viologens (Figure 4 and Table I). The maximal fraction may depend on the extent to which the quencher can penetrate into the core of the polymer latex particles. This is related to water penetration and hydrophobic interaction. In HV^{2+} or BV^{2+} quencher, about 80% of the carbazole units were quenched. Those viologens can diffuse deeply into the latex particles by displacements of the hydrated or penetrated water due to hydrophobic interaction. We can therefore propose that this polymer latex is porous and flexible (not hard) within the latex beads.

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Registry No. (NaSS)·(DMA)·(VCZ) (copolymer), 99966-50-4; Py^+, 13441-45-7; MV^{2+}, 4685-14-7; EV^{2+}, 46713-38-6; BV^{2+}, 47082-19-9; HV^{2+}, 47369-13-1.

References and Notes

(1) (a) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543. (b) Thomas, J. K.; Almgren, M. "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 2, p 559. (c) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1983**, *87*, 4529. (d) Miyashita, T.; Murakata, T.; Yamaguchi, Y.; Matsuda, M. *J. Phys. Chem.* **1985**, *89*, 497.
(2) (a) Yamaguchi, Y.; Miyashita, T.; Matsuda, M. *J. Phys. Chem.* **1981**, *85*, 1369. (b) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188. (c) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4279.
(3) (a) Tunuli, M. S.; Fendler, J. N. *J. Am. Chem. Soc.* **1981**, *103*, 2507. (b) Nomura, T.; Escabi-Perez, J. R.; Sunamoto, J.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1484.
(4) (a) Miyashita, T.; Matsuda, M. *Polym. Commun.* **1984**, *25*, 138. (b) Meisel, D.; Matheson, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6577.
(5) DellaGuardla, R. A.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 990.
(6) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.
(7) Frank, A. J.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1979**, *83*, 716.
(8) (a) Suen, C-H.; Morawetz, H. *Macromolecules* **1984**, *17*, 1800. (b) Kitano, H.; Sun, Z.-H.; Ise, N. *Macromolecules* **1983**, *16*, 1306.
(9) Rembaum, A.; Chang, M.; Richards, G.; Li, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 609.
(10) Pekcan, O.; Winnik, M. A.; Croucher, M. D. *J. Colloid Interface Sci.* **1983**, *95*, 420. Pekcan, O.; Winnik, M. A.; Egan, L.; Croucher, M. D. *Macromolecules* **1983**, *16*, 699. Winnik, M. A.; Hua, M. H.; Hougham, B.; Williamson, B.; Croucher, M. D. *Macromolecules* **1984**, *17*, 262.
(11) Johnson, G. E. *J. Phys. Chem.* **1974**, *78*, 1512.
(12) Yokoyama, M.; Tamamura, T.; Atsumi, M.; Yoshimura, M.; Shirota, Y.; Mikawa, H. *Macromolecules* **1975**, *8*, 101.
(13) $E_{cz^+/cz^*} = E_{cz^+/cz} - \Delta E_{ex} = -2.74$ V.
(14) Taniguchi, Y.; Nishina, H.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1646.
(15) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.
(16) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous System"; Marcel Dekker: New York, 1970.
(17) Rhem, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.
(18) Rodgers, M. A. J.; Becker, J. C. *J. Phys. Chem.* **1980**, *84*, 2762.
(19) Lakowicz, J. R. "Principles of Fluorescence Spectroscopy"; Plenum Press: New York, 1983; Chapter 9.

Fluorescence and Energy Migration in 2-Vinylnaphthalene Alternating and Random Copolymers with Methyl Methacrylate and Methacrylic Acid

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ABSTRACT: The fluorescence of alternating and random copolymers of 2-vinylnaphthalene with methyl methacrylate [P(2VN-*alt*-MMA) and P(2VN-*co*-MMA)] and methacrylic acid [P(2VN-*alt*-MA) and P(2VN-*co*-MA)] has been studied. The alternating copolymers have essentially no excimer fluorescence, unlike the random copolymers. The fluorescence decay of the alternating copolymers can be fit satisfactorily to a single exponential while the random copolymers require a three-exponential fitting function. The fluorescence quenching of these copolymers was compared with that of an excimer-free copolymer P(2VN-*co*-MMA) with ca. 3% naphthalene and a small-molecule model, 2-ethylnaphthalene. The energy migration distance (L_s) deduced from the former experiments showed that L_s for the alternating copolymers were approximately twice that of the random copolymers.

Introduction

Singlet energy migration in polymers with pendant aromatic groups has been studied extensively.[1-5] It is well-known that excimer formation can occur at adjacent chromophores[5] or non-nearest neighbors[6] and can act as a trap to terminate energy migration. Thus it is expected that changing the local concentration and/or mutual orientation of chromophores in the polymer coil will affect excimer formation with an concomitant change in energy migration rate. It has been reported by Nakahira et al.[1] that excimer formation in naphthyl polymers could be reduced by introducing bulky groups on the chromophore. However, in this case the energy-transfer rate was also reduced. In the present work, alternating naphthyl copolymers have been prepared in which the chromophores are separated equally and with sufficient chromophore separation to prevent excimer formation.

There are a few reports of photophysical studies of alternating copolymers in the literature. In 1974 Fox et al.[7] included an alternating copolymer of 2-vinylnaphthalene and methyl methacrylate in their studies and demonstrated that excimer formation was essentially eliminated. The present paper can be regarded as an extension of this earlier paper. In 1975 Wang and Morawetz[8] studied co-

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Table I
Preparation and Characterization of Copolymers

	feed, mmol					polymerization		GPC/THF	naphthalene	
polymer	MMA	MA	2VN	Et_2AlCl	TMSiMA	AIBN, mg	condition	M_n[g]	UV	NMR
P(2VN(3%)-*co*-MMA) (model)	9.43		0.28			6.5	*b* (34%[e])	1.2×10^4	3.76	
P(2VN-*alt*-MMA)	5.43		2.72	5.9			*a* (52%)	$\sim 5 \times 10^5$	48.5	48
P(2VN-*alt*-MA)			2.72	6.1	5.43		*a* (10%)[f]	4.2×10^5	40[c]	*d*
P(2VN-*co*-MMA)	3.77		3.31			9	*b* (32%)	1.9×10^4	43.0	46
P(2VN-*co*-MA)		2.79	2.86			6	*b* (4%)	1.4×10^4	45.4	*d*

[a] Toluene/1.8 mL/0 °C. [b] Benzene/5 mL/66 °C. [c] Only roughly estimated due to low solubility in THF. [d] Not performed due to low solubility in $CDCl_3$. [e] Approximate percent conversion. [f] Conversion for P(2VN-*alt*-TMSiMA) precursor polymer. [g] Based on polystyrene standards.

polymers of styrene and acenaphthylene and concluded that in the latter case certain alternating copolymers displayed prominent excimer fluorescence. Thus producing an alternating copolymer does not necessarily eliminate excimer formation. Even if excimer formation is prevented in an alternating copolymer, the average chromophore separation and/or orientation may not be conducive to facile energy migration as was pointed out in the preceding paragraph. In the present work we compare the singlet-state processes of excimer formation and energy migration in alternating and random copolymers of 2-vinylnaphthalene and methyl methacrylate or methacrylic acid. In agreement with the earlier work of Fox et al.,[7] the alternating copolymer displays no excimer fluorescence, in sharp contrast to the random copolymers. Singlet energy migration rates were estimated for the alternating and random copolymers by the method of comparative quenching,[9] using both a small-molecule model compound (2-ethylnaphthalene) and a model polymer containing a small mole fraction of 2-vinylnaphthalene. A significant rate of singlet energy migration was found for all copolymers with the latter model compound, and in all cases the estimated energy migration rate for the alternating copolymer exceeded that of the random copolymer. Thus it is concluded that in this case repressing excimer formation does not simultaneously diminish energy migration.

Experimental Section

A. Materials. The starting materials for sample preparation were 2-vinylnaphthalene (2VN), methacrylic acid (MA), ethylaluminum sesquichloride ($Et_2AlCl \cdot EtAlCl_2$) (all from Aldrich), methyl methacrylate (MMA) (J. T. Baker), and trimethylsilyl methacrylate (TMSiMA) (Petrarch Systems). Solvents used were diethyl ether (ACS, MCB), THF, toluene, methanol, benzene, and methylene chloride (all from Fisher Scientific). TMSiMA, $Et_2AlCl \cdot EtAlCl_2$, diethyl ether, methanol, benzene, and methylene chloride were used as received. All other reagents were purified very carefully since it was found that the dryness of starting materials was the key point to successfully produce an alternating copolymer.

2VN was sublimed twice under vacuum at ca. 30 °C (10^{-6} torr) and stored at low temperature (ca. −10 °C) over $CaCl_2$. MMA was washed by a Na_2CO_3 saturated solution three times to minimize any acid contamination, dried over $CaCl_2$ for 24 h, and then stored over CaH_2 for later use. Immediately before copolymerization MMA was fractionally distilled under a reduced pressure of N_2 gas. MA was also distilled twice under vacuum (~20 °C (10^{-6} torr)) before use. Toluene was distilled over sodium metal immediately before use. THF was passed through activated alumina (MCB) to remove peroxide, dried over CaH_2 overnight, and then fractionally distilled and stored under a positive pressure of N_2 gas.

B. Copolymerization. The random copolymers P(2VN-*co*-MMA) and P(2VN-*co*-MA) were synthesized by conventional radical polymerization methods. 2VN was dissolved in benzene, mixed with fresh MMA (or MA) in a polymerization tube to which AIBN was added as an initiator. Three freeze–pump–thaw cycles were employed to outgas the solution; then the polymerization tube was sealed and maintained at 60 °C for 12–24 h. The polymer was purified by three reprecipitations from CH_2Cl_2 into CH_3OH and then dried under vacuum.

The alternating copolymers P(2VN-*alt*-MMA) and P(2VN-*alt*-MA) were prepared by a slight modification of literature methods.[10] The MMA or TMSiMA was outgassed by three freeze–pump–thaw cycles. While the MMA or TMSiMA was at liquid N_2 temperature, the desired amount of Et_2AlCl was added through a septum mounted on a side arm with a clean, very dry syringe. The mixture was then degassed three more times. The degassed light yellowish-green mixture was brought to 0 °C and stirred for 5 min; then a N_2-bubbled 2VN toluene solution at 0 °C was added through the septum. This solution was degassed twice, sealed, and then stirred at 0 °C for 10 h. The viscosity of the solution was observed to increase gradually. This polymer solution was then poured into a large excess (ca. 10:1) of CH_3OH containing 3% (v/v) HCl. A white polymer precipitated and was purified by reprecipitating from THF into CH_3OH at least three times and dried under vacuum at 50 °C for 4 h. To obtain the P(2VN-*alt*-MA) polymer it is necessary to hydrolyze the P(2VN-*alt*-TMSiMA) polymer. The P(2VN-*alt*-TMSiMA) polymer solution was refluxed in a 1:10:1 (v/v) MeOH–THF–1% NaOH mixture for 10 h. HCl was then added to neutralize the NaOH, and this mixture was refluxed another 2 h. A white precipitate was obtained and washed with H_2O. Subsequent purification was the same as described above. In earlier reports of alternating copolymerization benzoyl peroxide was used as an initiator,[7] but for unknown reasons this method was unsuccessful in our hands. Reaction conditions are specified in more detail in Table I.

C. Characterization of Polymer. A Waters HPLC and four μ-Styragel columns (10^2, 10^3, 10^4, and 10^5 Å) were used to determine the molecular weights (M_n) of all polymers (Table I), using monodisperse polystyrene samples as standards.

Composition of each copolymer was determined primarily by using absorption spectra and proton NMR (Table I). The composition of the MMA copolymers determined from absorption spectra or the integrated ^1H NMR spectra in the alkyl and aromatic regions are consistent with each other. Unfortunately, this check was not possible for MA copolymers because of low solubility in $CDCl_3$.

The ^1H NMR spectrum of P(2VN-*alt*-MMA) is much more resolved than that of P(2VN-*co*-MMA). Our spectrum (Figure 1) for P(2VN-*alt*-MMA) is not identical with that of Hirabayashi et al.[10] since these latter workers studied the 2-(vinyl-α-*d*)-naphthalene polymer in *o*-dichlorobenzene at 150 °C. In future work on alternating copolymer systems we hope to use high-field NMR to assess the stereoregularity of these and related alternating copolymers.

D. Sample Preparation and Fluorescence Measurement. Three freeze–pump–thaw cycles were applied to all polymer solutions in THF. These solutions contained the same concentration of naphthyl groups (5×10^{-4} M) but different concentrations of CCl_4 for the quenching studies. The steady-state fluorescence spectra were recorded on a Spex Fluorolog 2 with a 450-W xenon lamp and a R508 photomultiplier using an excitation wavelength of 290 nm. The steady-state fluorescence quenching was determined from the intensity of naphthalene emission at 338 nm. Fluorescence lifetime measurements were performed on a conventional Ortec single-photon-counting instrument equipped with an uncooled RCA 8850 photomultiplier. However, an excitation wavelength of 316 nm was used due to the characteristics of the flash lamp used. For this reason a Corning CS-470 filter was used

Table II
Fluorescence Decay Parameters for Copolymers[a]

	I_M(340 nm)[b]			I_D(430 nm)[b]		
polymer	τ_1/A_1	τ_2/A_2	τ_3/A_3	τ_1/A_1	τ_2/A_2	τ_3/A_3
P(2VN-*alt*-MMA)	43.4/1.0					
P(2VN-*alt*-MA)	54.4/1.0					
P(2VN(3%)-*co*-MMA) (model)	1.6/0.608	49.2/0.392				
P(2VN-*co*-MMA)	3.0/0.655	11.8/0.329	52.3/0.016	2.0/1.050	4.0/−0.300	59.7/0.250
P(2VN-*co*-MA)	3.5/0.648	12.1/0.332	60.9/0.020	4.1/1.116	6.0/−0.537	71.6/0.421

[a] All in outgassed THF at ca. 20 °C. [b] Fit to $I(t) = \sum A_i \exp(-t/\tau_i)$. The number of terms indicated were required to obtain a satisfactory value of weighted χ^2 (<0.5 typical) and a random distribution of residual around zero. Unless otherwise noted all data taken over the range 0–200 ns. All lifetimes in nanoseconds.

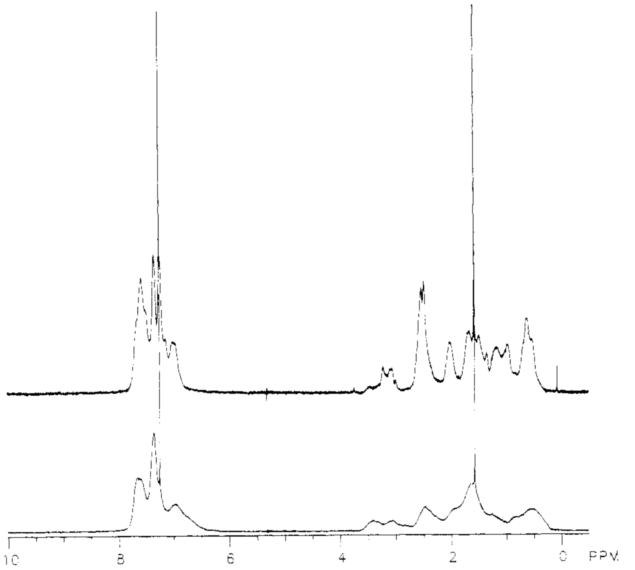

Figure 1. 500-MHz ^{1}H NMR of P(2VN-*alt*-MMA) (top) and P(2VN-*co*-MMA) (bottom) at room temperature in $CDCl_3$. The sharp superimposed peaks are solvent peaks.

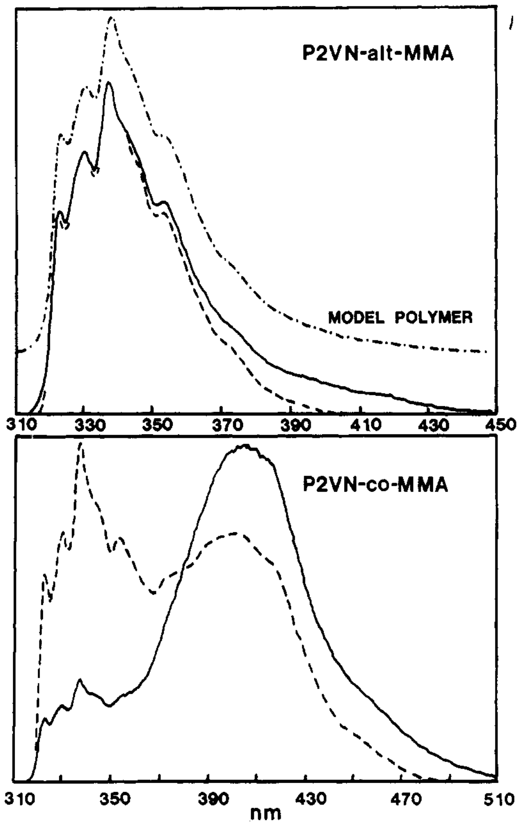

Figure 2. Steady-state fluorescence spectra of alternating and random copolymers P(2VN-*alt*-MMA) and P(2VN-*co*-MMA). The dashed line is the spectrum after the addition of CCl_4 ([CCl_4] = 0.04 M). The model polymer P(2VN(3%)-*co*-MMA) without added quencher is also presented (–·–), offset for ease of comparison with the alternating copolymer (fluorescence intensity in arbitrary units). Solvent: outgassed THF.

to eliminate any scattered excitation light. Details of instrumentation and deconvolution technique have been described elsewhere.[11] In the deconvolution method the following is minimized: $\chi^2 = \sum |I_{obsd}(t_i) - \int_0^{t_i} R_{obsd}(\tau)F(t_i - \tau)\, d\tau|^2 \omega(t_i)$, where $I_{obsd}(t_i)$ is the experimental fluorescence intensity at t_i, $R_{obsd}(t)$ is the instrumental response function determined by the time profile of the excitation wavelength scattered from a colloid solution, and $F(t)$ is a fitting function, which in our case will be a sum of exponentials. The weighting factor $\omega(t_i)$ was taken to be $I_{obsd}(t_i)^{-1}$. A fit was taken to be satisfactory if the same minimum of χ^2 was obtained for several choices of initial parameters in $F(t)$ and the plot of the weighted residual (given by $(I_{obsd}(t_i) - I_{calcd}(t_i))\omega(t_i)$) was randomly distributed around zero. We note for later reference we normalize our data such that the maximum value of $I_{obsd}(t_i)$ is unity. This allows different decay curves to be more easily compared. The actual number of counts in the channel with maximum intensity is given in the figure captions. Since many of the fluorescence decays have a fast and slow component, different time scales on the time-to-amplitude converter were used to collect data. If the longest lifetime value was the same within ca. 10% for a long- and short-time scale the short-time-scale fit was deemed satisfactory. For ease of comparison all fluorescence decays in this paper will be plotted over the same time interval.

Some fluorescence decays were measured at the Center for Fast Kinetics at the University of Texas using an Ar^+ laser operated mode-locked to produce very narrow excitation pulses and a polarizer set at the 54.6° magic angle to avoid polarization effects. The response function of this system has a width of ca. 400 ps. It was not possible to extensively outgas the solution used for these experiments. Hence these data are not included in Table II. There tended to be a short-lifetime component in all these decay curves, which may be in part a result of scattered light (only cutoff filters can be used in this system). The results obtained on this system were in substantial agreement with those obtained in our laboratory. One exception was the P(2VN-*alt*-MMA) polymer, which displayed a 25% component with a lifetime of ca. 2.8 ns.

Results

A. Fluorescence Spectroscopy (Solution Phase).

No excimer emission at 420 nm was observed for the alternating copolymers and the model polymer, but for the random copolymers the excimer band was the dominant feature. The P(2VN–MMA) and model polymer spectra are presented in Figure 2. It is noted that monomer emission for P(2VN-*alt*-MA) was red-shifted approximately 3 nm relative to the other polymers studied herein. This suggests a stronger interaction between the carboxylic group and naphthyl group in this polymer relative to the rest of the set. Otherwise, the spectral features of the P(2VN–MA) polymers are virtually identical with those of P(2VN–MMA). The emission spectra were observed to change very little upon quencher addition (except S/N ratio) for the alternating polymers and the model. For the former there is a slight decrease at longer wavelengths,

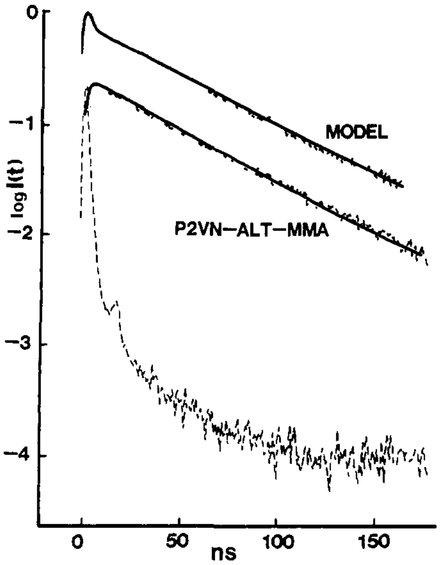

Figure 3. Comparison of the fluorescence decay of the monomer region (340 nm) for P(2VN-*alt*-MMA) (maximum counts 20732 or 3014) and P(2VN(3%)-*co*-MMA) model (maximum counts 32202 or 5626). Solvent: outgassed THF. Dashed line, lamp profile.

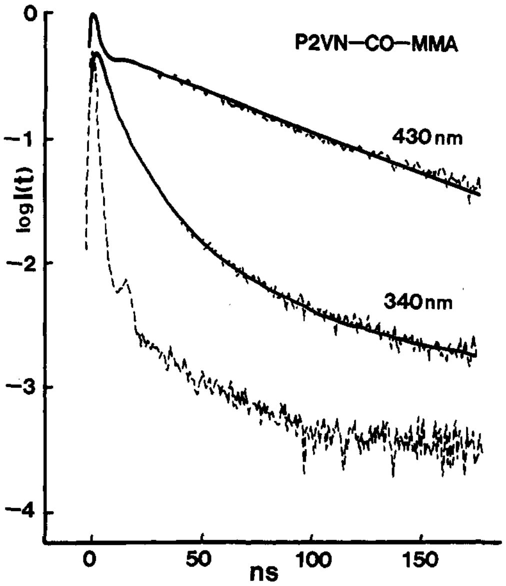

Figure 4. Comparison of the fluorescence decay of the monomer (340 nm) and excimer (430 nm) for P(2VN-*co*-MMA). Solvent: outgassed THF (see Figure 2).

which may be due to residual excimer formation. In contrast, for the random copolymers the excimer emission is diminished much more than monomer emission by addition of a quencher (see Figure 2). This is typical of other excimer-forming polymers.[9]

It was found that only a single exponential was required to satisfactorily describe the fluorescence decay curves for the time range 0–200 ns for the alternating copolymers. This feature implies either (1) a very uniform environment for the naphthalene moieties or (2) that energy transfer is so rapid that each singlet state experiences an average environment during its lifetime. In view of the nonexponential fluorescence decay of the model polymer (see below) we favor the second possibility. The alternating copolymer is not strictly a single exponential when examined over a longer time range of 0–400 ns. As discussed in section C, this has little effect on the calculated energy migration rate. Thus to a first approximation the excited-singlet-state kinetic scheme for alternating copolymers may be taken to be very simple with only one rate constant. We also note that the methacrylic acid copolymers have a longer lifetime than the corresponding methyl methacrylate copolymer (see Table II).

For the model polymer a dual-exponential decay function was required to fit the emission monitored at 340 nm. Since only ca. 0.03 mole fraction of naphthyl groups are present in the model polymer and given the absence of an excimer component in the spectrum, it is unreasonable to ascribe the short component to naphthalene–naphthalene interactions. Clearly the component with τ_m = 49.2 ns corresponds to "isolated naphthyl" units (i.e., this value is very close to the literature value[12] of τ for ethylnaphthalene, 54 ns). We speculate that the short component may correspond to naphthyl groups which happen to be sterically crowded by their neighboring ester groups. The fluorescence decay at 340 nm is compared in Figure 3 for the model copolymer and P(2VN-*alt*-MMA). This very marked nonexponentially persisted upon dilution of the polymer solution or going to a longer time scale (0–400 ns). The latter data yield different lifetimes, as might be expected for a multiple-exponential decay. We also observed a similar biexponential decay using a picosecond lifetime apparatus (see Experimental Section) in which all polarization effects could be rigorously removed. A second model polymer with 1.2% naphthalene was prepared and displayed a biexponential fluorescence decay. These two model polymers yield almost exactly the same $\langle \tau \rangle$ value as used in eq 5 (see section C). See Table II for a tabulation of preexponential factors and lifetimes.

The fluorescence decays for P(2VN-*co*-MMA) or P(2VN-*co*-MA) were more complicated and required a three-exponential decay function to fit satisfactorily the emissions monitored at either 340 nm or 420 nm, i.e.

$$I(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3} \quad (1)$$

The set of parameters A_i and τ_i were different for the monomer (340 nm) and excimer (430 nm) emissions (see Figure 4 and Table II). It is reasonable that different microenvironments[12] for the naphthyl groups lead to different photophysical behavior and hence multiexponential fluorescence decay. We will come back to this point in the Discussion. We note that our data at 340 nm for P(2VN-*co*-MMA) agree with analogous results for poly(1-vinylnaphthalene-*co*-acrylate) (P1VN-*co*-A) by Phillips et al.[13] very well.

One of the preexponential coefficients was negative for $I_D(t)$ (the excimer decay function) (see Table II). This suggests that some (but not all) of the excimer formation occurs via the classical Birks scheme, i.e., $^1M^* + M \rightarrow {}^1D^*$. Alternatively, some excimer formation may be occurring via exciton migration to an excimer-forming site.[14] Either of these mechanisms would yield a growing-in of the excimer fluorescence. However, $I_D(t)$ at $t = 0$ is not zero, which implies a part of the excimer population is formed via very rapid chromophore rotations and/or as a very rapid energy-transfer step on a time scale short compared to the time resolution of our instrument. Phillips et al.[13] have reported that the excimer fluorescence decay in P(1VN-*co*-MA) required a three-exponential decay function but did not present these fits because it was thought that photomultiplier transit time effects would invalidate a comparison of the fits in this spectral region with those in the monomer region. (For our experimental system we have not observed this effect in experiments with other fluorophores.) Two kinetic schemes were proposed based on the assumption that conventional (i.e., Birks' scheme) excimer formation kinetics existed, using the decay pa-

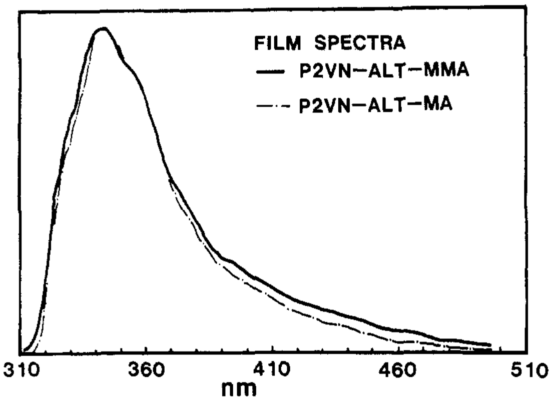

Figure 5. Fluorescence spectra for film of P(2VN-*alt*-MMA) and P(2VN-*alt*-MA).

Table III
Fluorescence Decay Parameters for Alternating Copolymer Films[a]

	I_M(338 nm)		I_D(425 nm)	
polymer	τ_1/A_1	τ_2/A_2	τ_1/A_1	τ_2/A_2
P(2VN-*alt*-MMA)	8.1/0.977	30.4/0.023	16.7/0.732	62.2/0.268
P(2VN-*alt*-MA)	11.2/0.950	26.5/0.050	20.9/0.659	57.2/0.341

[a] All outgassed, at ca. 20 °C.

rameters obtained for $I_M(t)$. We speculate that Phillips et al.[13] might have oversimplified their interpretation by this assumption.

B. Fluorescence Spectroscopy of Alternating Copolymers in Films. Films of the alternating copolymers were cast from THF in quartz tubes and outgassed at room temperature for ca. 20 h before fluorescence spectra were taken. The spectra for P(2VN-*alt*-MA) and P(2VN-*alt*-MMA) are compared in Figure 5. There is a loss of vibrational structure compared to the solution phase and the intensity for wavelengths greater than 400 nm is enhanced. The fluorescence decays more rapidly and can no longer be fit by a single-exponential decay function. Furthermore, the fluorescence decay is wavelength dependent, reminiscent of the random copolymers in solution (see Figure 6). The fluorescence decay parameters are summarized in Table III.

It would seem reasonable to interpret these film spectra in terms of monomer/excimer emissions. Compared to films of random copolymers the excimer component is still quite weak. There is nothing in the fluorescence decay parameters to suggest that the Birks scheme governs excimer formation in this system. It is interesting that the excimer state is so strongly repressed in films of these alternating copolymers compared to random copolymers. This result suggests that in the film state excimer formation is primarily an intrapolymer phenomenon.

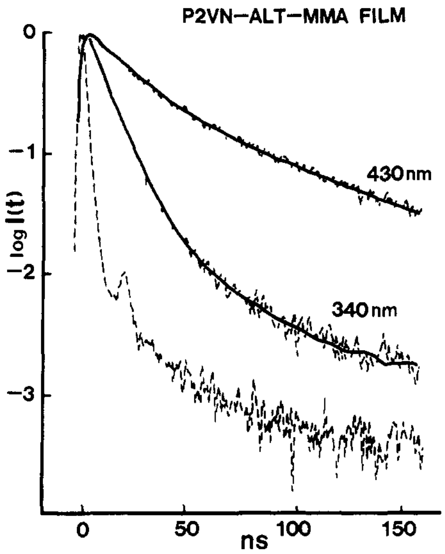

Figure 6. Fluorescence decay curves for films of P(2VN-*alt*-MMA) at wavelengths indicated (see Figure 2).

C. Fluorescence Quenching and Singlet Energy Migration in the Solution Phase. If an excited species is quenched by a collision with a quencher Q (CCl_4 in this study), the steady-state Stern–Volmer quenching constant, K_{SV}, provides a measure of the efficiency of quenching

$$I_0/I_Q = 1 + K_{SV}[Q] = 1 + k_q\tau_E[Q] \tag{2}$$

where k_q is the second-order quenching constant and τ_E is the excited-state lifetime. In this experiment the monomer fluorescence quenching by CCl_4 obeyed eq 2 and K_{SV} was obtained by a least-squares fit to a straight line. In order to obtain the quenching rate constant k_q it is necessary to obtain τ_E. Since the alternating copolymer singlet state decays approximately as a single exponential, τ_E is obtained straightforwardly (see below for the effect of the slight nonexponentiality).

For the random and model copolymer τ_E was taken to be a weighted average of the individual components. Our rationale for this is as follows. The average lifetime of a multiple-exponential decay function can be defined

$$\langle\tau\rangle = \int_0^\infty tI(t)\,dt \Big/ \int_0^\infty I(t)\,dt = \sum A_i\tau_i^2 / \sum A_i\tau_i \tag{3}$$

The relative quantum yield of the ith component is given by

$$\phi_i = \int_0^\infty A_i e^{-t/\tau_i}\,dt \Big/ \int_0^\infty I(t)\,dt = A_i\tau_i / \sum A_i\tau_i \tag{4}$$

If we assume that each component is independently quenched by Q with the same k_q value (e.g., the fundamental quenching interaction between Q and the monomeric naphthalene is the same regardless of the lifetime of the naphthalene moiety), then as an approximation I_0/I_Q can be treated as a sum of individual quenching relations, weighted by the relative quantum yield of each component; i.e.

$$I_0/I_Q = \sum\phi_i(1 + k_q\tau_i[Q]) = 1 + k_q[Q](\sum A_i\tau_i^2/\sum A_i\tau_i) = 1 + k_q\langle\tau\rangle[Q] \tag{5}$$

It is this equation that was used to derive k_q for the random copolymers. Note that this mode of analysis treats each lifetime component of the monomer fluorescence for the random copolymer as a kinetically independent species, which is not necessarily the case, and does not explicitly take into account excimer dissociation to re-form the monomer excited state. Our treatment does lead to a predicted simple linear dependence on [Q], which is experimentally observed. However, because of the approximations inherent in deriving k_q for the random copolymer from eq 5 the later comparisons with the alternating copolymers are subject to uncertainties. The values of k_q and τ_E for all systems are listed in Table IV.

As noted in Table II the lifetime analysis for P(2VN-*alt*-MMA) and P(2VN(3%)-*co*-MMA) is somewhat different in the 0–400-ns range. If these τ_i values are used to calculate $\langle\tau\rangle$ in eq 5, the resulting k_q values for these two polymers decreases to 2.30×10^9 and 1.27×10^9 $M^{-1}\,s^{-1}$, respectively.

The modified Smoluchowski–Einstein equation[15] was used to interpret k_q:

$$k_q = 4\pi N_0(D_N + D_Q + \Lambda_s)PR \times 10^{-3} \tag{6}$$

Table IV
Fluorescence Quenching of the Monomer and Energy-Transfer Parameters

polymer	K_{SV}, M^{-1}	k_q, × 10^{-9} M^{-1} s^{-1}	τ_E, ns	Λ_s/D_{CCl_4} a[a]	Λ_s/D_{CCl_4} b[b]	L_s, Å a[a]	L_s, Å b[b]
P(2VN(3%)-*co*-MMA) (model)	71.1	1.52	46.9[d]				
2-ethylnaphthalene	253.3	4.69	54.0				
P2VN(M)[c]		1.24		–0	–0	–0	–0
P(2VN-*alt*-MMA)	130.2	3.00	43.4	.974	0.28	113	42.6
P(2VN-*alt*-MA)	165.6	3.04	54.4	1.00	0.30	128	49.2
P(2VN-*co*-MMA)(M)[d]	32.9	2.30	14.3[d]	.513	–0	46.9	–0
P(2VN-*co*-MA)(M)[d]	41.8	2.40	17.4[d]	.579	0.02	55.0	7.8

[a] Using the model polymer and eq 7. [b] Based on the use of 2-ethylnaphthalene as a model compound and eq 8. [c] Monomer component of the homopolymer P2VN (see ref 9). [d] Weighted average used for τ_E; $\langle\tau\rangle = \sum A_i\tau_i^2/\sum A_i\tau_i$ (see text and eq 3 and 5).

where D_N and D_Q are the diffusion constants of the excited naphthalene and quencher, respectively, Λ_s is the singlet energy migration rate, P is the quenching probability per collision, R is the sum of radii for N and Q, and N_0 is Avogadro's number. In the analysis that follows it was assumed that the value of PR was the same in all copolymers as in the model polymer. Further, we also assumed $D_N \approx 0$ for a naphthalene chromophore attached on the polymer chain and $\Lambda_s \approx 0$ for the model polymer. These assumptions are similar to those made in earlier papers, except in the earlier work a small-molecule model compound was used.[9] As we will see using a small molecule substantially alters the final Λ_s values. From eq 6 one obtains

$$\Lambda_s/\bar{D}_{CCl_4} = (k_q^{poly} - k_q^{model})/k_q^{model} \qquad (7)$$

Equation 7 is different from the equation used in earlier studies[9,16] because of the use of a model polymer. If a small-molecule model is used

$$\Lambda_s/\bar{D} = (k_q^{poly} - (1/2)k_q^{model})/(1/2)k_q^{model} \qquad (8)$$

where $\bar{D} = (D_{CCl_4} + D_{model})/2$. On the basis of a one-dimensional random walk, the excitation diffusion length L_s can be evaluated from

$$L_s = (2\Lambda_s\tau_E)^{1/2} \qquad (9)$$

The derived values of Λ_s/D_{CCl_4} and L_s are also presented in Table IV. The assumed value for D_{CCl_4} is 1.5 × 10^{-5} cm^2/s[17] in the evaluation of Λ_s. We note that if monomeric ethylnaphthalene is used as the model compound (using eq 8), then the calculated values of L_s are significantly decreased. We presume this reflects a difference in the PR values for the monomeric model and polymeric models due to steric hindrance in the latter. We further note that the earlier conclusion that $\Lambda_s \approx 0$ for the homopolymer P2VN is verified with the polymeric model compound. Using the k_q values derived from lifetimes determined on the 0–400-ns time range yields $\Lambda_s/D_{CCl_4} \approx 0.81$. This provides some insight into the likely accuracy of this ratio. Thus we assert that for P(2VN-*alt*-MMA) the Λ_s/D_{CCl_4} ratio is in the range 0.8–1.0.

It is clear that energy transfer over significant distances is possible along the polymer chain in these alternating copolymers. The alternating polymers apparently exhibit more facile energy transfer than the random copolymers and the methacrylic acid copolymers have slightly larger L_s values than the methacrylate copolymers. However, the comparison between the alternating and random copolymers must be regarded as tentative because of the uncertainties in the k_q values for the latter, as discussed above.

Discussion

The absence of appreciable excimer fluorescence in alternating copolymers was expected based on the earlier work of Fox et al.[7] More surprising was the nearly monoexponential fluorescence decay, especially in view of the biexponential decay observed for the model methyl methacrylate polymer with 3 mol % naphthalene. To the extent that our polymers are like those of Hirabayashi et al.[10] one does not expect the naphthalene–ester or coil pairs in the alternating copolymer to exhibit strong stereoregularity. Thus we propose that energy transfer between naphthalenes tends to "homogenize" the local environment and leads to a single-exponential decay. From eq 9 we may write

$$L_s^Q = (\tau_E^Q/\tau_E^0)^{1/2}L_s^0 = (1 + K_{SV}[Q])^{-1/2}L_s^0 \qquad (10)$$

where the superscript Q or 0 refers to with and without quencher, respectively. Thus even at the highest quencher concentration $L_s^Q \approx 0.4L_s^0 \approx 48$ Å. If the average naphthalene–naphthalene nearest-neighbor separation is taken to be of the order of 6–8 Å, then the average number of transfers for an excited singlet lies in the range 17–6 for the no-quenching case to the maximum quencher concentration case (using L_s values in column a of Table IV). It is certainly reasonable that this is an adequate "sampling" of the various naphthalene environments to produce an average fluorescence decay rate. While the present work was not emphasized the film state, the relative complexity of the fluorescence decay of films of alternating copolymers is interpreted as the result of enhanced excimer formation and energy trapping.

The random copolymers studied herein were prepared for the purposes of providing a comparison to the alternating copolymer and were not studied extensively (cf. the Phillips et al.[13,18] study of poly(1-vinylnaphthalene-*co*-acrylate)). Where a comparison is possible our results are similar to theirs (i.e., the lifetime components for monomer fluorescence decay). These workers state that a single-exponential decay for naphthalene was observed only for a naphthalene mole fraction less than 0.005. Exactly why such a low mole fraction is required is not clear since the probability of neighboring naphthalenes (and excimer formation) is negligibly low at mole fractions significantly higher than this. Phillips et al.[13,18] do not observe a short-lifetime component in the monomer fluorescence for the polymer with the lowest mole fraction of naphthalene (0.13) for which data are reported. We conclude that the complex decay for the 3% naphthalene P(2VN-*co*-MMA) polymer is the result of different local environments of isolated chromophores interacting with neighboring ester groups and that this effect is not present in the 1-vinylnaphthalene polymers studied by Phillips et al.[13,18]

Phillips et al.[13,18] chose not to report their lifetime data for the excimer region, citing the errors that result from wavelength effects in the photomultiplier response function. Hence, we cannot compare our excimer data in Table II with theirs. On the basis of our experience with simple monomeric compounds (e.g., diphenylanthracene) that emit in the same region as the excimer, this wavelength effect is not very significant for lifetimes ≥2 ns, such that we believe that it is valid to compare our monomer and excimer data in Table II. Both $I_M(t)$ and $I_D(t)$ are nonzero at $t = 0$ and have a similar short-lifetime component. In the case of $I_D(t)$ this must correspond to excimer states that are populated very rapidly and cannot be time-resolved with our apparatus. The presence of a "buildup" in $I_D(t)$ (negative A_2 coefficient) is expected for the case that some excited monomer states may require either a bond rotation or energy transfer to an excimer-forming configuration. While we do not wish to ascribe any particular significance to the individual τ_i and A_i values (i.e., these do not correspond to independent populations of naphthalene moieties), the existence of some fluorescence buildup in $I_D(t)$ seems inescapable from our data. Such a buildup is not observed for simple model compounds that emit in the same region, so we do not think this observation is an experimental artifact.

One of the points of greatest interest to us in studying these alternating polymers is to determine if separating the naphthalene chromophores simultaneously suppresses excimer formation and energy transfer, similar to the earlier work of Nakahira et al.[1] On the basis of the method of comparative quenching (eq 7 and 8) it would seem that Λ_s is definitely not zero for the alternating copolymers. The analysis is especially straightforward in the comparison of the model copolymers and the alternating copolymers, where $k_q^{\text{model}} \approx (1/2)k_q^{\text{alt}}$ (see Table IV). Since the steric hindrance of the approach of the quencher to the naphthalene groups must be fairly similar in both cases, the product *PR* in eq 6 would be expected to be nearly equal, as required for a valid application of eq 7. In earlier work we[9] have used a small-molecule model (2-ethylnaphthalene) as a model in conjunction with eq 8. Results obtained with this model compound are also presented in Table IV. As can be seen the calculated Λ_s values obtained are significantly smaller. One would expect the proeduct *PR* to be larger for a free naphthalene molecule than a polymer-bound naphthalene based on steric effects. Thus eq 8 would be expected to systematically underestimate the value of Λ_s. For this reason we believe that use of a model polymer is to be preferred and hence regard the data in column a of Table IV as the more accurate.

Comparison of the alternating and random copolymers is clouded by the complexities of the multiexponential decay of the latter. Using eq 5 to obtain k_q yields and eq 7 for Λ_s/D_{CCl_4} gives Λ_s values for the random copolymers that are approximately one-half those of the alternating copolymer. Interestingly when the monomer quenching for the homopolymer P2VN is analyzed with eq 7, $\Lambda_s \approx 0$ is obtained, in agreement with the earlier conclusion.[9] It is plausible that the excimer represents a trap with respect to energy transfer, as has been mentioned several times in the preceding discussion. However, both P2VN and the P(2VN-*co*-MMA) or P(2VN-*co*-MA) polymers display facile excimer formation, with the ratio I_D/I_M being slightly larger for the homopolymer P2VN. Thus it would seem that increasing the density of excimer-forming sites (and possibly increasing the stability of the excimer by simultaneous interaction between three or more naphthalenes) does serve to decrease the average energy migration rate, in agreement with the theoretical analysis of Frank and co-workers. We note that our previous conclusion that $\Lambda_s \approx 0$ for P2VN has been criticized by Semerak and Frank[14] as inconsistent with the observed solution phase I_D/I_M ratio. We believe that the many assumptions implicit in the comparative quenching method invalidate Λ_s determinations when Λ_s/D_Q is small. If we estimate $\Lambda_s/D_{CCl_4} \leq 0.2$ for P2VN and take $\langle\tau_E\rangle \approx 7.4$ ns (the value used in our earlier publication), then $L_s \leq 21$ Å is obtained. Thus even with a relatively small Λ_s value some sampling of the region surrounding the point of initial photon absorption is significant.

Upon reflection it is not particularly surprising that Λ_s is significant for the alternating copolymers. The Förster radius (R_0) for self-transfer between 2-methylnaphthalene is 11.7 Å,[19] which is larger than the expected separation of naphthalene groups in the alternating copolymers. However, it is always possible that (1) the configurational constraints of the polymer limit the mutual orientation of neighboring chromophores, which can serve to either increase or decrease the effective R_0 or (2) the naphthalene separation is sufficiently small to invalidate the dipole expansion used to derive the R_0 formula. Presumably this would increase the transfer rate relative to the Förster formula $k_t = (R_0/R)^6(1/\tau_E)$. We close by noting that if an accurate naphthalene–naphthalene separation value were known for the alternating copolymers, then the energy hopping time could be estimated from

$$\Lambda_s = \langle R\rangle^2/2\tau_h \qquad (11)$$

If $\langle R\rangle$ is taken to be our crude estimate of ca. 6 Å, then $\tau_h \approx 0.1$ ns is estimated. This is not so different from the hopping rate deduced from studies of doped molecular crystals of naphthalene.[20]

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Registry No. P(2VN-*co*-MMA) (copolymer), 53640-71-4; P(2VN-*co*-MA) (copolymer), 100044-87-9; 2-vinylnaphthalene, 827-54-3; 2-ethylnaphthalene, 939-27-5.

References and Notes

(1) Nakahira, T.; Sasaoka, T.; Iwabuchi, S.; Kojima, K. *Makromol. Chem.* **1982**, *138*, 1239.

(2) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1982**, *15*, 424.

(3) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289.

(4) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.

(5) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.

(6) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.

(7) Fox, R. B.; Price, T. R., Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.

(8) Wang, Y.-C.; Morawetz, H. *Makromol Chem., Suppl.* **1975**, *1*, 283.

(9) Webber, S. E.; Avots-Avotins, P. E.; Deumie, M. *Macromolecules* **1981**, *14*, 105.

(10) Hirabayashi, T.; Nishikawa, Y.; Yokota, K. *J. Polym. Sci.* **1979**, *17*, 3823.

(11) (a) Delaire, J. A.; Rodgers, M. A. J.; Webber, S. E. *J. Phys. Chem.* **1984**, *88*, 6219. (b) Demas, J. N. "Excited State Lifetime Measurements"; Academic Press: New York, 1983.

(12) Ito, S.; Yamamoto, M.; Nishijima, Y. *Polym. J.* (*Tokyo*) **1981**, *13*, 791.

(13) Phillips, D.; Roberts, A. J.; Soutar, I. *Polymer* **1981**, *22*, 293.

(14) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 33 (see p 75).

(15) Voltz, R.; Laustriat, G.; Coche, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 1253.

(16) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 1741.

(17) Heisel, F.; Laustrait, H. *J. Chim. Phys.-Chim. Biol.* **1965**, *66*, 895.

(18) Phillips, D.; Roberts, A. J.; Soutar, I. *Polymer* **1981**, *22*, 427.

(19) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973.

(20) See the discussion of section 9.11.4.1 in: Birks, J. B., Ed. "Organic Molecular Photophysics"; Wiley: London, 1975; Vol. 2. In the context of molecular crystals there are two parameters that are considered: (1) τ_h, the hopping rate, and (2) *c*, the number of new sites visited by the exciton on each hop (in the limit of many hops). Thus while τ_h is found to be of the order of 0.1–0.3 ns, *c* is in the range 19–38, which is much larger than would be the case for a polymer. Hence there is some doubt as to whether the comparison of crystal and polymer τ_h values is meaningful.

Addition of Difluorocarbene to 1,4-Polybutadienes. Synthesis and Characterization of Novel Copolymers

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ABSTRACT: Difluorocarbene, generated under mild neutral conditions, adds cleanly to 1,4-*cis*- and -*trans*-polybutadienes to give cyclopropanated materials with complete retention of the double bond configuration. The addition can be effected to any desired degree of conversion by controlling the molar ratio of carbene precursor to the double bond, thus providing a series of novel copolymers. These fluorine-containing materials were characterized by thermal analysis, gel permeation chromatography, and high-field ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. The olefinic carbon resonances give the most detailed fine structure, which has been fully assigned to monomer sequence pentads. The addition of difluorocarbene takes place randomly to give a perfectly Bernoullian monomer sequence distribution, as well as an atactic stereosequence distribution.

Introduction

A carbene derives its important synthetic applications from cyclopropanation in a single key step in many target natural products, often with remarkable control of stereochemistry. A variety of carbenes have been shown to undergo reactions with double bonds along polymer backbones in much the same way as in simple alkenes.

Prior studies of the addition of methylene as well as dichlorocarbene to polybutadienes have been reported in the literature.[1,2] However, analogous reactions with difluorocarbene have not been examined heretofore. Surface modification of some polymer matrices by difluorocarbene has been claimed, despite lack of evidence of any direct chemical attachment of carbene fragments to the polymer.[3]

In the present study we examine the scope of the addition reaction of difluorocarbene (:CF_2) to both 1,4-*cis*- and -*trans*-polybutadienes. Since :CF_2 has a singlet ground-state electronic structure, it is possible to obtain these adducts without loss of the original configuration; i.e., the cis precursor polymer is expected to give only a cis adduct and the trans polymer a trans adduct. The properties of these novel fluoro copolymers depend on composition, which can be varied according to the extent of addition. High resolution multinuclear NMR methods are utilized to characterize the detailed microstructures of these materials.

Experimental Section

Materials. 1,4-*cis*-Polybutadiene (*cis*-PBD) was obtained from Aldrich Chemical Co. 1,4-*trans*-Polybutadiene (*trans*-PBD) was synthesized according to a literature procedure.[4] Both polymers had at least 98% isomeric purity as determined by ^{13}C NMR. (Trifluoromethyl)phenylmercury ($PhHgCF_3$) was obtained in about 40% overall yield from phenylmercuric hydroxide by the procedure of Seyferth.[5] Sodium iodide (Gold Label, 99.999% purity) was purchased from Aldrich and dried for 24 h at 140 °C under vacuum prior to use. Benzene and toluene were dried according to standard techniques and stored over molecular sieves under a nitrogen atmosphere. *cis*- and *trans*-5-decenes were obtained with better than 97% isomeric purity from Wiley Organics and used without further purification.

General Procedure for Cyclopropanation. The desired isomer of 1,4-polybutadiene was dissolved in either benzene or toluene (1% w/v)) with constant stirring under nitrogen. (Trifluoromethyl)phenylmercury (0.35–3.0 equiv with respect to double bonds) and dry sodium iodide (threefold molar excess with respect to $PhHgCF_3$) were added simultaneously to the polymer solution at room temperature. The mixture was vigorously stirred and heated to 80 °C, after which the reaction could be followed by the disappearance of $PhHgCF_3$ by TLC. Typical reaction times ranged from 20 to 30 h.

At the end of the reaction, the mixture was cooled to room temperature and filtered to remove insoluble materials (e.g., NaI, NaF, PhHgI, etc.). The filtrate was concentrated to one-third its original volume, whereupon more crystals of PhHgI appeared and were separated by centrifugation. The polymer was precipitated in a large excess of methanol containing 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant, collected, washed several times with methanol, and dried overnight under vacuum. The polymer was then purified by dissolving in chloroform and reprecipitating in methanol. The conversion of double bonds was determined from 500-MHz ^{1}H spectra (vide infra). If further double bond conversion was desired, the partially cyclopropanated material could be recycled through the above operation without any degradation.

Samples of *cis*- and *trans*-1,2-di-*n*-butyl-3,3-difluorocyclopropane were obtained by the above procedure from the respective olefins. Distillation under reduced pressure (20 torr) gave analytical samples of these compounds.

Analytical Methods. Molecular weights ($\bar{M}_w$ and $\bar{M}_n$) were measured by gel permeation chromatography on a Waters liquid chromatograph fitted with μ-Styragel columns and calibrated with monodisperse polystyrene standards. Thermal gravimetric analyses (TGA) were performed on a Du Pont 1090 thermal analyzer with a DSC cell and a Du Pont 951 thermal gravimetric analysis attachment.

NMR Measurements. The 500-MHz proton (^{1}H) NMR spectra of all samples were acquired at room temperature on a JEOL GX-500 spectrometer. Typically, a 7–10% (w/v) polymer solution in $CDCl_3$ was used. The extent of cyclopropanation was calculated by integration of the appropriate proton resonances.

The 50.31-MHz carbon-13 NMR spectra were recorded at 50 °C on a Varian XL-200 spectrometer, from $CDCl_3$ solutions containing at least 15% (w/v) polymer. The internal reference was tetramethylsilane (Me_4Si), and about 10000 transients were accumulated with a sweep width of 10 kHz in 32K of memory. Pulse repetition times were 5–15 s between 90° pulses (19.5-μs duration), and broad band proton decoupling was used. All quantitations were done with the integrated intensities of protonated carbons only.

The ^{13}C spin–lattice relaxation times (T_1) and nuclear Overhauser enhancements (NOE) were determined in order to choose appropriate delay times ($>5T_1$) for quantitatiion, and to deduce

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