Manufacture of Modified Poly(vinyl acetal) Showing Fluorescence and Molecular Recognition

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ABSTRACT: Poly(vinyl acetal) from poly(vinyl alcohol) and 4-dimethylaminobenzaldehyde (DMAB) is synthesized. Fluorescence behavior of the polymer is investigated in acetic acid glacial (HAc), dimethylsulfoxide (DMSO), and dimethylformamide (DMF) solvents. Fluorescence emission intensities of the polymer solutions are different with the change of concentration. The result suggests that the maximum fluorescence emission intensities of the polymer solutions depend on the optimal concentration of the polymer. It has been found that the fluorescence intensity of DMAB is dramatically lower than that of the polymer in the same chromophore concentration, and such phenomenon is termed as structural self-quenching effect (SSQE). The strong fluorescence of the polymer can be quenched by adding electron-deficient monomers which have no chromophore moieties such as lactic acid, adenine, etc., and their Stern–Volmer constants are determined. It is observed that the higher the electron deficiencies of the quenchers, the higher the Stern–Volmer constants, which means stronger quenching effect. The result indicates that the polymer can recognize these biologic small molecules. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2385–2390, 1999

Key words: poly(vinyl acetal); 4-dimethylaminobenzaldehyde; synthesis; fluorescence; quenching; molecular recognition

INTRODUCTION

Much attention has been paid to various fluorescent polymers bearing aromatic tertiary amino chromophores. Fluorescence behaviors of these vinyl monomers bearing aromatic tertiary amino chromophores have previously been investigated. Yamamoto et al.[1] reported that fluorescent dye compound containing 4-dimethylaminobenzaldehyde was able to recognize nucleic acids and to determine the number of microbial cells, cancer cells, or gene copies. Jiang et al.[2] reported the fluorescence behavior of 4-dimethylaminobenzaldehyde in solution. Li et al.[3] reported that the acrylic monomers bearing aromatic tertiary amino chromophores, such as N-(4-N',N'-dimethylaminophenyl) acrylamide (DMAPAA),[4] N-(4-N',N'-dimethylaminophenyl) methacrylamide (DMAPMA),[5] and 4-(N,N-dimethylamino) benzylmethacrylate (DMABMA),[6] showed an interesting photochemical and initiation behavior caused by the coexistence of the electron-accepting acrylic carbon–carbon double bond and the electron-donating chromophore moieties in the same molecule. The fluorescence intensities of these monomers are always much lower than those of their polymers in the same molar concentration of the chromophore residue. This phenomenon is termed as structural self-quenching effect to differ from the concentrational self-quenching effect caused by the concentrational factors as known thus far.

This article aims at reporting synthesis and fluorescence behavior of the polymer derived from

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poly(vinyl alcohol) and dimethylaminobenzaldehyde, as well as studying the fluorescence emission intensities of the polymer in different solvents and concentration, and pursuing the fluorescence of the polymer quenched by such biologic small molecules as lactic acid (LA), adenine (Ade), uracil (Ura), and thymine (Thy).

EXPERIMENTAL

Materials

Poly(vinyl alcohol) PVA-124 was obtained from Japan; average polymerization degree is ~ 2400–2500 (Shanghai Chemical Reagents Corp). LA, Ade, Ura, and Thy are biochemicals, chromatographic grade (Shanghai Chemical Reagents Corp). All the other reagents and solvents used were purified by conventional methods.

Polymer Preparation

The polymer was prepared as previously reported.[7] The reaction vessel used was a three-necked round bottom 250-mL flask fitted with an overhead stirrer, a thermometer, and a condenser. Water (100 mL) and 2 g (PVA-124) were charged into the flask. The reaction mixture was stirred at 100°C for 10 min. PVA-124 was entirely dissolved. The solution was cooled to 50°C. 4-Dimethylaminobenzaldehyde [6.5 g (43 mmol)] was dissolved in 40 mL acetic acid glacial (HAc) and 2 mL HCl (1 : 1) was added to the solution. The reaction mixture was stirred for 3 h.

After cooling, the reaction mixture was poured into basified methane alcohol (MeOH). The polymer precipitated was filtered off, washed with MeOH, and dried *in vacuo* at room temperature, and then raised to 40°C. The resulting polymer was a white solid state. Infrared (IR) was 642, 783, 826, 1196, 1405, 1584, 1601, 1750, 2902, 3410 KBr, cm^{-1}.
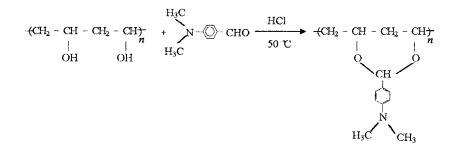
Measurements

IR spectroscopy was performed on a KBr disk with a AQS-20 spectrophotometer (Analect). Before the measurement, the disk was dried *in vacuo* at room temperature. Fluorescence and excitation spectra were measured at 25°C using a Hitachi Model-850 fluorescence spectrofluorimeter. The bandpasses were 5 nm for both the excitation and emission monochromators, respectively. The fluorescence and excitation spectra for the polymer solution were measured using a standard 1 cm quartz cell in side-face arrangement. Absorbance at the excitation wavelength was maintained at < 0.2 for fluorescence measurements to avoid the inner filter effect. Ultraviolet–visible (UV–VIS) absorption spectra of the polymer was measured at room temperature using a Model-756 MC UV–VIS spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of the Polymer

The synthesis of the polymer is shown in Scheme 1.

The direct aldehyde condensation technique[7,8] was used to prepare polymer directly from poly(vinyl alcohol) under mild conditions. The polymer had a rather poor solubility because of its high molecular weight and was reasonably soluble only in inorganic acid, HAc, dimethylsulfoxide (DMSO), and dimethylformamide (DMF), but insoluble in benzene, aliphatic compound, MeOH, alcohol, and chloroform. The resulting polymer was partly soluble in tetrahydrofurane (THF), acetone, and ethyl ether.

Degree of acetalization (%) was determined as described.[8] Therefore, the yield of aldehyde condensation was about 7.8%.
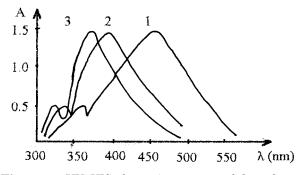
Figure 1   UV–VIS absorption spectra of the polymer solution, (1) in HAc, (2) in DMSO, (3) in DMF.

UV–VIS Absorption Spectra

As a general feature, it was observed that the absorption spectra and the wavelength of the absorption maximum of the polymer were little affected by the solvent, and there was also no significant concentration effect. As a consequence, any observed variation in the Stokes shift has to be attributed nearly exclusively to the change in the fluorescence band maximum (i.e., to lower the energy of the excited state of the dye molecules by particular reorientation and interactions).

The different polymer solutions showed different absorption bands in the visible region because of the interaction of polymer molecule and solvents. UV–VIS absorption spectra of the polymer solution were shown in Figure 1. Three UV–VIS absorption spectra were similar in the shape, but the position of the absorption maxima depend on the solvent. UV–VIS absorption spectrum of the polymer in HAc would be observed as a much larger red shift because HAc is a kind of stronger proton-donor solvent.

Fluorescence of the Polymer

The excitation and emission spectra of the different polymer solutions are shown in Figures 2–4. No excimer emission is observed for the polymer in HAc. This may be due to the formation of quaternary ammonium salt that prevents the formation of excimer. The long-wavelength bands in the fluorescence spectra of the polymer in DMSO and DMF may be of excimer origin. When excited, the chromophore moiety (A*) may form an excimer (AA)* with a chromophore moiety of the same chain in the ground state (A) that emits light at a longer wavelength than the separated chromophore moiety (A*). Emission spectra of the polymer in three solvents all show large shoulder
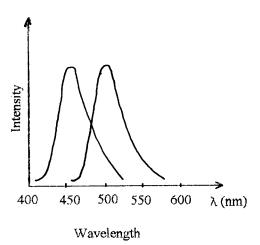

Figure 2   Excitation and emission spectra of the polymer in HAc.

bands which would be seen because of reabsorption of emitted light by fluorescent moieties.

Effect of Concentration

Figure 5 shows fluorescence emission intensity V_s concentration of the polymer solutions. Interestingly, fluorescence of the polymer solution becomes intense as the solution concentration increases. After reaching a maximum value (at the concentration of $4 \times 10^{-6}M$ in HAc and $1.6 \times 10^{-5}M$ in DMSO or DMF), the intensity decreases with the increase of concentration. The maximum concentration in HAc is smaller than that in DMSO or DMF. This phenomenon seems to be the reason for an interaction between the polymer and the solvent. As mentioned, the polymer in HAc can form quaternary ammonium salt, the interaction of fluorescent moieties in a polymer chain in HAc solution is
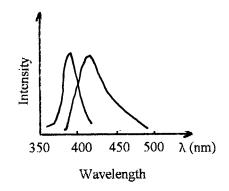

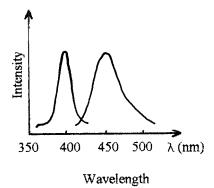**Figure 4**   Excitation and emission spectra of the polymer in DMF.

Figure 3 Excitation and emission spectra of the polymer in DMSO.

smaller than in DMF or DMSO because the quaternary ammonium salt cationic excludes each other. Therefore, relative fluorescence intensity of the polymer in HAc is stronger than that in DMF or DMSO. However, the interaction between polymer and HAc is stronger than that in DMF or DMSO. The polymer molecules

overlapping each other are stronger in HAc than in DMSO or DMF, so the maximum concentration in HAc is smaller than in DMSO or DMF. Stabilization of the excited state by interaction with the environment is much easier in a medium of low viscosity than in a highly viscous medium. The energy of the excited state of the dye molecule in a low molecular weight liquid is lowered by reorientation of the solvent molecules around the dye because of its increased dipole moment in the excited state. The degree of stabilization for a given fluorescent dye depends on several parameters, such as the polarity and steric features of the solvent molecules, and, of course, the mobility of the solvent molecules within the lifetime of the excited state.[9] Of course, besides this, the chemical structure and physical properties of the dye molecule itself determine the overall absorption and fluorescence behavior and are the controlling factors for the maximum Stokes shift that can be realized.
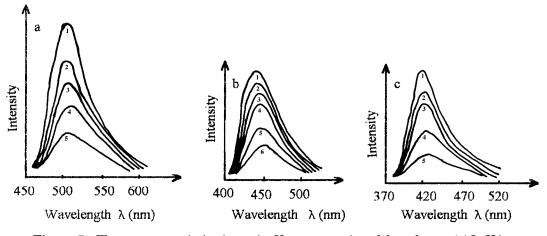

Figure 5 Fluorescence emission intensity V_s concentration of the polymer. (a) In HAc, (1) $4 \times 10^{-6}M$, (2) $2 \times 10^{-6}M$, (3) $3.2 \times 10^{-5}M$, (4) $1.6 \times 10^{-5}M$, (5) $1.33 \times 10^{-6}M$. (b) In DMSO, (1) $1.6 \times 10^{-5}M$, (2) $3.2 \times 10^{-5}M$, (3) $8 \times 10^{-6}M$, (4) $4 \times 10^{-6}M$, (5) $2 \times 10^{-6}M$, (6) $1.33 \times 10^{-6}M$. (c) In DMF, (1) $4.6 \times 10^{-5}M$, (2) $3.2 \times 10^{-5}M$, (3) $4 \times 10^{-6}M$, (4) $2 \times 10^{-6}M$, (5) $1.33 \times 10^{-6}M$.

Table I Properties of the Polymer

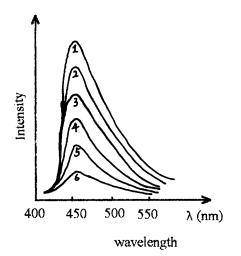| Solvent	Maximum Absorption Wavelength (nm)	Maximum Excitation Wavelength (nm)	Maximum Emission Wavelength (nm)	Maximum Concentration (M)	Relative Intensity
HAc	452	452	497	4×10^{-6}	high
DMSO	392	392	442	1.6×10^{-5}	low
DMF	385	385	417	1.6×10^{-5}	low

Figure 6 Fluorescence spectra of the polymer quenched by LA in DMSO.

$\lambda_{ex} = 392$ nm,   [polymer] $= 1.6 \times 10^{-6}M,$

[LA](M): (1) 0, (2) 0.02, (3) 0.04,

(4) 0.1, (5) 0.2, (6) 0.4.

Table I summarizes the absorption, emission, and excitation maximum wavelength data, the maximum concentration value corresponding to maximum fluorescence emission and relative intensity. The maximum absorption, excitation, and emission wavelength of the polymer in HAc is longer than in DMSO and DMF. As mentioned above, the phenomenon is the reason for an interaction between the polymer molecule and solvent molecule.

Fluorescence Quenching

To understand the effect of the quenchers on the fluorescence of the polymer, electron-deficient compounds such as LA, Ade, Thy, and Ura, which have no chromophore moieties, are added to the polymer solution. Just as we expected, the fluorescence of the polymer can be quenched by these biologic small molecules. As a representative one, the quenching spectra of the polymer by LA is shown in Figure 6.

The data were analyzed conventionally by the Stern–Volmer equation

$$I_0/I_q = 1 + K_{SV}[Q]$$

where I_0 and I_q are the unquenched and quenched fluorescence emission intensities, re-
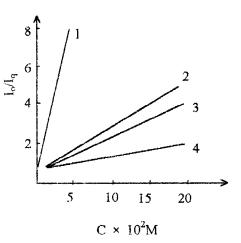

Figure 7 Stern–Volmer plots of the polymer quenched by different quenchers in DMSO. 1, LA; 2, Ura; 3, Ade; 4, Thy; [polymer] $= 1.6 \times 10^{-5}M$.

spectively; K_{SV} is the Stern–Volmer constants. The Stern–Volmer plots of different quenchers for the polymer are shown in Figure 7. The Stern–Volmer constants calculated from the slopes of these straight lines indicate that the quenching efficiencies of these biologic small molecules increase in the order of Thy, Ade, Ura, and LA, as summarized in Table II.

CONCLUSIONS

The direct aldehyde condensation technique was used to prepare poly(vinyl acetal) directly from poly(vinyl alcohol) under mild conditions. The yield of aldehyde condensation was about 7.8%. The relative fluorescence intensity of the polymer in HAc is stronger than in DMF or DMSO. The maximum absorption, excitation, and emission wavelength of the polymer in HAc

Table II   Stern–Volmer Constants of Different Quenchers

Quencher	K_{SV}	Quencher	K_{SV}
LA	173	Ade	13
Ura	18	Thy	5

The polymer can recognize these biologic small molecules and their concentration, according to their Stern–Volmer constants.

is longer than in DMSO or DMF. The maximum concentration corresponding to maximum fluorescence emission intensity is smaller in HAc than in DMF or DMSO. The fluorescence of the polymer can be quenched by biologic small molecules such as LA, Ura, Ade, and Thy. The quenching efficiencies of these biologic small molecules increase in the order of Thy, Ade, Ura, and LA. The polymer can recognize these biologic small molecules and determine their concentration, according to their Stern–Volmer constants.

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