ_f = 525 nm



C120(440)

λ_a = 353 nm

λ_f = 427 nm



C339

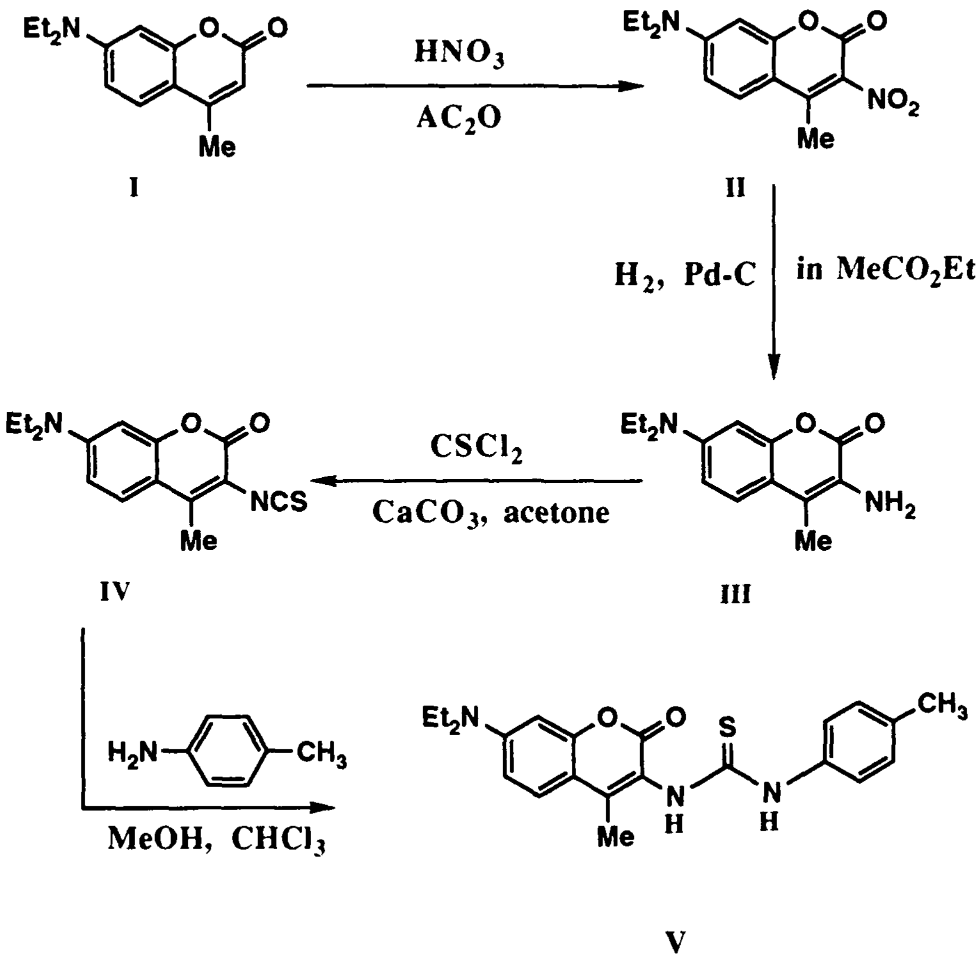
λ_a = 378 nm

λ_f = 442 nm

Ethanol solution

Scheme 2

Synthesis of coumarin derivatives



Scheme 3

Synthesis of PMAA-coumarin conjugate

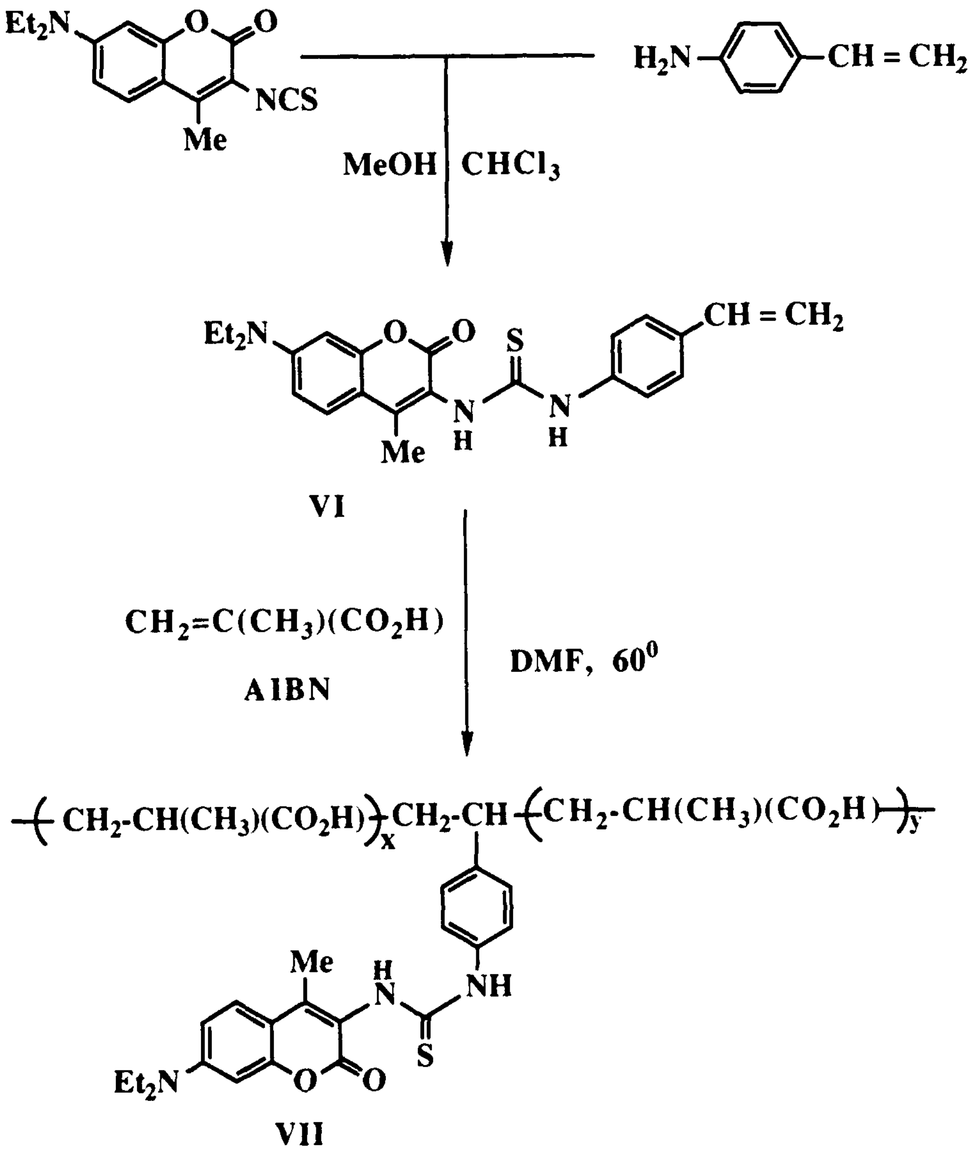


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Table 1. Solubility of coumarin dyes in aqueous poly(methacrylic acid)[a]

medium	C1	C35	C102	C153
water	1.0 x 10^{-4} M	5.8 x 10^{-6} M	1 3x 10^{-5} M	2.0 x 10^{-6} M
0.1% PMAA (pH 3)	1.1 x 10^{-3} M	1.0 x 10^{-4} M	3.5 x 10^{-4} M	2.2 x 10^{-5} M
1.0% PMAA (pH 3)	2.0 x 10^{-3} M	1.1 x 10^{-3} M	5.2 x 10^{-4} M	2.1 x 10^{-4}M

[a] 0.1% and 1.0% PMAA solutions correspond to concentrations of 0.012 M and 0.12 M residues of the polymer respectively.

Table 2. Photophysical parameters of coumarin 1 in solvents and in aqueous PMAA at pH 3 and at different P/D[a]

medium	λ_a (nm)	λ_f (nm)	Φ_F[b]	P (r)[b]
ethanol	373	443	0.59	0.02 (0.01)
water	385	467	0.07	0.02 (0.01)
P/D = 10	385	440	0.15	0.10 (0.07)
P/D = 50	385	438	0.23	0.13 (0.09)
P/D = 100	385	435	0.28	0.16 (0.11)
P/D = 500	384	434	0.44	0.23 (0.17)
P/D = 1000	384	434	0.52	0.31 (0.23)
P/D = 1500	384	434	0.54	0.32 (0.24)
P/D = 2000	384	434	0.55	0.32 (0.24)

[a] [dye] = 10 μM, pH was maintained by adding dilute aqueous HCl and NaOH solutions, P/D = [PMAA residue]/[dye]

[b] excitation at the long wavelength absorption band.

Table 3. Photophysical parameters of coumarin dyes in different media[a]

dye	medium	λ_a (nm)	λ_f (nm)[b]	P (r)[b]
C1	ethanol	373	443	0.01 (0.01))
	water	385	467	0.06 (0.04)
	aq. PMAA	385	432	0.32 (0.24)
C102	ethanol	389	462	0.01 (0.01)
	water	397	483	0.01 (0.01)
	aq. PMAA	399	447	0.29 (0.21)
C35	ethanol	402	500	0.03 (0.02)
	water	414	534	0.01 (0.01)
	aq. PMAA	403	468	0.31 (0.23)
C153	ethanol	422	525	0.01 (0.01)
	water	435	548	0.01 (0.01)
	aq. PMAA	422	488	0.31 (0.23)
C120	ethanol	353	427	0.02 (0.01)
	water	343	435	0.02 (0.01)
	aq. PMAA	341	437	0.02 (0.01)
C339	ethanol	378	442	0.01 (0.01)
	water	374	457	0.01 (0.01)
	aq. PMAA	372	456	0.04 (0.03)

[a] [dye] =10 μM; for aq. PMAA, [residue] = 10 mM and pH = 3.0

[b] excitation at the long wavelength absorption band

Table 4. Fluorescence quantum yield and lifetime data for coumarin dyes in different media[a]

dye	medium	Φ_F[b]	τ_F (ns)[b]	χ_r^2
C1	ethanol	0.73	3.3	1.7
	water	0.09	< 0.5	
	aq. PMAA	0.64	4.7 (89%), 0.70 (11%)	1.8
C35	ethanol	0.09	0.85	4.2
	water	0.03	< 0.5	
	aq. PMAA	0.49	5.8 (96%), 1.8 (4%)	1.8
C153	ethanol	0.38	4.8	1.2
	water	0.10	< 0.5	
	aq. PMAA	0.62	6.6	2.4
C102	ethanol	0.95	4.9	1.4
	water	0.95	5.8	1.2
	aq. PMAA	1.00	5.4	2.7

[a] [dye] = 10 μM; for aq. PMAA, [residue] = 10 mM and pH = 3.0

[b] excitation at the long wavelength absorption band

Table 5. Radiative and non-radiative rate constants for coumarin dyes in different media[a]

Dye	Medium	$k_f \times 10^{-7}$ (s^{-1})	$k_{nd} \times 10^{-7}$ (s^{-1})
C1	ethanol	22.	8.2
	water	18.	182
	aq. PMAA	14.	7.7
C35	ethanol	11.	10.
	water	6.0	194
	aq. PMAA	8.4	8.8
C153	ethanol	7.9	13.
	water	20.	180
	aq. PMAA	9.4	5.8
C102	ethanol	19.	1.0
	water	16.	0.86.
	aq. PMAA	18.	0.38

[a] [dye] = 10 μM; for aq. PMAA, [residue] = 10 mM and pH = 3.0

Table 6. Photophysical parameters of PMAA-coumarin covalent conjugate as compared to the model compound in aqueous PMAA solution [a]

System		λ_a (nm)	λ_f (nm)	$\Phi_F{}^b$	P^b	τ_F(ns)^b	$\chi_r{}^2$
V	ethanol	373	465	0.10	0.02	< 0.5	-
	P/D 1600 (pH 3)	395	448	0.32	0.29	3.5 (79%), 0.9 (21%)	2.3
	P/D 1600 (pH 8)	395	480	0.07	0.03	< 0.5	-
conjugate	pH 3	390	458	0.65	0.31	4.2	3.4
						3.8 (83%), 7.1 (17%)	0.7
	pH 8	388	480	0.23	0.21	2.9 (71%) 0.5 (29%)	3.1

[a] for the model compound and conjugate, [dye] = 5 μM

[b] excitation at the long wavelength absorption band

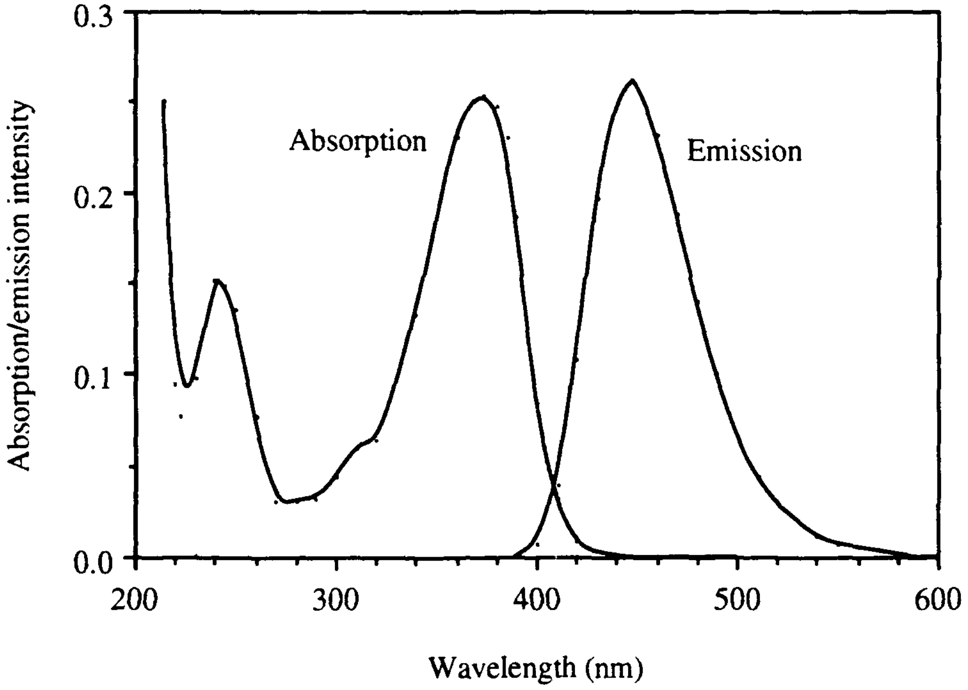

Figure1. Absorption and emission spectra of coumarin 1 (10 μM) in ethanol.

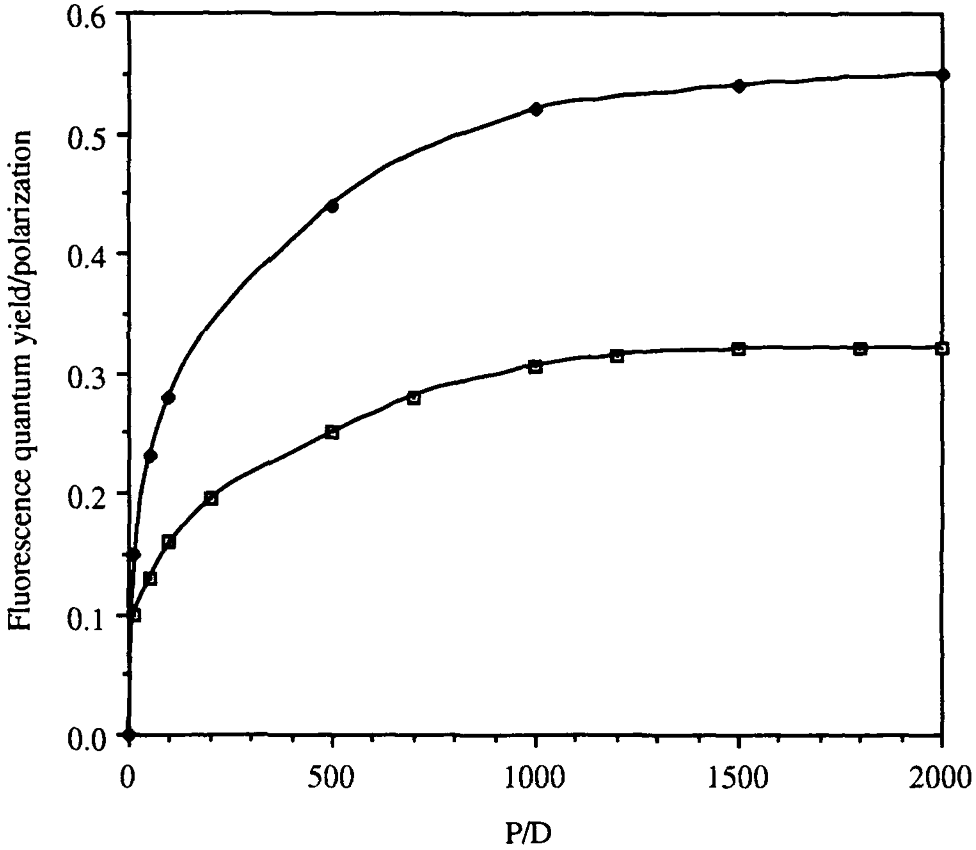

Figure 2. Dependence of fluorescence quantum yield (diamond) and polarization (square) of coumarin 1 upon addition of polymer; P/D = [PMAA residue]/[dye]; aqueous solution of C1 = 5 μM and pH = 3.

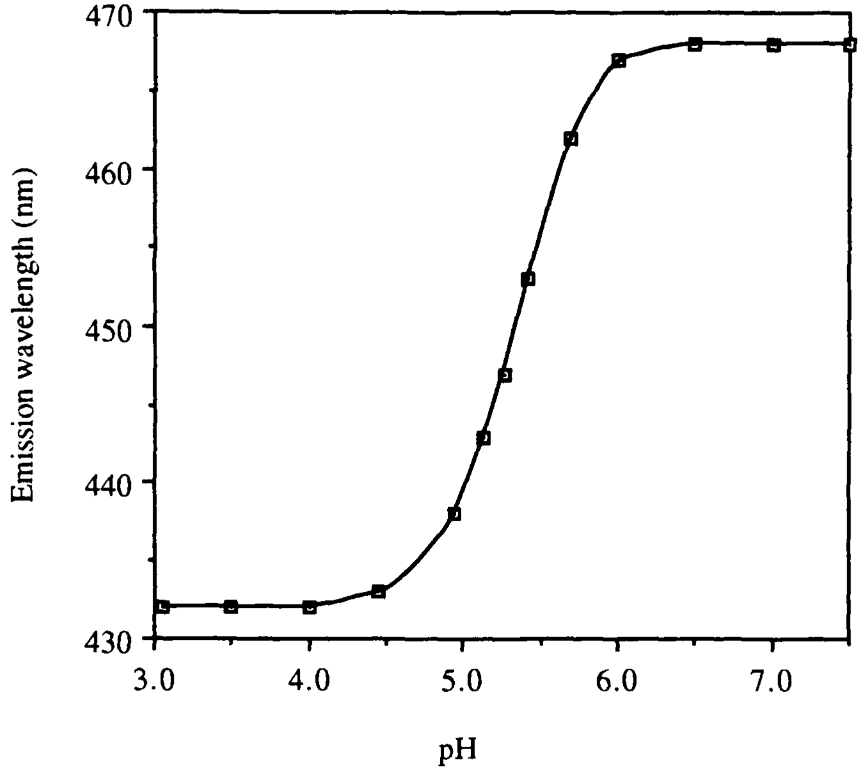

Figure 3. Emission wavelength of coumarin 1 (10 μM) in aqueous PMAA (P/D 1000) at different pH values (λ_{ex} = 428 nm)

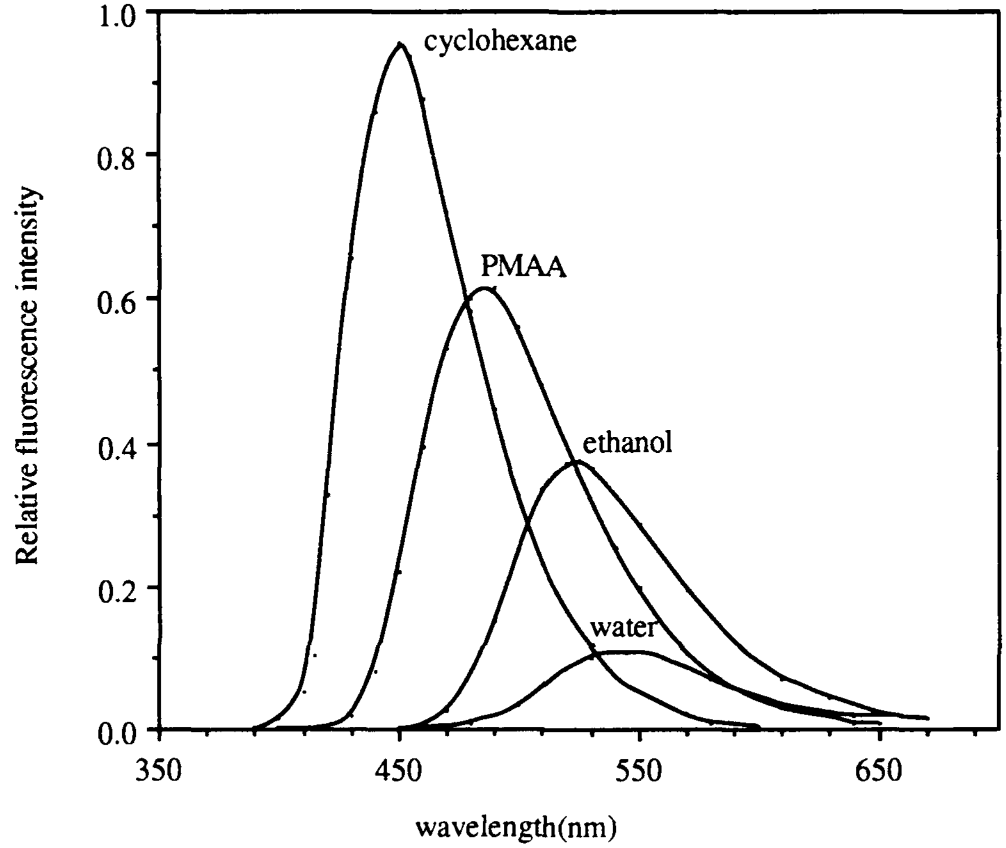

Figure 4. Emission spectra of 10 μM coumarin 153 in different media; for PMAA solution, pH = 3 and P/D = 1000.

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