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13. ABSTRACT (*Maximum 200 words*)

The solubilization of laser dyes in water with the aid of the polyelectrolyte, poly(methacrylic acid) (PMAA) has been studied. An important strategy was the isolation of dye species in the "hypercoils" associated with the polyelectrolyte, as it is found at moderately acidic pH. Polymer-bound dyes in water display markedly enhanced emission yield, lifetime, and polarization. Dye materials are also less susceptible to photodegradation, since they are isolated in polymer domains away from adventitious quenchers. Also examined in the study was the possibility that two dyes could be co-bound within polymer domains and that energy transfer between the two would result in "downshifting" of output emission wavelengths. Of the various amphiphilic media used for solubilizing organic dyes in water (e.g., detergent micelles, cyclodextrins), PMAA shows the greatest promise in terms of fluorescence enhancement and compartmentalization or organized assembly of additives. These studies show promise for the protection of the dyes against undesirable photodegradation under flash excitation. The results provide also some direction in the use of absorption and emission properties of organic chromophores in polymeric hosts in applications in microelectronics or photonics.

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PHOTODEGRADATION AND PHOTOPHYSICS OF LASER DYES

FINAL TECHNICAL REPORT

Guilford Jones, II

June 30, 1994

U. S. ARMY RESEARCH OFFICE

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PHOTODEGRADATION AND PHOTOPHYSICS OF LASER DYES

Introduction

The current study was a new project, funding for which began on September 1, 1989. Work was suspended at the end of calendar 1990, due to lack of funds for year II. A second year of funding was provided for work that commenced in June, 1991. Funding was again suspended at the end of year II, May 31, 1992; no-cost extensions of the contract were approved through March 1, 1994, awaiting a third year installment for the grant.

Objectives of the program included the study of the effects of medium on the fluorescence properties of a series of coumarin and rhodamine 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 PMAA polyelectrolyte, as it is found at 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 dyes bound to PMAA through the attraction to hydrophobic interior sites or, alternatively, through covalant attachment to polyelectrolyte. In the latter case, dye remains bound in the polymer domain through the conformational transition of globular polymer to a charged rod-like structure. Also examined in the study was the possibility that two dyes could be co-bound within polymer domains and that energy transfer between the two would result in "downshifting" of output emission wavelengths. This phenomenon was demonstrated for PMAA-co-bound coumarin dyes. Of the various amphiphilic media used for solubilizing organic dyes in water (e.g., detergent micelles, cyclodextrins), PMAA shows the greatest promise in terms of fluorescence enhancement, the isolation of dye molecules in polymer domains (and controls thereon), and opportunities for compartmentalization or organized assembly of additives.

These studies show promise for the solubilization by polymers of laser dyes in water and the protection of these dyes against undesirable photodegradation under flash excitation. These investigations are directed to the improvement of performance for dye lasers. The present results are also important in terms of the ability of dye fluorophores, through changes in photophysical properties, to "report" 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.

The results of this work have been reported in two conference papers, two journal articles, a completed Ph. D. dissertation, and a submitted manuscript.

Outline of Research Findings

The improvement in the flourescence emission properties of laser dyes solubilized in novel aqueous media has been studied. The influence of the solvent medium and polymer and other additives on photophysical and photochemical properties including flourescence quantum yields, lifetimes, and polarization, has been investigated. The coumarin and rhodamine families of dyes were selected for study as representative of relatively hydrophobic molecules or ions that could be sequestered in microdomains created by the"hypercoiling" of selected polyelectrolytes. These polymer structures are adopted when the macromolecules are folded into globular conformations under certain conditions in water. Poly(methacrylic acid) (PMAA) behaves in this fashion for aqueous dilute solutions at pH 3.0. Experiments conducted to date include measurement of fluorescence quantum yields, lifetimes, and anisotropy (polarization). These parameters for the dyes under study are highly dependent on solvent polarity and viscosity. The results reveal sharp changes in photophysical properties on binding the coumarins and rhodamines in the PMAA hydrophobic "pockets". Quantum yields and lifetimes of fluorescence are raised, signifying a relatively "dry" interior for the polymer globule; polarization measurements further reveal a high local (not bulk) viscosity.

Significant enhancement of solubility of the dyes in water was observed in the presence of high concentrations of PMAA (P/D > 500) at low pH (< 5). For some dyes a significant blue shift of the emission maximum and enhancement of fluorescence quantum yield were observed. Highly polarized fluorescence (P ~ 0.3) of the PMAA solubilized dyes indicated the presence of dye molecules in the hydrophobic microdomain of the PMAA hypercoil. The extent of solubilization and alteration of photophysical parameters were found to be dependent on dye structure (e.g., rigidity of the 7-amino-nitrogen, presence of trifluoromethyl group at position 4). The study was also extended to some rhodamine dyes and interesting alterations of photophysical parameters were observed upon binding of dye molecules to globular PMAA. Aggregation of these cationic dyes in moderately concentrated aqueous solution was found to be retarded by addition of the polymer.

The transition from the hypercoiled conformation (pH 4-8) can be followed readily by reference to coumarin fluorescence wavelength, quantum yield and polarization data. 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-lie conformation at higher pH's at which charged carboxylate units engage in electrostatic repulsion. 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. Flash photolysis data have been obtained for coumarin 1 (and for the covalent analog) for which a low yield of dye triplets can be observed. Observation of the longer lived (msec) intermediate depends strongly on PMAA binding; the triplet is exceptionally long-lived under conditions in which dye is incorporated in hypercoiled polyelectrolyte.

Personnel

Principal Investigator:

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Research Assistants - Graduate Students:

M. A. Rahman (B. Sc., M. Sc., University of Dhaka, Ph. D., Boston University)

Mr. Rahman was supported under the project for two calendar years. His thesis is devoted primarily to the subject area of the ARO-funded research.
"The Photophysics and Photochemistry of Organic Laser Dyes under Conditions of Binding to Polymethacrylic Acid in Water" (thesis defense, April, 1992)

M. S. Farahat (B. S. Renssalear Polytechnic Inst., M. S., Worchester Polytechnic Inst.)

Mr. Farahat provided technical support to the program for approximately nine months; he completed his thesis work (defense, March, 1993) in another subject area.

Conference Reports and Journal Articles

1. G. Jones, II and M.A. Rahman, "Novel Environments for Laser Dyes" in *Proceedings of the International Conference on Lasers '89*, D.G. Harris and T.M. Shay, Ed., STS Press, McLean VA, 1990.

2. M. A. Rahman and G. Jones, II, "Photophysical Properties of Coumarin Dyes in Aqueous Solutions of Poly(methacrylic Acid), *Abstracts, National Meeting of the American Chemical Society*, Boston, Massachusetts, 1990.

3. G. Jones, II and M. A. Rahman, "Fluorescence Energy Transfer between Coumarin Laser Dyes Co-bound to Poly(methacrylic acid) in Water," *Chem. Phys. Lett.*, **200**, 241 (1992).

4. G. Jones, II and M. A. Rahman, "Photophysics of Laser Dyes Bound to Poly(methacrylic acid) in Water," *Optics Commun.*, **97**, 140 (1993).

5. 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. Phys. Chem.*, 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 as the result of DOD-supported work that was initiated during 1979-83.[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 the 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. This change in state of protonation accompanies a rise in bulk medium pH in the range of 4-8 as carboxylic acid moieties are deprotonated. Particularly pertinent to the present work are the recent reports of the behavior of fluorescence probes of the microenvironment of PMAA coils,[10,11] where organic fluorophores have been incorporated into polyelectrolyte domains through electrostatic or covalent attachment.

Provided here is a sampling of the results of our 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.

Selected Results and Discussion

Enhancement of solubility of coumarin dyes in water by addition of poly(methacrylic acid). 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.

Alteration of photophysical parameters of coumarin 1 on solubilization in aqueous poly(methacrylic acid): Coumarin 1 (C1) was taken as representative of the family. 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. An emission wavelength of 443 nm for PMAA solutions corresponds to a micropolarity similar to that of benzene by comparison of the sovatochromic data for C1 in different solvents. 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 1. The flourescence polarization value (P) increases sharply with the addition of polymer in the low P/D regime.

The effect of PMAA conformation on binding of coumarin 1 with the polymer has been examined by emission titration. Figure 2 shows the variation of emission wavelength of the dye in 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 (i.e., a gradual release of the dye molecules from the polymer domain to the bulk aqueous medium is observed). The transition region for emission wavelength resembles the conformational transition of the polymer. At a 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 ~ 0.02) values of fluorescence polarization.

Photophysical parameters of some other coumarin dyes in aqueous poly(methacrylic acid). Since for coumarin 1 the effect of PMAA solubilization on the photophysical properties of the dye attains an optimum effect at P/D 1000, and since the hypercoiled conformation of the polymer (at lower pH) is most suitable in situating dye molecules 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 value 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. More polar 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.

Fluorescence quantum yield and life-time 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. The fluorescence lifetime values of the dyes in different media are also presented in Table 4.

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 3 along with the emission spectra of the dye in different other solvents. It is evident that PMAA hypercoil is much more non-polar than ethanol.

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 were examined in aqueous solution at two different pH's (3 and 8) where PMAA is known to have two distinct conformational forms (hypercoil and elongated rod, respectively) and the results are presented in Table 5. Also presented in Table 5 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. The 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 unconjugated coumarin dyes under similar conditions indicates considerable restriction to the rotation of the covalently bound chromophore, even when the dye is attached to the open polymer coil for which considerable exposure to water is expected.

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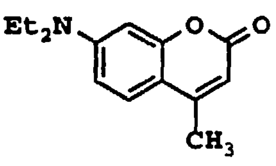
Scheme 1

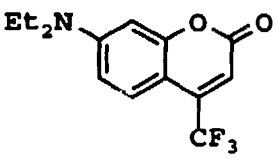
Structure of coumarin dyes



C1(460)

$\lambda_a = 373$ nm

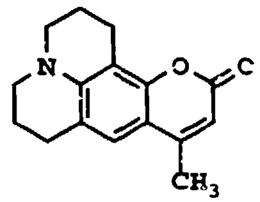
$\lambda_f = 443$ nm



C35

$\lambda_a = 402$ nm

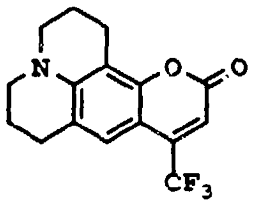
$\lambda_f =$ 50[illegible] nm



C102(480)

$\lambda_a = 389$ nm

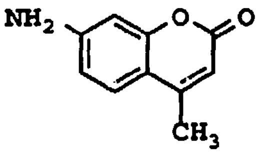
$\lambda_f = 462$ nm



C153(540A)

$\lambda_a = 422$ nm

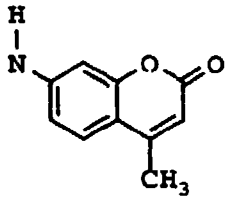
$\lambda_f = 525$ nm



C120(440)

$\lambda_a = 353$ nm

$\lambda_f = 427$ nm



C339

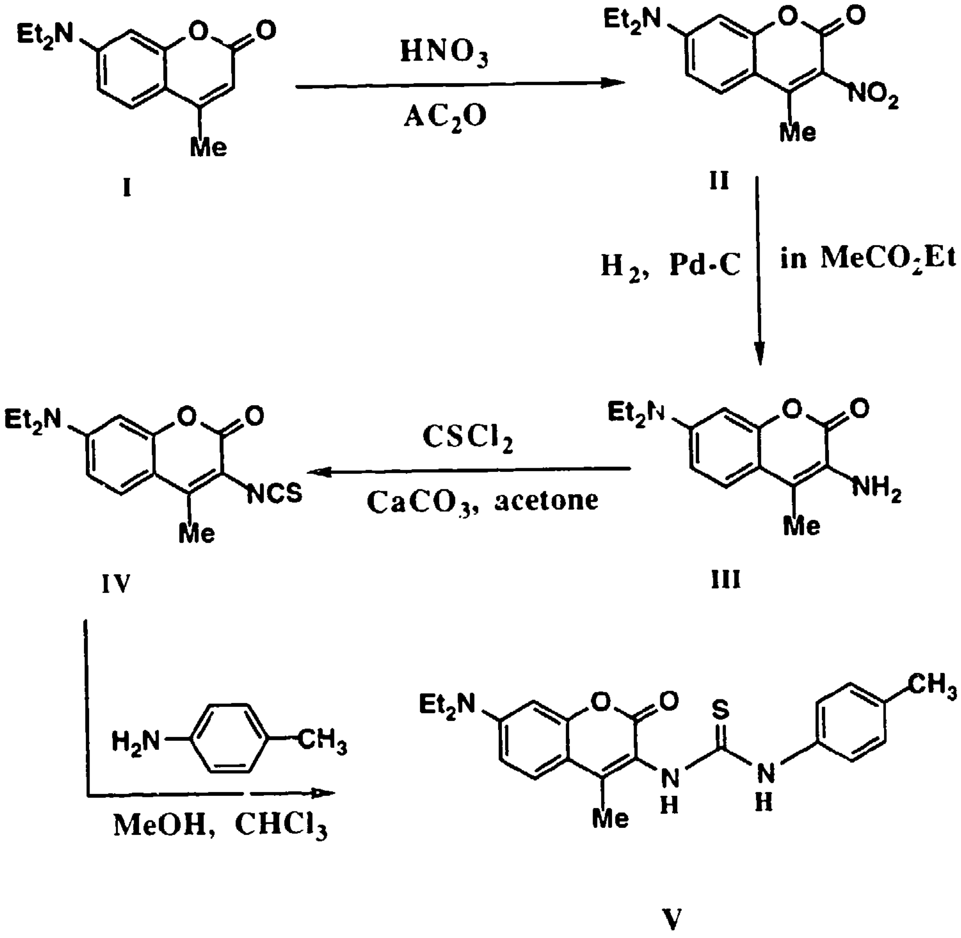
$\lambda_a = 378$ nm

$\lambda_f = 442$ nm

Ethanol solution

Scheme 2

Synthesis of coumarin derivatives



Scheme 3

Synthesis of PMAA-coumarin conjugate

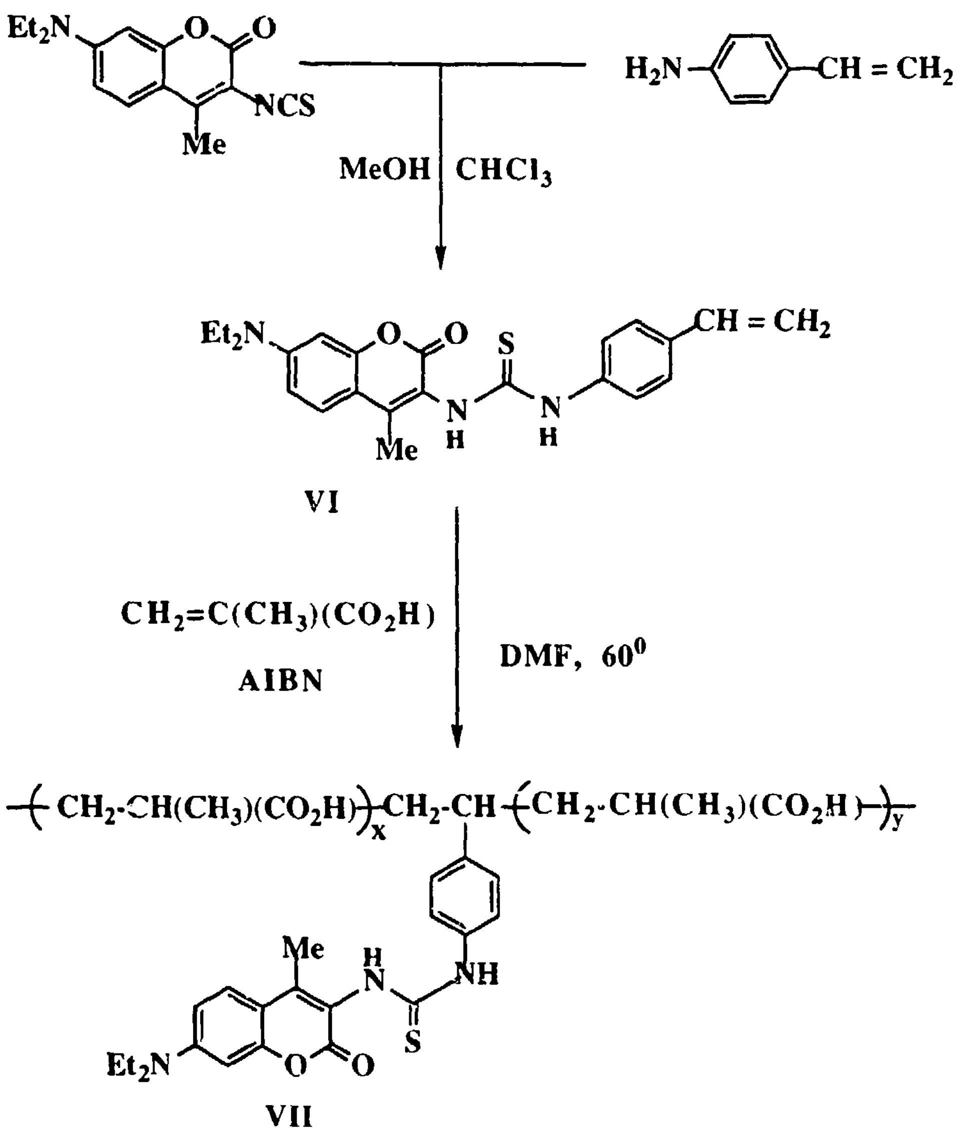


Table 1. Solubility of coumarin dyes in aqueous poly(methacrylic acid) [a]

medium	C1	C35	C102	C153
water	1.0×10^{-4} M	5.8×10^{-6} M	1.3×10^{-5} M	2.0×10^{-6} M
0.1% PMAA (pH 3)	1.1×10^{-3} M	1.0×10^{-4} M	3.5×10^{-4} M	2.2×10^{-5} M
1.0% PMAA (pH 3)	2.0×10^{-3} M	1.1×10^{-3} M	5.2×10^{-4} M	2.1×10^{-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 was done on the long wavelength absorption band.