degree of polymer chain expansion as well as the length and bulkiness of side groups.

The qualitative data presented in this article will be elaborated on in a more quantitative manner by means of time-resolved fluorescence spectroscopy determining directly the rate of molecular motion.

Acknowledgment. The authors are greatly indebted to Professor M. Sisido and Dr. N. Kitamura for their valuable discussions.

Registry No. (BMA)(12) (copolymer), 116911-34-3; (CHMA)(12) (copolymer), 116911-35-4; (DDMA)(12) (copolymer), 116911-36-5; (MMA)(12) (copolymer), 112925-63-0; DDDMAB, 77016-80-9.

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Association of Hydrophobic Polymers in Water: Fluorescence Studies with Labeled (Hydroxypropyl)celluloses

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ABSTRACT: The occurrence in water of interpolymeric association between fluorescently labeled (hydroxypropyl)cellulose was demonstrated on the basis of nonradiative energy transfer between chromophores attached to different polymer chains. The two polymers were a pyrene-labeled (hydroxypropyl)cellulose (HPC-Py/438) containing on average 0.5 pyrene per chain and a fluorene-labeled (hydroxypropyl)cellulose (HPC-Flu/33) containing on average three fluorene groups per chain. Energy transfer between fluorene, the energy donor, and pyrene, the energy acceptor, was detected in aqueous solutions of HPC-Py/438 and HPC-Flu/33 for total polymer concentrations as low as 0.02 g L^{-1}. No energy transfer occurred between the labels when the two polymers were dissolved in methanol or dioxane. The steady-state and time-dependent fluorescence spectroscopy of HPC-Flu/33 is described. In water, methanol, and dioxane the polymer exhibited an emission of intensity I_M centered at 317 nm due to isolated excited fluorenes and an emission of intensity I_E centered at 395 nm due to fluorene excimers. In a given solvent the ratio I_E/I_M remained constant over the concentration range of 0.01 to 0.1 g L^{-1}. The ratio was larger for polymer solutions in water (0.49) than in dioxane (0.14).

Introduction

The architecture of organized systems in water reflects a delicate balance of forces. Coulombic forces, ion pair formation, hydrogen bonding, and hydrophobic interactions all contribute to the stability of self-assembling natural systems, such as micelles, vesicles, or membranes. Synthetic polymers also form organized assemblies. These provide attractive options for the design of functional devices. Tools for the study of microdomains in solutions are numerous.[1] They yield information on parameters such as the size and distribution of the microdomains, their electric charge, or their hydrophobicity. The experiments described here use fluorescence techniques to study aggregates of an industrially important polymer, (hydroxypropyl)cellulose (HPC). This polymer is an additive in many commercial materials, such as paints, inks, cosmetics, pharmaceuticals, foods, ceramics, and coatings.[2] It is a water-soluble polymer prepared from cellulose by attachment of hydroxypropyl ether groups to the glucose hydroxyl substituents. Minor chemical modifications of the polymer structure can alter dramatically the solution properties of cellulose ethers. An intriguing example is that

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of the hydrophobically modified cellulose ethers in which long-chain hydrocarbon groups are attached covalently to a small number of hydroxyalkyl groups. The materials are soluble in water, but they exhibit an anomalous, large increase in solution viscosity which has been attributed to intermolecular association of the alkyl chains.[3] Another example is that of fluorescently labeled (hydroxypropyl)celluloses. While introducing less than one fluorescent label per chain on average does not alter significantly the solution properties of the polymer, severe changes occur when the level of labeling is larger. This situation is reflected, for example, by a decrease of the solubility in water of the polymer and by modifications of the cloud point of aqueous solutions. These effects have been reported previously in the case of several pyrene-labeled (hydroxypropyl)celluloses (HPC-Py).[4,5] They were attributed tentatively to the formation of polymer aggregates triggered by hydrophobic forces between the pyrenyl labels. With the spectroscopic tools available it was not possible to demonstrate in an unambiguous manner that the pyrene/pyrene interactions were interpolymeric and that aggregates were formed at very low polymer concentrations. To clarify this point a series of experiments based on energy transfer between two different chromophores has been performed. Their results are reported here.

Nonradiative energy transfer between two fluorescent dyes is an extremely powerful tool to characterize the distances between pairs of chromophores in biological macromolecules[6] as well as in synthetic polymeric systems.[7] Examples of recent applications of this technique to synthetic polymers include the study of polymer compatibility in blends,[8] of polymer chain interpenetration in solution,[9,10] and of the morphology of polymer colloids[11] and polymeric micelles.[12] Closest to the system under investigation here is that of the interpolymeric association in water between cationic and anionic polymers, a phenomenon examined by energy transfer in pioneering experiments reported by Nagata and Morawetz.[13] Their experiments monitored the efficiency of energy transfer in aqueous solutions containing mixtures of naphthyl- and anthryl-labeled charged and neutral polymers. They observed an enhanced efficiency of energy transfer when the energy donor (naphthyl group) and the energy acceptor (anthryl group) were attached to polymers carrying charges of opposite sign.

In the present study mixtures of pyrene-labeled and fluorene-labeled HPC were employed. The fluorene/pyrene pair of chromophores has been used with great effectiveness by Watanabe and Matsuda to detect and quantify nonradiative energy transfer within graft copolymers.[12] Here the fluorene label was attached to HPC by an ether linkage using a reaction scheme developed for the preparation of HPC-Py. Fluorene-labeled HPC (HPC-Flu/33) presents interesting features from the point of view of the spectroscopy of the fluorene chromophore, as highlighted by the occurrence of a very strong excimer emission when the fluorene concentration is as low as 10^{-6} M. The first part of this article is devoted to the spectroscopic properties of HPC-Flu/33. From the results of the energy-transfer experiments between HPC-Py and HPC-Flu/33, the existence of interpolymeric interactions in water is demonstrated for polymer concentrations as low as 20–50 ppm. Corresponding experiments between labeled HPC and low molecular probes are also reported. They allow comparison of the efficiency of energy transfer between free chromophores and chromophores attached to polymer chains.

Experimental Section

Materials. (Hydroxypropyl)cellulose (HPC, Klucel L, Hercules Inc.) was purchased from Aldrich Chemicals Co. The manufacturer's literature claims a molecular weight of 100 000. A recent reference reports $M_{sedimentation}$ = 82 000[14] and another 73 000 with M_n = 36 000.[15] The preparation and characterization of the pyrene-labeled (hydroxypropyl)cellulose samples HPC-Py/438 and HPC-Py/56 are described elsewhere.[5] The denominators in HPC-Py/438 and HPC-Py/56 represent the average number of glucose units per pyrene group in the polymers. 9-Fluorenemethanol (99%, Aldrich Chemicals Co.) was purified by recrystallization from hexanes (mp 102–103 °C, lit. 102–103 °C).[16] 2-Aminopyridine (99%, Aldrich Chemicals Co.) was recrystallized from hexanes (mp 57–58 °C, lit. 57.5 °C).[17] Pyrene (99%, Aldrich Chemicals Co.) was purified by repeated recrystallizations from absolute ethanol and subsequent sublimation. *p*-Toluenesulfonyl chloride (Gold Label, Aldrich Chemicals Co.) was used without purification. Water was deionized with a Millipore Milli-Q water purification system. Spectroscopic grade methanol and dioxane were used for spectroscopic measurements.

Synthesis. 9-Fluorenylmethyl Tosylate (2).[18] To a solution of 9-fluorenemethanol (1, 1.0 g, 5.1 mmol) in chloroform (10 mL, flushed through alumina) were added first pyridine (0.82 mL, 10.2 mmol) and then *p*-toluenesulfonyl chloride (1.45 g, 7.6 mmol) in small portions over 5 min. The mixture was stirred under nitrogen at ~23 °C for 18 h. The reaction mixture, diluted with dichloromethane (20 mL), was extracted successively with 10% aqueous HCl (twice), water (twice), aqueous 5% $NaHCO_3$ (twice), water (once), and brine (once). The organic layer was dried over $MgSO_4$, filtered, and evaporated to give a crystalline material, which was purified by crystallization from ethyl acetate to yield **2** (990 mg, 56%): mp 111–112 °C; λ_{max} 267, 289, and 300 nm; ^1H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 4.23 (m, 4 H), 7.1–7.9 (m, 12 H) ppm; IR (KBr) 1600, 1360 (s), 1170 (s); M^+, *m/e* 350.

Fluorene-Labeled (Hydroxypropyl)cellulose (HPC-Flu/33). A solution of 9-fluorenylmethyl tosylate (540 mg, 1.5 mmol) was added to a solution of HPC (4.0 g) in dimethylformamide (DMF, 20 mL). The HPC had previously been dried by azeotropic distillation of water from solutions of the polymer in toluene (20 mL, three times). Then sodium hydride (200 mg, 60% dispersion in oil, washed with dry hexanes) in DMF (1 mL) was added, and the mixture was allowed to stand overnight. Excess base was neutralized with diluted acetic acid (5 mL, 3:1 v/v with water). Solvents were removed at 55 °C at reduced pressure. The residue was dissolved in tetrahydrofuran (THF, 50 mL). Addition of hexane (30 mL) led to the precipitation of the polymer, which was separated by decanting off the supernate. This reprecipitation was repeated three times. The final product was dried in vacuo (3.4 g). This material was redissolved in THF (100 mL). Some insoluble material [250 mg, white powder, tentatively identified as poly(dibenzofulvene)] was separated by centrifugation (12 000 rpm) of this solution. The supernate was concentrated to 50 mL. Repeated precipitations of the polymer into hexanes, followed by drying in vacuo at 60 °C, yielded HPC-Flu/33 as an amorphous solid (2.85 g). Through the use in tandem of UV–visible and refractive index detectors for the GPC analysis, it was determined that the fluorenyl groups were covalently linked to the polymer, that the chemical transformation did not alter significantly the molecular weight and the molecular weight distribution, and that the sample contained less than 0.05% UV-absorbing low molecular weight impurities. The concentration of fluorene chromophores incorporated into the polymer was determined by UV absorption measurements in methanol as 8.9×10^{-5} mol per g of polymer, using 9-fluorenemethanol (λ_{max} 265 nm, ϵ 20 000, λ_{max} 300 nm, ϵ 6300)[18] as a model compound. With a value of 36 000 for the M_n of HPC, it can be estimated that the sample contains on average 1 fluorene chromophore per 33 glucose units or ~3 fluorenes per chain.

Instrumentation. ^1H NMR spectra were recorded at 80 MHz with a Brucker WP-80 spectrometer. Spectra were run in chloroform-*d* containing 0.1% Me_4Si as an internal standard. UV–visible spectra were recorded with a Hewlett-Packard 8450A diode array spectrometer. Molecular weights and molecular weight distributions were estimated by gel permeation chromatography (GPC), using a Hewlett-Packard 1090 instrument equipped with a 1037A refractive index detector and a 8294A diode array UV–visible detector set at 280–310 nm. The columns used were PL-gel 50 Å, 500 Å, 1000 Å, 10,000 Å, and 10^5 Å. Spectral grade THF

Table I
Summary of Energy-Transfer Experimental Conditions

donor	acceptor	solvent	[pyrene], mol L^{-1}	[fluorene], mol L^{-1}	[Flu]/[Py]	HPC,[a] ppm
HPC-Flu/33	HPC-Py/438	water	1.1×10^{-6}	5.6×10^{-6}	5	200[b] to 2
HPC-Flu/33	HPC-Py/56	methanol	8×10^{-7}	7.6×10^{-6}	10	100[c]
HPC-Flu/33	Py	water	4×10^{-7}	2×10^{-6}	5	25
Flu-MeOH	HPC-Py/438	water	1.1×10^{-6}	5.7×10^{-6}	5	150
Flu-MeOH	Py	water	4×10^{-7}	2×10^{-6}	5	0

[a] Total polymer concentration. [b] HPC-Flu/33, 50 ppm; HPC-Py/438, 150 ppm. [c] HPC-Flu/33, 60 ppm; HPC-Py/56, 40 ppm.

(BDH) was used as the solvent with a flow rate of 1.0 mL min^{-1}. Steady-state fluorescence spectra were measured on a SPEX Fluorolog 212 spectrometer equipped with a DM3000A data system. The temperature of the water-jacketted cell holder was controlled by a Neslab water circulating bath. The temperature of the sample fluid was measured with a thermocouple. Fluorescence decay measurements were made with a home-built time-correlated single photon counting instrument in the laboratory of Professor M. A. Winnik, Chemistry Department, University of Toronto, Toronto, Canada.[20]

Fluorescence Measurements. The emission spectra were not corrected, except when specified and for all spectra used in quantum yield determinations. A calibrated tungsten lamp (NBS, Washington, DC) was used to determine the correction factors in units of either wavelengths or wavenumbers. The excitation spectra were measured in the ratio mode. For measurements of fluorene spectra and for energy-transfer experiments the band paths were set at 1.8 nm (excitation) and 3.6 nm (emission). The excitation wavelength was 290 nm. For measurements of the I_1/I_3 ratio of the pyrene emission, the excitation band paths were set at 3.6 or 7.2 nm and the emission band paths at 0.9 nm. The excitation wavelength was 330 nm. Solutions in methanol and dioxane were degassed by vigorous bubbling of argon for 1 min immediately prior to the measurement. Aqueous solutions were not degassed, since it was found that emission intensities were unaffected by degassing. Spectra were run at 25 °C. Quantum yields were calculated by integration of peak areas of corrected spectra measured in wavenumber units, using 2-aminopyridine in 0.1 N H_2SO_4 as a standard ($\Phi = 0.60$).[21] Beer's law corrections were applied for optical density changes at the excitation wavelength (290 nm). Corrections were made as well for refractive index differences. For HPC-Flu/33 the ratio of excimer emission intensity (I_E) to monomer emission intensity (I_M) was estimated after spectral corrections either from the ratio of peak heights at 395 nm and at 317 nm, respectively, or from the ratio of peak areas. In the latter case the excimer emission was obtained by subtraction from the total spectrum of the emission of 9-fluorenemethanol normalized at 317 nm. The two values were proportional. The values reported here were calculated from peak heights.

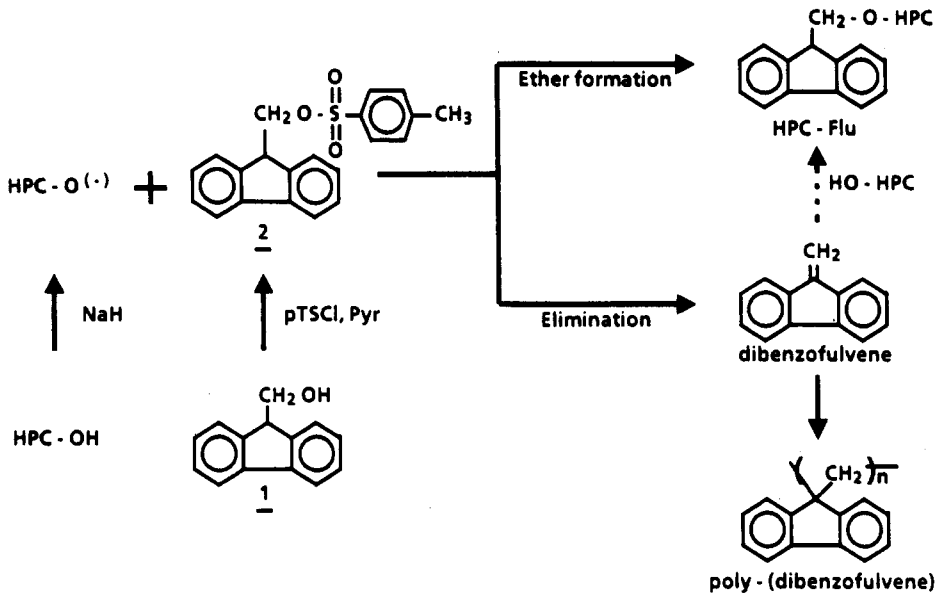
Samples for Spectroscopic Analysis. HPC-Py and HPC-Flu/33 solutions in water were prepared by allowing the polymer to swell and then dissolve at room temperature. They were allowed to stand for 24 h, either at room temperature or at 5 °C, before they were diluted to a known total volume. The polymer concentrations were approximately 100 ppm for HPC-Flu/33 and HPC-Py/56 and 300 ppm for HPC-Py/438. For energy-transfer measurements, solutions of HPC-Flu/33 and of HPC-Py were mixed (Table I). The absorbance at the excitation wavelength (290 nm) was kept low (<0.04), to avoid radiative transfer of the excitation energy. Solutions containing either HPC-Flu/33 or HPC-Py were also at hand. The concentrations of the chromophores were the same as in the mixture in order to allow easy comparisons of absorption and emission intensities. No changes were observed when spectra were recorded immediately after mixing or after allowing the solutions to stand for 24 h. A small decrease (20%) of the efficiency of energy transfer was observed after 7 days. For the energy-transfer experiments between pyrene and HPC-Flu/33 the solutions were made up in the following manner: first, a saturated aqueous pyrene solution was obtained by filtration of a suspension of pyrene in water (stirred overnight); this solution was then added to a solution of HPC-Flu/33 in water. Solutions prepared by filtration of a pyrene suspension in an aqueous HPC-Flu/33 solution presented reproducible but unusual features in their absorption and fluorescence spectra which will not be discussed here.

Results

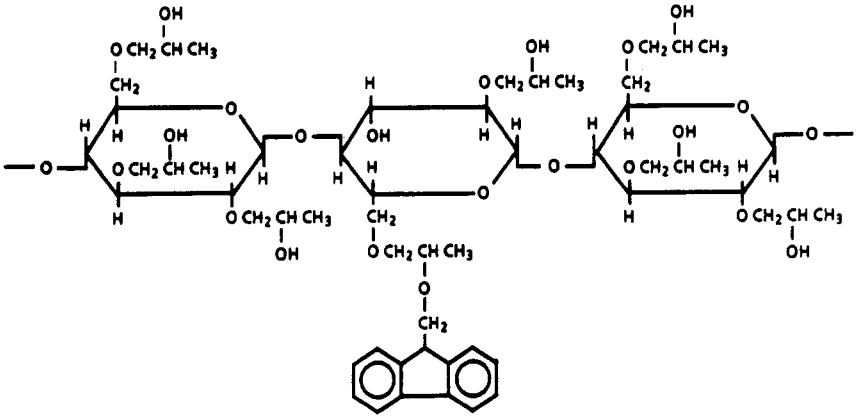
Fluorescence Spectroscopy of Fluorene-Labeled (Hydroxypropyl)cellulose (HPC-Flu/33). Attachment of the fluorene label to HPC was achieved by reaction of the sodium alkoxide of HPC with 9-fluorenylmethyl tosylate (**2**) prepared from the corresponding alcohol. It was anticipated that under these conditions the tosylate **2** may undergo an elimination reaction in competition with ether formation (Figure 1).[22] However, this side reaction did not dramatically reduce the yield of labeling, nor did it hamper the purification of the labeled polymer. The presence of a minor component, insoluble in THF, in addition to HPC-Flu/33 was taken as evidence for the formation of dibenzofulvene, which can undergo facile base-catalyzed polymerization under the reaction conditions. Repeated precipitations gave the labeled polymer in high purity, as established by GPC analysis.

Excitation and Emission Spectra. Excitation and emission spectra of HPC-Flu/33 were recorded in water, methanol, and dioxane. In all three solvents the fluorescence spectrum was characterized by two emissions: an emission centered at 315 nm (intensity I_M), attributed to locally excited fluorene chromophores ("monomer emission"), and a broad emission centered at 387 nm, attributed to fluorene excimers (intensity I_E) (Figure 2). A close examination of the corrected excimer fluorescence reveals that the emission band presents a shoulder at 411 nm, suggesting that the polymer-linked fluorenes form more than one type of excimer. This observation was confirmed by fluorescence decay measurements (see below). The ratio of excimer to monomer emission was higher in water (0.49) than in methanol (0.20) and dioxane (0.14). It did not change significantly when the concentration of polymer in solution was increased from 10 to 100 ppm. It is tempting to conclude from this observation that in this concentration range the excimers form between fluorenes attached to the same polymer chain, rather than between fluorenes belonging to different chains. While this may be true in dioxane and methanol, the situation in water is different, as proven by the results of experiments presented later in this paper. Excitation spectra of HPC-Flu/33 in dioxane monitored at 317 and 395 nm were identical, and the maxima corresponded to those in the UV absorption. In contrast, in water the excitation spectra for the monomer and excimer were different. The general features of the two spectra are the same, but the excitation spectrum for the excimer is red-shifted by 4 nm (see Table II). It is the excitation spectrum for the excimer that corresponds to the UV absorption spectrum.

Quantum Yields of Fluorescence. As a matter of course the spectra of HPC-Flu/33 were compared to those of the model compound, 9-fluorenemethanol. In all the measurements it appeared qualitatively that the total emission of fluorene attached to HPC was much weaker than that of the model coompound, for solutions of iden-



HPC - OH: (hydroxypropyl) cellulose
pTSCl: p - toluenesulfonyl chloride
Pyr: Pyridine



HPC - Flu

Figure 1. Synthetic scheme for the preparation of fluorene-labeled (hydroxypropyl)cellulose (HPC-Flu/33).

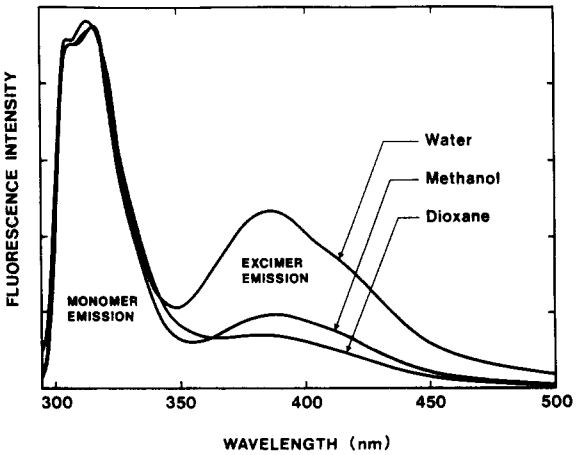


Figure 2. Corrected fluorescence spectra of HPC-Flu/33 (0.1 g L^{-1}) in water, methanol, and dioxane; λ_{exc} = 290 nm.

tical chromophore concentrations. To confirm this observation the fluorene fluorescence quantum yields were measured for solutions of HPC-Flu/33 and 9-fluorenemethanol in water, dioxane, and methanol (Table III). The quantum yields of fluorescence measured for 9-fluorenemethanol (0.50–0.64) were of the same order of magnitude as that reported for fluorene in cyclohexane (0.80)[23a] and in ethanol (0.54).[23b] In HPC-Flu/33 the total fluorene quantum yield had decreased by a factor of 7–10.

Table II
UV Absorption and Excitation Spectra Data for HPC-Flu/33 and 9-Fluorenemethanol in Various Solvents

	UV absorption spectra		excitation spectra (HPC-Flu)	
solvent	λ_{max}, nm (FluMeOH)	λ_{max}, nm (HPC- Flu)	λ_{max}, nm (monomer)[a]	λ_{max}, nm (excimer)[b]
water	300, 289	303	298	303
dioxane	300, 289	302, 291	301	302
methanol	299, 288	302, 290	301	302

[a] λ_{em} at 317 nm. [b] λ_{em} at 395 nm.

Table III
Fluorescence Quantum Yields of HPC-Flu/33 and 9-Fluorenemethanol in Various Solvents

	water	methanol	dioxane
Flu-MeOH	0.50	0.64	0.53
HPC-Flu	0.05	0.08	0.08

Table IV
Fluorescence Decay Measurements for HPC-Flu/33[a,b]

	water		methanol	
	τ, ns	prefactor	τ, ns	prefactor
monomer[c]	τ_1, 4.2	a_1, 0.73	τ_1, 4.3	a_1, 0.60
	τ_2, 6.0	a_2, 0.27	τ_2, 8.0	a_2, 0.40
excimer[d]	τ_1, 1.9	a_1, 0.78	τ_1, 2.2	a_1, 0.65
	τ_2, 13.5	a_2, 0.14	τ_2, 15.0	a_2, 0.23
	τ_3, 32.7	a_3, 0.08	τ_3, 33.1	a_3, 0.12
	$\langle\tau\rangle$, 19.5		$\langle\tau\rangle$, 20.9	

[a] Intensities were fit to a sum of exponentials: $I(t) = \sum a_i \times \exp(-t/\tau_i)$. Fits to three exponential terms were employed when fits to two exponentials were clearly inadequate. [b] The angular brackets indicate mean lifetimes calculated from the data. [c] λ_{exc}, 280 nm; λ_{em}, 317 nm. [d] λ_{exc}, 280 nm; λ_{em}, 395 nm.

This fact is diagnostic of either a high incidence of fluorene self-quenching by a nonemissive process or a significant shortening of the lifetime of excited fluorenes. This self-quenching takes place in the three solvents examined, but it is especially evident in water.

Lifetime Measurements. The monomer fluorescence decay of HPC-Flu/33 in methanol showed a nonexponential profile which could be fit to a sum of two exponential terms (Table IV). The best fit ($\chi^2 = 1.13$) was obtained for decay times of 2.5 ns ($a_1 = 0.42$) and 7.3 ns ($a_2 = 0.58$). A marginally acceptable fit resulted ($\chi^2 = 1.43$) when the longer decay time was fixed at 8.0 ns, the value of the decay time of the model compound 9-fluorenemethanol in methanol. The shorter lived component was then assigned a decay time of 4.3 ns. Fluorescence decay measurements on an aqueous solution of HPC-Flu/33 also showed a nonexponential decay for the monomer emission. This decay could not be fit well to a sum of two exponential terms. Nonetheless it is reported here as a sum of two exponential terms with decay times of 4.2 and 6.0 ns ($\chi^2 = 1.80$). The longest decay time was set to be identical with that of the model compound in water (6.0 ns, single-exponential decay). Assuming that the prefactors of the exponential decay terms are proportional to the relative amounts of each emitting species, it can be shown that the shorter lived component is the main contributor to the monomer emission. The complexity of the fluorescence decay of the fluorene monomer emission reflects the heterogeneity of the sample. Not only can the fluorene groups be attached to chemically different positions on the glucose rings of the polymer, but also there exists a distribution of fluorene separations on the polymer, and various polymer chains contain different numbers of chromophores. However, both in water and in methanol the monomer decay profiles may be interpreted in terms of two distinct fluorene populations, the largest one having a shorter lifetime and the minor one having a decay behavior similar to that of isolated 9-substituted fluorenes.

The fluorescence decay profile for the excimer emission of HPC-Flu/33 in water did not show any growing-in component, but only a complex decaying curve. The profile could be fit to a sum of three exponential terms with decay times of 1.9, 13.5, and 32.7 ns ($\chi^2 = 1.22$) (Table IV). The absence of a rising component implies either that all but a very small fraction of the excimer emission arises from ground-state aggregates of fluorene or that the excimer forms faster than the resolution (<1 ns) of the measurement. This situation was already encountered for solutions of pyrene-labeled HPC. In this case, evidence from picosecond fluorescence studies pointed strongly toward the presence of preformed pyrene ground-state dimers or aggregates.[24] A similar situation was found for samples in methanol, where the excimer profile of HPC-Flu/33 did not show a rising component. The nonexponential excimer decay profile could be fit to a sum of three exponential terms with decay times of 2.2, 15.0, and 33.1 ns ($\chi^2 = 1.18$). This behavior is different from that of pyrene-labeled HPC solutions in methanol, for which the excimer profile exhibited both a growing-in component and a decaying component, as expected for dynamic excimer formation.[25] The complexity of the excimer decay profiles of HPC-Flu/33 in water and in methanol provides additional evidence for the presence of more than one type of fluorene excimer, as implied by the steady-state measurements.

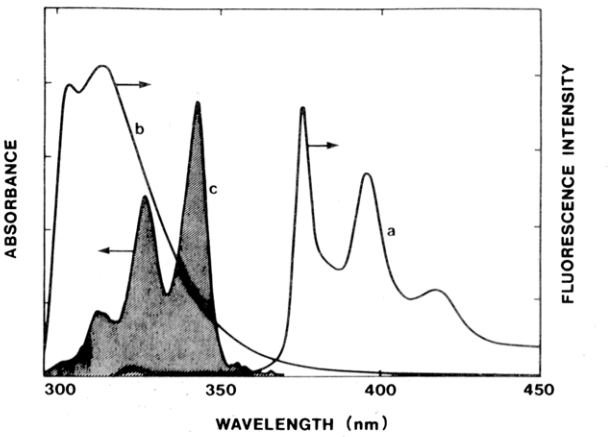


Figure 3. Fluorescence spectra of aqueous solutions of (a) pyrene-labeled (hydroxypropyl)cellulose (HPC-Py/438, 0.2 g L^{-1}) and of (b) 9-fluorenemethanol (6.9×10^{-6} M); $\lambda_{exc} = 290$ nm. The shaded spectrum (c) represents the UV absorption of HPC-Py/438 (0.4 g L^{-1}) in water.

Energy-Transfer Experiments. Spectroscopically, the fluorene-pyrene pair is well suited for nonradiative energy-transfer experiments, since the emission spectrum of fluorene (energy donor) overlaps well with the absorption spectrum of pyrene (energy acceptor) and there exists a window in the UV spectrum where the absorption of fluorene is much stronger than that of pyrene, thus allowing selective excitation of donor (fluorene) in the presence of acceptor (pyrene) (Figure 3). In this study of HPC–HPC interactions in water, pyrene and fluorene have been used in turn as labels and as probes. In one case the experiments focused on the energy transfer between two labeled polymers, HPC-Py and HPC-Flu/33. In a second approach, the energy transfer between a labeled polymer and a fluorescent probe, either HPC-Flu/33 and pyrene or HPC-Py and 9-fluorenemethanol, has been studied.

Solutions of Donor- and Acceptor-Labeled Polymers. Aqueous and methanolic solutions of mixtures of fluorene- and pyrene-labeled HPC were examined (Table I). The emissions spectra of aqueous solutions of HPC-Py, HPC-Flu/33, and of a mixture of the two polymers at the same concentrations are shown in Figure 4. It is immediately apparent that the pyrene emission is greatly enhanced in the presence of HPC-Flu/33. More subtle features of the spectra become apparent upon closer examination. The first observation concerns the fluorene emission. Neither the monomer nor the excimer emission decreases to any significant degree in the presence of HPC-Py. This should not come as a surprise. Not only are the fluorene chromophores present in large excess, but they also undergo efficient nonradiative self-quenching, as discussed earlier. Energy transfer to pyrene can originate from any excited fluorene, irrespective of its fate in the absence of acceptors. It is, however, an unfortunate situation from the point of view of the experiments pres-

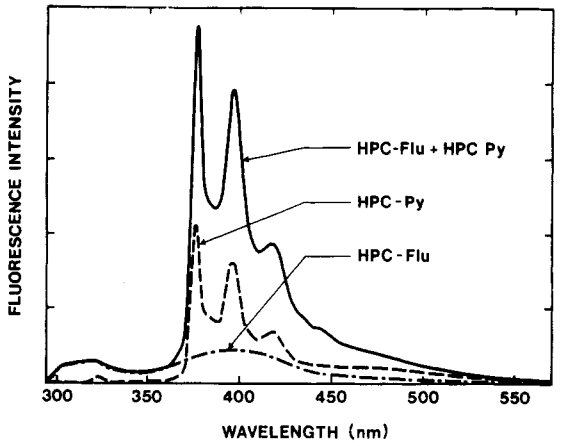


Figure 4. Fluorescence spectra of aqueous solutions of fluorene-labeled (hydroxypropyl)cellulose (HPC-Flu/33, 0.05 g L^{-1}), pyrene-labeled (hydroxypropyl)cellulose (HPC-Py/438, 0.15 g L^{-1}), and a mixture of the two polymers [HPC-Flu/33 (0.05 g L^{-1}) and HPC-Py/438 (0.15 g L^{-1})]; λ_{exc} = 290 nm.

ented here, since it prevents one from obtaining meaningful information from the ratio of the donor and acceptor emission intensities as a tool to monitor changes in the energy transfer. This ratio has proven to be extremely useful in other related systems.[8-12] The second observation deals with details of the pyrene emission spectrum. In the absence of HPC-Flu/33 the fluorescence spectrum of HPC-Py/438 is characterized by a strong emission due to isolated excited pyrenes ("monomer" emission) with maxima at 377 and 397 nm and a weak emission centered around 480 nm due to excimer emission. As in the case of fluorene-labeled HPC the excimer emission originates mostly from the excitation of preformed ground-state pyrene dimers. The emission spectrum of a mixture of HPC-Py and HPC-Flu/33 excited at 345 nm was similar to but not identical with that of a solution of HPC-Py alone: the monomer emission was unaffected, but the excimer emission had a lower intensity. This reflects the fact that HPC-Flu/33 disrupts the pyrene dimers to a certain extent. When the mixture is excited at 290 nm the observed pyrene emission is a superposition of the emission due to directly excited pyrenes and of that due to pyrenes excited by energy transfer. It is possible to isolate the emission resulting from energy transfer, by subtraction from the spectrum of the mixture of the contributions of flluorene and directly excited pyrene. This was done, and the pyrene emission spectra arising from the two processes were normalized at 377 nm. The emission of the directly excited pyrene presents an excimer emission, but the emission resulting from energy transfer does not.

The influence of polymer concentration on the efficiency of energy transfer was examined. Three different effects were monitored. First, the relative ratio of fluorene to pyrene chromophores was increased from 5 to 10. This did not change the observed intensity of the pyrene emission by a significant amount. Next, for a given pyrene to fluorene molar ratio (5), the total polymer concentration was decreased from 200 to 2 ppm. For each polymer concentration the intensity of pyrene emission due to energy transfer was evaluated in the following manner. The total pyrene emission was taken as the half-sum of the emission intensities at 377 and 397 nm of the spectrum obtained after subtraction of the fluorene emission normalized at 317 nm. The intensity of the pyrene emission resulting from energy transfer (I_{ET}) was calculated from this value by subtraction of the contribution of the directly excited pyrene of corresponding concentration. Since the pyrene concentration changed for every measurement, the

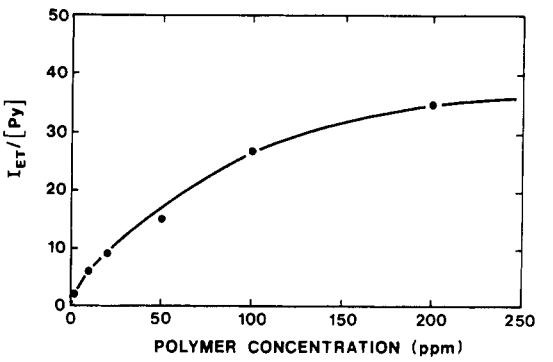


Figure 5. Reduced intensity of the pyrene emission due to energy transfer ($I_{ET}/[Py]$) as a function of the total labeled (hydroxypropyl)cellulose concentration.

intensity I_{ET} was divided by the pyrene concentration for each measurement. This value was plotted against the total polymer concentration (Figure 5). Significant energy transfer between HPC-Flu/33 and HPC-Py takes place when the total polymer concentration is as low as 50 ppm. It becomes negligible only at concentrations lower than 5 ppm. Finally the effect of added unlabeled HPC was examined. The concentrations of HPC-Flu/33 and HPC-Py/438 were maintained constant, while the total HPC concentration was increased from 200 to 5000 ppm. In all cases the results were time dependant. At high HPC concentration (>2000 ppm) the efficiency of energy transfer decreased continuously with time and became negligible after 7 days. In the 200–500 ppm concentration range, complex phenomena were observed, indicative of the influence of time aging on the aggregation properties of HPC in water. Similar aging effects have been reported recently by Georgelos and Torkelson in a study of the thickening behavior of dilute aqueous polyethylene oxide solutions.[26]

A solution in methanol of HPC-Flu/33 (60 ppm) and HPC-Py/56 (40 ppm) was used to investigate the occurrence of energy transfer between chromophores attached to different polymers in a solvent other than water. In this case the molar ratio of fluorene to pyrene was 10 and an HPC-Py sample of higher level of labeling was employed. No energy transfer between fluorene and pyrene was detected under these conditions: the emission spectrum of the mixture of the two polymers was identical with the spectrum created by addition of the spectra of the two polymers in separate solutions at the same concentration. The pyrene emission was not enhanced.

Solutions of a Low Molecular Weight Probe and a Labeled Polymer. HPC-Flu/33 and Pyrene. Experiments with the pyrene probe yield information both on the polarity of the probe environment and on the distances between the probe and the fluorene tag on the polymer. The spectrum of pyrene exhibits a characteristic fine structure which is sensitive to the environment of the probe. A useful tool to determine the polarity of the pyrene environments is the ratio I_1/I_3 of the intensity of the highest energy band ([0,0] band) to that of the third band ([0,2] band).[27a] This ratio has been reported for pyrene in a wide range of solvents.[27b] The general trend is that I_1/I_3 increases with increasing solvent polarity. For pyrene in water and in aqueous polymer solutions at 25 °C the ratio I_1/I_3 was lower in the presence of HPC-Flu/33 (1.75) than in water (1.80) or in the presence of HPC (1.85). This indicates that on average in polymeric solutions pyrene resides in a polymer-rich environment and that the polarity sensed by the probe is different in HPC and in HPC-Flu/33. Similar experiments to probe the polarity of HPC-Py are very difficult, since in this case the label

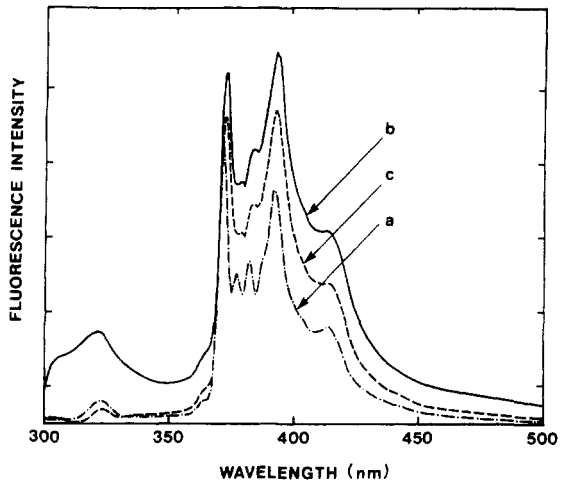


Figure 6. Fluorescence spectra of pyrene in water and in an aqueous solution of fluorene-labeled (hydroxypropyl)cellulose (HPC-Flu/33, 0.025 g L^{-1}); λ_{exc} = 290 nm: (a) pyrene ($\sim 4 \times 10^{-7}$ M) in water; (b) pyrene ($\sim 4 \times 10^{-7}$ M) in aqueous HPC-Flu/33 (0.1 g L^{-1}); (c) spectrum obtained by subtracting from (b) the emission of HPC-Flu/33 at the same concentration.

and the probe absorb at almost identical wavelengths.

To detect nonradiative energy transfer between HPC-Flu/33 and pyrene, the emission spectra of aqueous solutions of pyrene, HPC-Flu/33, and a mixture of HPC-Flu/33 and pyrene were measured under the same conditions and at the same concentrations (Figure 6). The emission of pyrene was enhanced in the presence of HPC-Flu/33, although not as much as in the case of mixtures of HPC-Py and HPC-Flu/33. The fluorene emission intensity was hardly affected by the presence of pyrene, as observed already in the labeled polymer experiments.

HPC-Py and 9-Fluorenemethanol. No significant energy transfer was observed in an aqueous solution of 9-fluorenemethanol (donor, probe) and HPC-Py/438 (acceptor, label). A solution of the two low molecular weight probes, 9-fluorenemethanol and pyrene, was examined as well with chromophore concentrations identical with those used in labeled polymer/probe experiments. In this case absolutely no energy transfer between 9-fluorenemethanol and pyrene was detected.

Discussion

Fluorescence Spectroscopy of Fluorene-Labeled (Hydroxypropyl)cellulose. Evidence from UV absorption and fluorescence indicates that there are two light-absorbing species in aqueous solutions of HPC-Flu/33: isolated fluorenes and ground-state dimers or higher aggregates. Both species absorb light at 290 nm. Excited isolated fluorenes undergo either radiative decay to the ground state (λ_{max}(emission) = 317 nm) or nonradiative quenching. Isolated excited fluorenes could also form excimers by diffusion-controlled encounter with ground-state fluorenes. This last pathway has to be ruled out since fluorescence decay measurements gave no evidence for a rising component in the excimer time-dependent fluorescence profile. The excimer emission has to be attributed to the excitation of preformed fluorene ground-state dimers. Precedents for this situation exist. Saigusa and Itoh reported the formation and spectroscopy of ground-state fluorene dimers during supersonic expansion of fluorene in helium.[28] Fluorescence emission from the excited van der Waals fluorene dimers was characteristic of an excimer emission with a maximum at 360 nm and a decay time (about 60 ns) longer than that of the monomer (about 20 ns). Excimer formation was postulated to occur by a small rearrangement of the geometry of the ground-state dimer. The dynamic fluorene excimer which has been observed in concentrated solutions of fluorene derivatives[28] was described as consisting of two parallel molecules displaced along their short axis by about one carbon–carbon bond length to minimize intermolecular π electronic repulsion and maintain a high degree of symmetry.[29] The interplanar separation between the two fluorene molecules was estimated to be ca. 3.5 Å.

While studies of fluorene derivatives in solution and in the gas phase help to understand the spectroscopy of HPC-Flu/33, the situation of the polymer is more complicated because of additional constraints imposed by intra- and interpolymeric interactions. The existence of ground-state fluorene dimers in water, and possibly methanol, is directly related to the solution properties of HPC. Their formation and stability are driven by hydrophobic forces working in the following manner. The number of hydrogen bonds between water molecules which are broken or disrupted by the nonpolar fluorene groups is minimized when two or more fluorenes come in close proximity. The nonpolar dimers are surrounded by a cage of highly organized water molecules bound together by tight hydrogen bonds. Thus the dimer formation in water has a positive entropy and a positive enthalpy. At room temperature the entropic term dominates, rendering the free energy of dimer formation favorable (negative). Other aspects of the fluorescence of HPC-Flu/33 merit further attention. For example, neither the monomer nor the excimer have simple fluorescence decay profiles. A rigorous interpretation of these observations will require the time-dependent studies to be performed on a much shorter time scale. The sizeable quenching of fluorescence emission that results from attachment of fluorene to HPC is also puzzling. Comparison of steady state and time-dependent data suggests that the quenching is a static phenomenon rather than dynamic. A similar effect was not observed in the case of the pyrene label. This decrease in quantum yield is probably a consequence of a high incidence of fluorene self-quenching, a phenomenon reported also in highly concentrated fluorene solutions in toluene.[30]

Energy-Transfer Measurements. Nonradiative energy transfer between an energy donor (D) and an energy acceptor (A) originates in dipole–dipole interactions. For isolated pairs of chromophores which fulfill the requirements for energy transfer by this mechanism, the transfer efficiency is a well-defined function of the distance, r, between the donor and the acceptor. According to Förster's theory the probability $P(ET_{D\to A})$ of energy transfer from a donor to an acceptor per unit time is given by[31]

$$P(ET_{D\to A}) = \frac{9000(\ln 10)\kappa^2\Phi_0\upsilon}{128\pi^5 n^4 N r^6 \tau}\int_0^\infty \frac{f(\upsilon)\epsilon(\upsilon)}{\upsilon^4}\,d\upsilon = \frac{1}{\tau}\frac{R_0^6}{r^6} \quad (1)$$

where κ^2 is a function of the mutual orientation of donor and acceptor, Φ_0 is the quantum yield of the donor fluorescence in the absence of an acceptor, n is the refractive index of the medium, N is Avogadro's number, τ is the lifetime of the donor in the absence of the acceptor, $f(\nu)\,d\nu$ is the normalized fluorescence intensity of the donor in the wavenumber range ν to $\nu + d\nu$, $\epsilon(\nu)$ is the absorption coefficient at the wavenumber ν, R_0 is defined by eq 1 and is given by

$$R_0^6 = 8.8 \times 10^{-25}\Phi_0\kappa^2 n^{-4} J \quad (2)$$

J being the integral in eq 1. The energy transfer competes

with spontaneous decay of the donor, characterized by the rate constant $1/\tau$. Thus the probability p that the donor will not be deexcited within the time, t, following excitation is given by eq 3, and the efficiency, E, for energy transfer is expressed by eq 4:

$$-\frac{1}{p}\frac{dp}{dt} = \frac{1}{\tau}\frac{R_0^6}{r^6} \tag{3}$$

$$E = \frac{R_0^6}{R_0^6 + r^6} \tag{4}$$

Thus the efficiency of transfer is 50% when $r = R_0$. The R_0 value between pyrene and fluorene was calculated to be approximately 37 Å, for a quantum yield of fluorene emission of 0.66.[12] Since in the case of HPC-Flu/33 the quantum yield of fluorene emission is much lower, the R_0 value may also decrease. A decrease of the intrinsic quantum yield by a factor of 10 (see Table III) gives an approximate value of R_0 of 25 Å.

The efficiency of energy transfer will be affected significantly by the density of energy acceptors around the energy donor: the higher the density of acceptors Py around the donor Flu in an active sphere of radius R_0, the more effective the energy transfer from Flu to Py. The importance of this factor is immediately apparent when one compares the results of experiments with low molecular weight probes to those with labeled polymers. In the case of small molecules, energy transfer takes place when the two interacting chromophores diffuse toward each other during the lifetime of the donor. At the micromolar concentrations employed here the probability of this event is extremely low. Indeed no energy transfer takes place between pyrene annd 9-fluorenemethanol under these circumstances. By contrast, in the case of polymer-bound chromophores, diffusion of the polymers is negligible on the time scale probed by energy transfer. The chromophore motions are limited by the rate of conformational transitions of the chain molecules. When there exist no interpolymeric interactions in solution the probability of energy transfer between labels on two different chains is very low. This is the situation of HPC (0.1 g L^{-1}) in methanol. No energy transfer is detected. In water, in contrast, efficient energy transfer is observed between labels attached to different polymer chains. This phenomenon can only be explained in terms of a strong interpolymeric mutual attraction, which brings the two chromophores into proximity. This attraction results in the formation of polymeric aggregates which were detectable by the experiments described here at polymer concentrations as low as 0.02 g L^{-1}. This fact is unique in solutions of synthetic polymers.

The exact nature of the donor and acceptor species responsible for the energy transfer between HPC-Flu/33 and HPC-Py is difficult to ascertain. In principle energy transfer can occur between two types of donors, excited fluorenes and excited fluorene dimers, and two acceptors, isolated pyrenes and ground-state dimers. Energy transfer originating from fluorene excimers must be a minor component, since the absorption of either pyrene or pyrene dimers is extremely weak in the 350–450-nm spectral window in which the fluorene excimer emits. Energy transfer from excited fluorenes to pyrene ground-state dimers is excluded also, since there is no evidence for pyrene excimer emission from energy transfer. Therefore the observed energy transfer takes place mostly between isolated fluorenes and isolated pyrenes.

A final point on the interactions between HPC-bound fluorene and pyrene chromophores merits discussion. It concerns the detailed mechanism of energy transfer between the two chromophores. The following evidence from the excitation spectra of the mixture of HPC-Flu/33 and HPC-Py indicates that energy transfer between fluorene and pyrene may occur by more than one mechanism. Excitation spectra of an aqueous solution of HPC-Flu/33 and HPC-Py were monitored at several wavelengths and compared to those of solutions containing either HPC-Py or HPC-Flu/33. The excitation spectra of the mixture of HPC-Py/438 and HPC-Flu/33 present bands attributed to the pyrene chromophores (from 310 to 360 nm) and bands due to the fluorene chromophores (from 295 to 305 nm). A comparison of the spectra monitored at different wavelengths yields insights into the nature of the light-absorbing species. Most revealing are the spectra monitored at 380 and 480 nm (Figure 7). The general features of the spectra are the same, but there are significant shifts in band positions. The bands due to the pyrene chromophores in the spectrum monitored at 480 nm (pyrene excimer) are red-shifted by about 3 nm compared to those of the spectrum monitored at 380 nm (pyrene monomer). This feature observed also in the spectra of HPC-Py/438 in the absence of HPC-Flu/33 is an indication of the presence of two distinct absorbing species, isolated pyrenes and ground-state dimers or aggregates.[4] By contrast, focusing on the spectral range attributed to the fluorene chromophores (295–305 nm), it is not possible to detect any shift in band maxima between the excitation spectra monitored at 380 and 480 nm. In both cases the band of longest wavelength occurs at 303 nm, a position assigned to fluorene dimers. This indicates that energy transfer takes place between excited fluorenes and both isolated pyrenes and aggregated pyrenes. Therefore one cannot discount the occurrence of short-range interactions between the chromophores by a Dexter-type mechanism.[32]

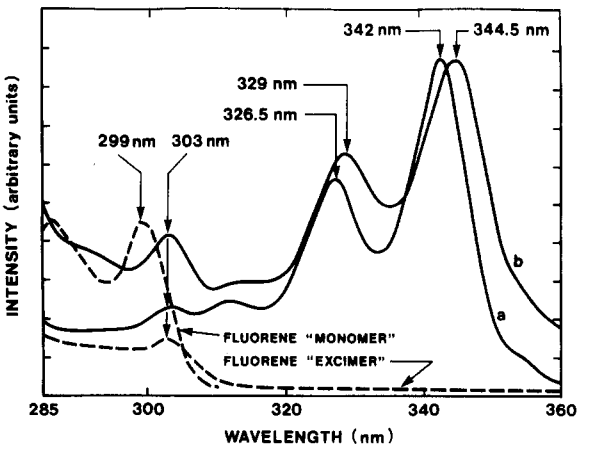


Figure 7. Excitation spectra of a mixture of HPC-Py/438 and HPC-Flu/33 in water (full line) monitored at 380 nm (a) and 480 nm (b) and of a solution of HPC-Flu/33 in water (dashed line) monitored at 317 nm (fluorene "monomer") and 380 nm (fluorene "excimer"). Spectra a and b were normalized at the wavelength of highest intensity.

Conclusion

Interpolymeric associations of fluorescently labeled (hydroxypropyl)celluloses were monitored by experiments based on energy transfer between energy donors (fluorene) and energy acceptors (pyrene) attached to different polymer chains. No energy transfer was observed in a methanolic solution of fluorene-labeled HPC and pyrene-labeled HPC. In water, energy transfer between the two labeled polymers was detected at total polymer concentrations as low as 0.02 g L^{-1}. This phenomenon was explained in terms of a strong interpolymeric mutual attraction which brings

the two chromophores into proximity and results in the formation of interchain aggregates at very low polymer concentration. Aggregates occur in water but not in alcohols or in a good solvent for HPC such as dioxane or methanol.

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Registry No. HPC, 9004-64-2.

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Miscibility and Immiscibility of Polyamide Blends

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ABSTRACT: The solution behavior of blends of an amorphous aromatic polyamide, nylon 3Me6T, in a homologous series of aliphatic polyamides has been interpreted in terms of a recently introduced mean-field binary-interaction model. Founded on the premise that the polyamides in question can be treated as copolymers composed appropriately of methylene, amide, and phenyl mers, it has been possible to estimate the segmental interaction parameters, χ_{ij}. Using these values, a cartographic survey of the phase behavior of additional binary blends of aromatic/aliphatic polyamides has been conducted and found to correlate well with the experimental observations described here and in the literature.

Introduction

Although lacking in completeness, the Flory-Huggins approach[1,2] is often relied upon to provide a convenient and readily acceptable insight into the thermodynamics of polymer-polymer blends. The necessary negative Gibbs free energy of mixing, ΔG, is the primary requirement in order that two polymers are miscible. Additional prerequisites are also necessary; however, these restrictions are well understood to originate from the delicate balance between the entropic and enthalpic contributions to ΔG, although in the limit of high molar mass polymers, the entropic contribution is usually regarded to have a negligible impact upon the free energy balance. A further simplification, introduced by setting aside the free volume or equation of state contribution to ΔG, has shifted the focus of attention to the enthalpic term.[3] Accordingly it has been generally believed that a favorable or exothermic interaction between segments, or portions of segments, of different polymer species is the dominant factor promoting polymer-polymer miscibility.

Recent developments,[4-6] however, incorporating a mean-field binary interaction model, have shown that it is possible to accommodate the unusual phase behavior of blends of random copolymers by the inclusion of an unfavorable or repulsive interaction between the segments or mers comprising the copolymers. Essentially, this type of treatment assigns a segmental interaction parameter, χ_{ij}, to individual mers of each polymer and computes an overall value of the Flory interaction parameter, χ_{blend}, in order to predict phase behavior. This simple approach has been applied with great efficacy to account for a varied body of experimental observations.[7-14] Similarly it will also

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