from both monomer and stereosequences. However, spectrum c in this Figure shows the simplification achieved at >98% conversion, where nine well resolved lines appear. These lines evolve from stereochemical triads; the heterosteric geminal fluorines in *mr* and *mm* environments give rise to AB quartets, whereas the homosteric geminal fluorines in the symmetrical *rr* environment give a singlet. More detailed ^{19}F assignments of these triad components are not made in the present study.

Conclusions

Difluorocarbene generated from PhHgCF$_3$ under mild, neutral conditions adds to *cis*- and *trans*-1,4-polybutadienes very efficiently with retention of double bond configuration. These adducts can be prepared with any desired level of the geminal difluorocyclopropane moiety, and form a new class of fluorocopolymers. Complete conversion results in the structural equivalent of a 1:1 (ethene–3,3-difluorocyclopropene) copolymer.

The mode of difluorocarbene addition to the polybutadienes is strictly random in both monomer and stereosequence. Thus the crystallinity initially present in *trans*-PBD is destroyed at intermediate conversions, and studies are presently under way to characterize additional properties of these materials.

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Registry No. 3, 99966-95-7; 4, 99966-96-8; PhHgCF$_3$, 24925-18-6.

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Formation and Relaxation of an Excited Complex in a Polymer

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ABSTRACT: The dynamic fluorescence spectroscopy of an excimer-forming polymer (I) and an exciplex-forming polymer (II) is reported in comparison with the corresponding dimer model (III) and monomer model (IV), respectively, in dilute solution. The rise profile of intrapolymer excimer in I is faster than that of III, although diffusion of polymer-bonded chromophores is slower than for the small molecule. The reason is believed to be the high local concentration of chromophores in I. In the case of exciplex formation by II, the mode of excited-state interaction is mostly interpolymer and the formation of the exciplex is completed within a time of the order of 100 ps. The corresponding monomer model (IV) forms the exciplex more slowly. Loose polymer association prior to excitation accounts for the fast rise of the exciplex emission in II. The time-resolved fluorescence of II shows a gradual red shift of the exciplex emission beyond 100 ns, whereas IV does not exhibit this shift. This is an indication that solvation and other relaxation processes forming the stable exciplex state in II are slow. Also, excimer formation by I does not show a time-dependent wavelength shift since the relaxation of the excimer is less than that of the exciplex. Fluorescence lifetime measurements with a fixed wavelength for the polymer must therefore be made with care.

Excited-state interaction in polymer systems is a rapidly growing area of research as a basis for photopolymers and for understanding photophysicochemical phenomena in molecular aggregate systems.[1] Energy migration and transfer, interaction of the excited chromophore with molecules in the ground state leading to excimer formation, exciplex formation, dimerization, electron transfer, and other phenomena are unit processes of photoresponsive functions in polymers and molecular aggregate systems. These excited-state interactions are useful probes not only for photopolymers but also for the study of polymer

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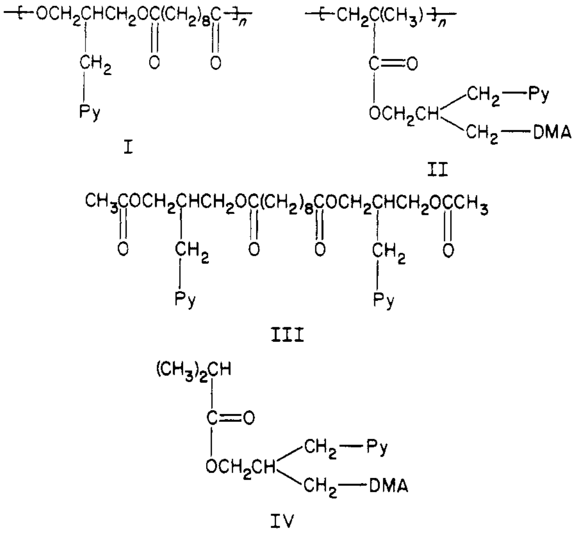
Chart I



Py: 1-pyrenyl, DMA: 4-*N*,*N*-dimethylaminophenyl

properties. For example, miscibility of two polymers has been conveniently probed by the measurement of energy migration between them.[2]

As a result of recent advances in fluorescence lifetime and time-resolved fluorescence measurements, it is now possible to look into the dynamic aspects of excited-state interactions and subsequent relaxation processes in polymers in the picosecond regime.

We report here our recent time-resolved measurements of excimer and exciplex formation in polymers that were formerly discussed on the basis of stationary fluorescence spectroscopy.[3]

Experimental Section

The preparation of samples I, II, III, and IV has been reported.[3] All solvents used were spectrophotometric grade. The sample solutions were purged with argon for more than 20 min and then sealed. The rise and decay of fluorescence and time-resolved fluorescence spectra were measured by means of a single photon counter. The instrument made in the Institute for Molecular Science is equipped with an argon ion laser–dye laser combination with a cavity damper (pulse width: ~6 ps; repetition: 0.8 MHz, 315.6 nm) and operated at 5.12 ps/channel. The wavelength scan between 350 and 600 nm was programmed at 1.2-nm intervals so that the wavelength-resolved rise and decay profiles of emission can be determined automatically and a time-resolved emission spectrum thus obtained. Details of this instrument have been reported.[4]

For fluorescence lifetime measurement in the nanosecond region, a single photon counter with a computer program for two-component decay analysis (PRA system 3000) was employed.

Results and Discussion

The samples are a polyester (I) bearing pendant 1-pyrenyl groups ($\bar{M}_w$ = 10 400, $\bar{M}_w/\bar{M}_n$ = 1.3, fractionated by preparative GPC) and an exciplex-forming polymethacrylate (II) ($\bar{M}_w$ = 6300, fractionated by preparative GPC) shown in Chart I. As their small molecular model compounds, the corresponding dimer model (III) for the polyester and monomer model for the polymethacrylate (IV) were used.

In previous publications,[3a] we reported that both I and III form intramolecular excimer and that no intermolecular excimer formation is observed below a chromophore concentration of 10^{-4} M. On the other hand, II exhibits strong interpolymer association even below 10^{-5} M, as revealed by concentration-dependent exciplex formation.[3b] The extent of association depends strongly on molecular weight and solvent. The corresponding monomer model shows only intramolecular exciplex formation. In either I or II, the total amount of excimer or exciplex is much larger than for the corresponding dimer or monomer model compounds. In particular, II shows almost no monomer emission of pyrene. Since excimer and exciplex formation are diffusion-controlled processes that are supposedly slower in polymeric systems, the fast rise of the excited complex emission in polymers may indicate the presence of a conformation favorable for excimer or exciplex formation.

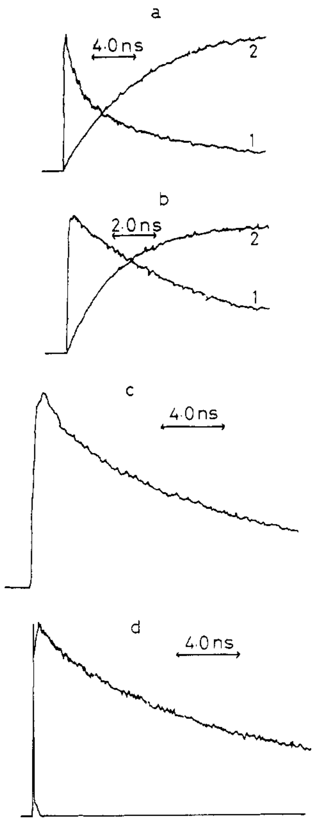


Figure 1. Rise profile of excimer (I, III) and exciplex (II, IV): (a) III in toluene, monitor at 377 nm (monomer emission) (1) and 480 nm (excimer emission) (2); (b) I in toluene, monitor at 377 nm (monomer emission) (1) and 480 nm (excimer emission) (2); (c) IV in 2-methyltetrahydrofuran (MTHF), monitor at 500 nm; (d) II in MTHF, monitor at 500 nm. Excitation at 315.6 nm.

There has been a long dispute on the participation of energy migration in excimer formation in polymers to facilitate excimer formation.[5] However, this is rather unlikely for pyrene in the present systems. The $S_1 \leftarrow S_0$ transition of pyrene is forbidden, so that the efficiency of long-range energy migration should be small. Our previous measurements on fluorescence depolarizations of I in a glassy matrix,[6] in which excimer formation is not observable, indicated that the extent of fluorescence depolarization is limited, showing the frequency of energy migration within the excited lifetime of pyrene to be small. Participation of energy migration in exciplex formation is even more unlikely since pyrene units have quencher neighbors (DMA) in II.

The participation of polymer association in the ground state in exciplex formation is unequivocally shown in Figure 1. Excimer formation in I is faster than in III but the difference is small. The rise of exciplex in II is much faster than that of excimer in I. Both excimer and exciplex being diffusion-controlled, the rates of excimer/exciplex formation should be about the same when two isolated species encounter to form an excimer/exciplex. The rise

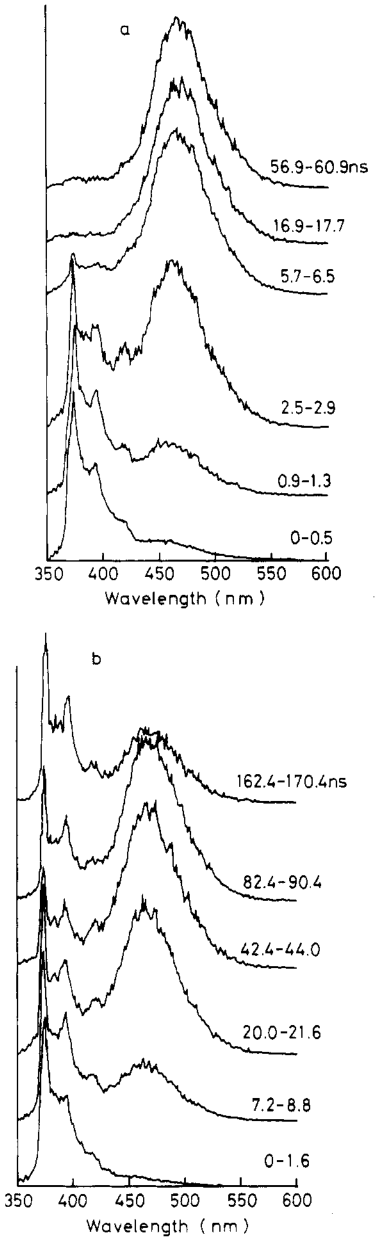


Figure 2. Time-resolved fluorescence spectra of (a) I, and (b) III in toluene. Excitation at 315.6 nm.

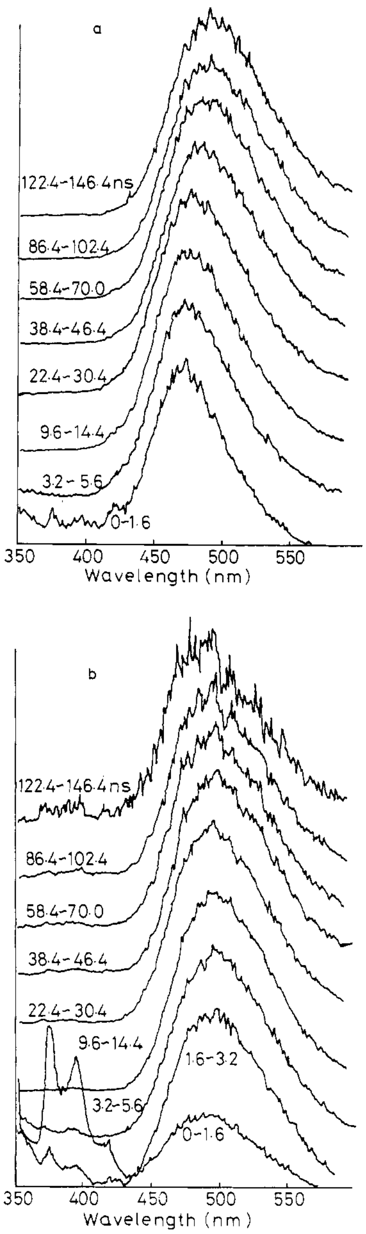


Figure 3. Time-resolved fluorescence spectra of (a) II, and (b) IV in MTHF. Excitation at 315.6 nm.

time of exciplex in II is very short. However, an apparent delay of 100 ps is observed after the laser pulse. Although we cannot exclude the partial contribution of a preformed exciplex site (i.e., well-arranged pair of chromophores leading to instantaneous exciplex formation after excitation), the majority of exciplexes are formed with small segment motions, as shown by the short but clear delay of exciplex emission after excitation. The exciplex rise profile of IV, which does not associate, is of the order of nanoseconds.[7]

Differences in the rate of formation of exciplex and excimer in polymers are attributed to differences in the pairing of chromophores. Exciplex-forming polymers having regularly repeating chromophores tend to associate, as confirmed by the concentration-dependent exciplex intensity and also by the observation of a concentration-dependent diffusion current in pulse polarography.[8] The driving force of the polymer association is suggested to be dipole–dipole interaction induced by very weak electron donor–acceptor interactions between pyrene and DMA in the ground state that cannot be detected as charge-transfer absorption.[9] This polymer association is a kind of loose interaction to facilitate interpolymer exciplex formation but cannot be considered as a preformed exciplex site giving rise to instantaneous exciplex emission.

Excimer formation is intramolecular for both I and III and the different rates in I and III are explained as due to local differences of chromophore concentration which cannot be distinguished from a favorable entropy term in the case of intramolecular excimer formation.[3a]

Besides the difference between intra- and interpolymer modes of interaction, the excimer and exciplex are intrinsically different. While excimer formation requires a close approach of like chromophores to 3–4 Å to bring about exchange interaction, exciplex formation follows primary electron transfer at a distance much greater than 3–4 Å and requires considerable reorientation of chromophores and solvent reorganization during the relaxation process to the stable form of the exciplex.

Time-resolved fluorescence spectra in Figures 2 and 3 reveal interesting contrasts between the polymer and the monomer model as well as excimer and exciplex. The shape of the excimer emission is unaffected by time resolution, indicating that relaxation to the stable excimer

Table I
Fluorescence Lifetime of Exciplex[a]

	decay component, ns			
	IV		II	
fitting range, %	τ_1	τ_2	τ_1	τ_2
0–70	3	114	3	36
0–90	3	117	8	65
15–100	5	116	20	96

[a] τ_1 is the minor component, <5% for IV and <20% for II. [II] = 2×10^{-5} M or [IV] = 1.5×10^{-5} M in 2-methyltetrahydrofuran (MTHF) at room temperature. Excitation: 345 nm. Monitor: ~440 nm.

state is either undetectably fast or unimportant. Also, these results support the presence of only one energy level for the excimer. If there are more than two excimers having different energy levels and different lifetimes, the shape of the excimer emission would change as a function of time after excitation.

Unlike excimer, the exciplex in a polymer shows a definite relaxation process, as shown in Figure 3. It is reasonable that relaxation should be slower in the polymer than in the monomer model. At the present time, however, we cannot decide whether the wavelength shift reveals gradual relaxation of an exciplex species or the presence of multiple exciplex species, each having a different energy level. Under these circumstances the conventional method of lifetime measurement results in a nonexponential decay curve. Within the framework of a two-component analysis, when the fast-rise component is neglected, the apparent lifetime components τ_1, τ_2 fluctuate depending on the range of channels analyzed (Table I). Although we do not understand the physical meaning of τ_1 and τ_2, these values are constant for IV but not for II. In particular, τ_2 of II becomes longer, approaching the value for IV upon shifting the analyzing channels toward the tail of the decay curve. When τ_2 of IV corresponds to the lifetime of the fully relaxed exciplex, the present results are very consistent. The exciplex lifetime is longer after relaxation, as expected.

The time-dependent shift of the fluorescence is a strong warning concerning fluorescence lifetime analysis in a polymer based on measurements at a fixed wavelength. If the fluorescence shift is indeed attributable to a gradual relaxation process, the lifetime analysis must be based on the integrated intensity of the corrected time-resolved spectra. This practice is extremely laborious and no such attempt in a polymer system has been reported to date.

Registry No. I (copolymer), 65289-73-8; I (SRU), 65289-38-5; II, 80683-28-9; III, 73535-83-8; IV, 80628-91-7.

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Preparation and Characterization of Polymeric Solid Electrolytes from Poly(alkylene sulfides) and Silver Salts

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ABSTRACT: Polymeric solid electrolytes have been prepared by complex formation between silver salts and various poly(alkylene sulfides). The polymer–salt complexes of poly(pentamethylene sulfide) (P5S) and $AgNO_3$ have total ionic conductivities comparable to poly(ethylene oxide). Infrared spectroscopy indicates ion pairing between Ag^+ and NO_3^- ions. The transference number for Ag^+ in P5S·$AgNO_3$, ca. 0.9, is much higher than that of most other polymeric solid electrolytes.

Introduction

Most of the recent research on solvent-free polymer electrolytes has concentrated on poly(ethylene oxide) (PEO, I) or poly(propylene oxide) (PPO II) complexes with alkali metal salts.[1-3] These complexes have been investigated extensively in attempts to understand the factors that govern ion transport, and they also are under evaluation as electrolytes in high-energy-density batteries.[4,5]

$$\text{PEO, } (CH_2CH_2O)_n$$
I

$$\text{PPO, } (CH_2CH(CH_3)O)_n$$
II

Polymer–salt complex formation appears to be enhanced by a high concentration of polar groups in the polymer, high polymer chain flexibility, which permits the polymer to more easily solvate the cation, low lattice energy of the salt, and low cohesive energy density of the polymer.[6] To test these ideas and to delineate the chemical variables that influence the formation and function of polymer electro-

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