Localization of Excitations by Electron-Donating Side Groups in the Novel Copolymer Poly[methylphenyl-co-methyl-4-(dimethylamino)phenylsilane]

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Received: February 15, 1994; In Final Form: May 3, 1994*

The effect on the coherence length of excitations in polysilane copolymers due to electron-donating (dimethylamino)phenyl (DMAP) side groups is investigated by time-resolved and steady-state fluorescence studies. In the case of poly(methylphenylsilane) the lowest excitonic state has been shown to delocalize over several tens of monomer units. Steady-state studies of the novel copolymers indicate three emitting species which can be assigned to three fluorescence lifetimes identified by time-resolved experiments. A fast lifetime of a few tens of picoseconds corresponds to the delocalized lowest excited state. A second delocalized excitation with a short lifetime and a third "self-trapped exciton" with a coherence length of approximately a single silicon bond are also proposed. The size of the delocalized excitations in the copolymers exhibits a strong dependence on the concentration of the electron-donating DMAP side group. The coherence length of the excitations can be predicted by a simple statistical treatment of the distribution of homogeneous chain segments terminated at each end by DMAP side groups. Consequently, a perturbation of the backbone states due to the electronic nature of the DMAP side groups is proposed to be the origin of the force which defines the size of the exciton.

Introduction

Polysilanes exhibit a large electronic third-order susceptibility, efficient charge transport in the form of highly mobile holes, and a readiness to undergo photodecomposition. In the past decade a great deal of interest has been shown in these σ -conjugated polymers due to their potential applications as photoresist,¹ photoconductors,² one-dimensional semiconductors,³⁻⁵ nonlinear optical materials,⁶⁻⁸ and precursors in polymer syntheses.⁹ An understanding of the excited-state dynamics and the delocalization of excitations is important from the viewpoint of controlling these optical and conductive properties. For a recent review of the photochemical and photophysical properties and applications of the polysilane high polymers, the reader is referred to the article by Miller and Michl.¹⁰

Strong evidence of the σ conjugation in polysilanes is given by the shift in the sharp one-photon absorption peak in the nearultraviolet region (\sim 350 nm) with increasing chain length¹¹⁻¹⁴ indicative of the delocalization of the excitations. A transition has also been identified in polysilanes by two-photon absorption^{15,16} and electroabsorption¹⁷ and has been shown to lie about 0.9 eV higher in energy than the single-photon absorption peak. The single-photon peak has been assigned a $\sigma - \sigma^*$ excitonic transition^{10,18-21} in alkyl-substituted polysilanes, and the coherence length of this excitation has been shown to be in the range 20-40 silicon atoms in poly(methylphenylsilane).²² Anisotropy studies have shown the $\sigma - \sigma^*$ transition dipole to lie along the silicon backbone.¹⁹ The absorption and photoluminescence behavior of the polysilanes has been described in terms of a distribution of chain segments^{18,23} with transfer of the excitations to the longer, lower-energy segments before photoluminescence, which manifests itself as a narrowing in the fluorescence emission and a red shift from the absorption peak. The geometry of the chain segments has been proposed to be all trans terminated at each end of by an abrupt conformational kink such as a gauche twist,¹⁸ limiting the persistence length of excitations to be shorter than the full polymer chain. At low temperatures where the structures are more homogeneous, the size of the excitations can be modeled by introducing a small random energy disorder into the linear chain.^{24,25} The absorption and photoluminescence from arylsubstituted polysilanes^{10,19,22,26} have led to models suggesting mixing of the ring and backbone states leading to proposed excitations which are similar to σ - σ ^{*} but have some π characteristic, $\pi(\text{ring})-\sigma^*$, and $\pi-\pi(d\text{Si})$ composed of the vacant silicon d orbitals.

The aim of the present work is to investigate the dependence of the delocalization length of the excitations on the concentration of an electron-donating side group. By introducing electronic perturbations in the backbone states, we could systematically modify the electronic and nonlinear optical properties of conjugated polymers. A range of polysilane copolymers of the type $(SiRMe)_{1-x}(SiR'Me)_x$ were R = phenyl and R' = (dimethylamino)phenyl (DMAP) of different x, where x is the percentageconcentration of the electron-donating side group, were studiedby steady-state and time-resolved fluorescence spectroscopy andfluorescence depolarization spectroscopy. A simple statisticalmodel for the chain length distribution as a function of side groupconcentration will be presented, and a strong correlation betweenthe predicted and experimentally determined excitation lengthswill be shown.

Experimental Section

Sample Preparation. The copolymers shown in Figure 1 were synthesized using the monomers methyl-4-(dimethylamino)phenyldichlorosilane and dichloromethylphenylsilane; the latter is commercially available and was dried over CaH_2 and distilled before use. The former was prepared in the following manner. An addition funnel was charged with 4-(dimethylamino)phenyl bromide (100 g, 0.5 mol) in 200 mL of diethyl ether, and this solution was added slowly to a slurry of lithium powder (96.94 g, 1.0 mol) in 200 mL of dry diethyl ether at 25 °C over 4 h. The solid residue was filtered through a coarse fritted disk funnel, and a clear orange solution was obtained. Subsequently, the lithium reagent was added dropwise to a solution of methyltrichlorosilane (70.5 mL, 0.6 mol) in 400 mL of dry diethyl ether at 25 °C over 2 h, and the mixture was stirred overnight. The

0022-3654/94/2098-7359\$04.50/0 © 1994 American Chemical Society

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[•] Abstract published in Advance ACS Abstracts, June 15, 1994.



Figure 1. General structure and composition of the polysilanes.

precipitated salt was then removed by filtration, and the colorless liquid residue was washed with toluene, evaporated, redissolved in hot toluene/diglyme (8/2), and filtered. A colorless residue remained after evaporation. Kugelrohr distillation followed by a Vigreux distillation (98–100 °C, 0.24 Torr) gave the pure product (mp 45 °C, white crystals). The compound was found to be unstable in CHCl₃.

The copolymers (6CO, 30Co, 60Co, and 70Co) were synthesized using the feed ratios (methyl-4-(dimethylamino)phenyldichlorosilane:dichloromethylphenylsilane) 6:94, 2:8, 1:1, and 8:2, and ¹H-NMR integration of the dissolved products revealed that the ratios in the second and last case were 3:7 and 7:3 while the other two products mimicked the feed ratios.

The poly[methyl-4-(dimethylamino)phenylsilane] homopolymer (100Hom) was prepared in the following manner. Sodium spheres (0.71 g, 31 mmol) were dispersed in 25 mL of refluxing dry toluene. Methyl-4-(dimethylamino)dichlorosilane (3.0 g, 13 mmol) was dissolved in 25 mL of toluene and added dropwise to the sodium dispersion at reflux. The mixture was stirred and the progress of the reaction monitored by GLPC. After the complete disappearance of the starting material, the mixture was cooled to 25 °C and the solid was obtained by filtration under nitrogen, dried for 2 h at 25 °C, and subsequently extracted with hot H₂O to remove the salt. The remaining fraction was dissolved in 25 mL of hot toluene, the solution was filtered, and 50 mL of 2-propanol was added. The resulting precipitate was dried in vacuo to yield 0.235 g (6.7%).

Optical Measurements. The steady-state emission and excitation spectra were measured using a Perkin-Elmer LS50 spectrofluorometer in solution in THF. Time-resolved fluorescence studies using a time-correlated single photon counting technique were performed on flowed solutions in THF ($\sim 10^{-5}$ mol) with a sample reservoir of 0.5 L necessary due to the high photosensitivity of polysilanes. The excitation source was the frequencydoubled output of a cavity dumped dye laser, synchronously pumped by the second harmonic of a mode-locked Nd:YAG laser. The fluorescence emission was collected at the magic angle and was detected by a $6-\mu m$ microchannel plate (Hamamatsu R3809) PMT after wavelength discrimination using an apertured double monochromator in subtraction mode (American Holographic DB-10). The instrument function of the system obtained by scattering from pure solvent in the flow cell was faster than 20 ps. Data were collected using a multichannel analyzer interfaced to an IBM PC. Depolarization studies were performed by alternately measuring fluorescence decays with an motorized analyzer aligned parallel and perpendicular to the pump polarization.

The fluorescence lifetimes were determined by convoluting the instrument response with an exponential decay model using an iterative procedure to minimize the residuals. The decay spectra for excitation from 300 nm to the red edge of the absorption spectrum were obtained, and initially each fluorescence decay curve was individually fitted to the multiexponential decay model.



Figure 2. Absorption spectra and extinction coefficients at the peak absorption wavelength.

The entire set of decay curves across the excitation range were then globally fitted, ensuring that the global fit maintained reasonable agreement with the results of the individual fits. The global fitting was performed using Global Unlimited (University of Illinois), which is based on a singular valve decompositionalgorithm.

Results

Steady-State Measurements. The polysilanes exhibited a strong absorption in the near-ultraviolet (Figure 2), as indicated by the large extinction coefficient per silicon unit, which is typical of the alkyl- and aryl-substituted polysilanes.¹⁰ The absorption peaks are typically about 20–30 nm wide, which is 5–15 nm narrower than alkyl-substituted polysilanes such as poly(di-*n*-hexylsilane) and appear to be free of vibrational structure. The absorption maxima are also shifted to longer wavelengths by 15–25 nm when compared with the spectra of alkyl-substituted polysilanes.

The shift in the absorption maximum to lower frequencies with increasing concentration of the DMAP substituent in the copolymers is probably due to a direct electronic effect. When the aryl group is insulated from the backbone by alkyl linkages, the absorption spectra have been shown to resemble much more closely those of the alkyl polysilanes,^{14,19} which strongly suggests that the shift we observe is not a result of side chain induced conformational changes. The continual shift in the absorption peak of the copolymers with respect to PMHom as the concentration of electron-donating side group is increased indicates a decrease in the lowest transition energy due to mixing of the DMAP ring states with the backbone states. In the case of the copolymers an absorption at around 280–290 nm may be indicative of excited states localized on the monomer, since N,N-dimethylnitroaniline has its absorption peak at 297 nm. The intensity of this transition increases as the concentration of the DMAP side group increases.

The steady-state emission spectrum for excitation in the region 300-350 nm for 30Co, which is typical of all the copolymers, is shown in Figure 3. Two emitting species may be clearly identified: a narrow emission at 370 and 420 nm which shows some structure. A shoulder at about 345 nm may indicate the presence of another single emitting species although this is less clear. The steady-state emission spectra for each material for excitation at 320 nm is shown in Figure 4. The 370-nm emission is present in all the copolymers; however, the relative strength of the emission at 420 nm can be seen to increase with increasing concentration of the electron-donating side group. The phenylmethyl homopolymer, PMHom, exhibits a single, narrow emission at 360 nm, typical of the delocalized exciton emission previously been reported.¹⁹

Fluorescence Lifetimes. Time-resolved fluorescence decays for the polysilanes were obtained for excitation wavelengths in the



Emission Wavelength (nm)

Figure 3. Steady-state emission spectra of 30Co for excitation in the region 300-350 nm.



Figure 4. Steady-state emission spectra for the polysilanes at an excitation wavelength of 320 nm.

region 300–365 nm at 5-nm intervals and at emission wavelengths of 370 and 420 nm. PMHom was studied in the same excitation region but at an emission wavelength of 355 nm, the peak emission wavelength. The fluorescence lifetimes were fitted by convoluting a multiexponential decay model with an experimentally determined instrument function and minimizing the sum of the residuals using software based on the Marquoit-Levenburg algorithm. Each fluorescence decay was fitted individually. Then, a global fit for each material across the excitation spectrum was performed which constained the lifetimes to be the same for each excitation wavelength. The results of the individual fits seeded the global fit to ensure that realistic global lifetimes were obtained by the fitting procedure, and other minima in the fitting "plane" were avoided. The results of the global fit are shown in Tables 1 and 2.

The fit to the PMHom decays resulted in a single discrete lifetime of 85 ps, consistent with previous results.²² The substituted polysilanes exhibited three discrete exponential lifetimes of ~ 50 , ~150, and ~500-1000 ps, the exact values depending on the material and detection wavelength. The individual fit procedure indicated that the lifetimes are largely independent of excitation wavelength. The multiexponential decay is not thought to be as a result of photodegradation as is often the case with alkylsubstituted polysilanes. The phenyl-substituted polymers are more robust, and a large (0.5 L) flow reservoir was used and refreshed at each new excitation wavelength. The amplitude of each exponential term in the total decay may be plotted as a function of excitation wavelength to yield a time-resolved excitation spectrum. The time-resolved excitation spectra of 6Co at emission wavelengths of 370 and 420 nm are shown in Figures 5a, and b, respectively. These spectra are broadly typical of the excitation spectra for all the copolymers.



Figure 5. Time-resolved excitation spectrum for 6Co at an emission wavelength of (a) 370 nm and (b) 420 nm.

Figure 5a,b shows that the fast lifetime, which is typical of a delocalized excitation, is predominant at the 370-nm detection wavelength, and the longest lifetime has the most significant amplitude at the 420-nm detection wavelength. This correlates well with the previous comments based on a consideration of the emission spectrum at 370 and 420 nm originating from a short and a long lifetime species, respectively. It therefore seems reasonable to associate the fast lifetime with the emission at 370 nm and the long lifetime with the emission at 420 nm.

Size of the Excitations and the Effect of the DMAP Side Groups. Tables 1 and 2 summarize the fluorescence characteristics for excitation at the peak absorption wavelength and at emission wavelengths of 370 and 420 nm, respectively. (The results for PMHom were obtained at an emission wavelength of 355 nm.) The results of Kim *et al.*²² for PMHom are given in Table 1 for comparison. The total quantum yield for fluorescence was obtained by comparison to a known standard, in this case *p*-bis-(2-(5-phenyloxazolyl))benzene, and the contribution of the emissions at 370 and 420 nm were determined from the steadystate emission spectrum.

The absorption peak of each copolymer was fitted with three Gaussian line shapes corresponding to the three emitting species of the time-resolved spectra. The parameters for this fit were not chosen arbitrarily; the central wavelengths and bandwidths of the transitions were obtained from fits to the time-resolved excitation spectra in the region of the absorption peak. Using these parameters, the absorption spectra could be fitted very satisfactorily to three line shapes using standard fitting procedures. From the extinction coefficient per monomer unit integrated over the absorption band the radiative lifetime, $\tau_{si,r}$, based on a single Si–Si unit shown in Tables 1 and 2 can be calculated.²⁷ In a standard manner, this may be compared with the radiative lifetime of the emitting species obtained from the measured fluorescence

TABLE 1:	Fluorescence	Parameters Obtained	at an Emission	Wavelength o	of 370 nm fo	Excitation at the	Absorption Peak
Wavelengths	i			_			-

material	fluorescence lifetime τ_f $(10^{-12} s)$	quantum yield $\phi_{\rm f}$	measured radiative lifetime $\tau_{\rm f}$ (10 ⁻⁹ s)	absorption coefficient esi	calculated radiative lifetime (Si–Si unit) $\tau_{Si,r} (10^{-9} s)$	coherence length $ au_{{ m Si},{ m r}}/ au_{ m r}$ (Si–Si units)
PMHom	85	0.18	0.48	11 767	18.1	37
PMHom ^a	73	0.11	0.67	12 000	22.7	34
6Co	949	0.031	30.6	2645	31.7	1.0
	134	0.008	16.8	622	210.6	12.5
	35	0.011	3.2	1876	78.9	24.7
30Co	786	0.033	23.8	3557	38.5	1.6
	253	0.009	28.1	1021	280.3	10.0
	28	0.001	28.0	1361	231.5	8.3
50Co	489	0.014	34.9	2187	48.0	1.4
	189	0.016	11.8	1244	171.9	14.5
	36	0.0016	22.5	3280	70.7	3.1
70Co	487	0.0068	71.6	1134	92.2	1.3
	184	0.019	9.7	1713	91.6	9.4
	57	0.0016	35.6	2224	99.8	2.8
100Hom	675	0.0016	421	Ь	Ь	Ь
	166	0.015	11.1	3941	107.2	9.6
	71	0.057	1.2	2101	43.7	36.4

^a From: Kim, Y. R.; Lee, M.; Thorne, J. R. G.; Hochstrasser, R. M. Picosecond reorientations of the transition dipoles in polysilanes using fluorescence anisotropy. Chem. Phys. Lett. 1988, 145, 75-80. ^b Amplitude of transition too small to accurately determine these parameters.

TABLE 2: Fluorescence Parameters Obtained at an Emission Wavelength of 370 nm for Excitation at the Absorption Peak Wavelengths

material	fluorescence lifetime τ_f $(10^{-12} s)$	quantum yield $\phi_{\rm f}$	measured radiative lifetime $\tau_r (10^{-9} s)$	absorption coefficient esi	calculated radiative lifetime (Si–Si unit) $\tau_{Si,r} (10^{-9} s)$	coherence length $\tau_{Si,r}/\tau_r$ (Si-Si units)
6Co	1150	0.034	33.8	2645	31.7	0.94
	300	0.030	10.0	622	210.6	21.1
	32	0.011	2.9	1876	78.9	27.1
30Co	924	0.027	34.2	3557	38.5	1.1
	327	0.008	40.9	1021	280.3	6.9
	34	0.0002	170.0	1361	231.5	1.4
50Co	554	0.013	42.6	2187	48.0	1.1
	219	0.0073	30.0	1244	171.9	5.7
	49	Ь	Ь	3280	70.7	Ь
70Co	467	0.0061	76.6	1134	92.2	1.2
	190	0.008	24.1	1713	91.6	3.8
	57	Ь	Ь	2224	99.8	Ь

^a The homopolymers have very low emission at 420 nm and are therefore omitted from the table. ^b Extremely low amplitude prohibits accurate calculation of these parameters.

lifetime and fluorescence quantum yield to give an approximate value for the size of the excitation in monomer units.²²

Since the fast lifetime species has been assigned to the emission at 370 nm, we consider the data in Table 1 in our discussion of the coherence length of the corresponding excitation. PMHom exhibits the expected delocalization of about 40 silicon units; however, as the concentration of DMAP side groups is increased, the size of the excitations can be seen to fall rapidly. In fact, the excitation appears to be fully localized in the case of the 50% copolymer. In 100Hom the excitation appears to extend once more over about 40 silicon units. In the case of the longest lifetime we consider the data of Table 2.

The excitation corresponding to this emission at 420 nm appears to be localized onto approximately a single monomer unit independent of the degree of substitution of electron-donating side group. This is consistent with the long fluorescent lifetime and broad emission which is typical of a localized excitation.

The excitation corresponding to the middle lifetime of about 150 ps appears to extend over about 10 silicon units independent of the degree of substitution. However, the contribution of this emission to the total fluorescence quantum yield calculated from the area under the steady-state emission spectrum is somewhat ambiguous unlike the emissions at 370 and 420 nm. We shall therefore restrict our discussion to the excitonic and localized emissions which are of primary interest.

Fluorescence Anisotropy. Fluorescence anisotropy decay measurements were performed at detection wavelengths of 370

and 420 nm and in both cases for excitation at 300 nm and on the red edge of the absorption spectra at about 365 nm. For excitation at 300 nm the anisotropy was zero even at very short time in all cases since excitation at higher energy provides many pathways via which the polarization information may be lost rapidly. The results of excitation on the red edge for 70Co which are typical of the copolymers are shown in Figures 6a, and b, for 370- and 420-nm emission, respectively.

The decays start from an initial value of 0.4, the theoretical maximum, since irradiation on the red edge of the absorption spectrum excites only the lowest-energy chromophores which reduces the pathways by which polarization information is lost, thereby maximizing the correlation between absorbing and emitting transition moments. The decays are nonexponential but appear to consist of an initial rapid decay occurring on a time scale of a few tens of picoseconds and a second longer decay with a time constant of about 100 ps. Due to the loss of fluorescence signal after 1 ns the anisotropy could not be studied on this time scale; however, within this limit the anisotropy does not decay to zero.

It is likely that energy trapping by the longer, lower-energy segments with transition dipoles in different orientations is responsible for the fast initial loss of anisotropy.¹⁸ Since the anisotropy decays are the same for all the materials studied, this process must be assumed to be an intrinsic property of the polysilane backbone and not dependent on the substituents or copolymer ratios. The longer time scale depolarization may be



Figure 6. Anisotropy decays of 70Co excited on the red edge of the absorption peak taken at emission wavelengths of (a) 370 and (b) 420 nm.

due to cross chain dipole-dipole energy transfer or motion of the excitation within the chain segment.²² Successive changes in the transition dipole orientation due to this motion along a not quite linear chain segment would reduce the anisotropy but probably not to zero as the data shows.

Discussion

Steady-state fluorescence measurements have clearly revealed two emitting species in the copolymer at 370 and 420 nm which have been identified from the time-resolved studies as having a fast lifetime of a few tens of picoseconds and a much longer lifetime of many hundreds of picoseconds, respectively. By a consideration of the radiative lifetimes of these emissions and a calculated radiative lifetime of a monomer unit, the size of these excitations has been determined. The fast emission originates from a highly delocalized excitation of about 36 silicon units and the longer lifetime to at most a few (ca. 1) monomer units.

The most highly delocalized excitation at 370 nm is proposed to be of σ - σ^* type since it is typical of the fast lifetime delocalized excitons reported in other polysilanes. The extent of the mixing of ring π character to the ground and excited states of this transition is not clear. Harrah and Zeigler¹⁹ have reported results that in aryl-substituted polysilanes suggest a π (ring- σ^* transition, and this may account for the second delocalized excitation. However, this excitation would be expected to be as delocalized as the first which is not the case. The second excitation might arise from conjugation of the ring and backbone states^{28,29} in which the excited state is constructed from the vacant silicon d orbitals or a mixing of these and the ring states.

The 420-nm emission appears to show some vibrational structure which would not be consistent with the excimer model

which has been suggested in some polysilanes.^{30,31} The spacings of these vibrations are approximately 300 cm⁻¹ which are similar to observations by Harrah and Zeigler, 19 who reported vibrational fine structure in low-temperature emissions from poly(methyln-propylsilane). The steady-state emission spectrum presented by Harrah and Zeigler strongly resembles the spectrum obtained in the case of the copolymers with a fluorescence peak at about 370 nm and a second much broader peak at 420 nm. However, time-resolved studies showed that the longer wavelength peak was phosphorescence in poly(methyl-n-propylsilane) with a lifetime of about 1 ms. In the case of the copolymers the emission at 420 nm has a lifetime of around 1 ns and therefore cannot be phosphorescence. A similar broad, structured emission was demonstrated by Wilson and Weidman³² in alkyl-substituted polysilanes and silynes, and in this case the localizing force is attributed to branching in the polymer structure. High degrees of branching resulted in the complete loss of the excitonic emission which does not occur in the copolymers studied here, suggesting that branching is not responsible for trapping the excitations in this case. The exact electronic nature of the transition which results in the emission at 420 nm is not clear; however, a broad emission which is highly Stokes shifted and exhibits a longer fluorescence lifetime has been reported in oligomers^{33,34} and described as a "self-trapped" exciton. This excitation is proposed to exist on three silicon bonds³⁴ which in the case of the copolymers may indicate a highly localized excitation at a DMAP site flanked by two phenylmethylsilicon units. To model the dependence of the size of the excitations on the electronic perturbations introduced by the electron-donating side groups, the distribution of homogeneous chain segment lengths which define the size of the excitations is considered. If we assume that the distribution of DMAP side groups in the copolymer is random, then for a concentration x of this side group, the normalized probability of fluorescence from a homogeneous chain of either SiPhenylMe units or SiDMAPMe units of length n terminated at each end by the other species is given $by^{35,36}$

$$P_{n,x} = (anx^2(1-x)^{n-1}) + (bnx^{n-1}(1-x)^2)$$
(1)

The first term in (1) is the probability associated with homogeneous SiPhenylMe segments and the second with SiDMAPMe segments, where a and b are weighting factors (summing to unity) which modify the distribution to account for differences in the photophysical properties of the two chromophores.

The fluorescence measurements must yield some mean value for size of the excitations, and for a given concentration x the mean value of homogeneous chain segment length in the distribution may be calculated from the distribution in (1) by the summation

$$\langle n \rangle = \sum_{n} n P_{n,x} \tag{2}$$

The resulting mean homogeneous chain segment length is shown as a function of concentration of DMAP side group in Figure 7a along with the experimentally determined coherence length data for the fast lifetime excitonic species. The asymmetry in the data is fitted by values of a and b of 0.6 and 0.4, respectively. The need for this asymmetry is clear from the data, but it is not obvious whether it arises from different steric effects due to the two side groups, different quantum yields of the two chromophores, or the delocalization being restricted for some reason in the SiDMAPMe segments. Concentrations close to 0 and 1 are not well treated by this model since it does not take into account the combined effect of electronic perturbations and conformational changes which are presumably significantly only in the "very near homopolymers". However, the ability of such a simple model to predict the size of excitations measured by fluorescence experiments strongly suggests that the homogeneous chain segments



Figure 7. (a) Coherence length of the s-s^{*} delocalized excitation (solid triangles) calculated from fluorescence emission measurements at 370 nm and the mean homogeneous chain segment length fit (dotted line) derived from a statistical probability distribution of homogeneous chain lengths. (b) Percentage contribution of the localized excitation to the total emission at 420 nm (solid triangles) and the calculated form of the fluorescence signal from short segments of 1-3 units based on the probability distribution (dotted line).

define the coherence length. The electron-donating nature of DMAP side groups is the most likely cause of the electronic perturbations in the backbone states.

The contribution of the localized emission at 420 nm to the total fluorescence shown in Figure 7b is fitted by the total probability of fluorescence from short homogeneous chains calculated from (1) and multiplied by a scalar factor to yield the total detected fluorescence signal. The best fit was achieved by summing up to chain lengths of three silicon-silicon units which corresponds closely to the proposed size of the "self-trapped" exciton.³⁴ The asymmetry in the data is best fitted by strongly weighting the probability distribution (a = 0.1, b = 0.9) in favor of emission from short chain segments of SiDMAPMe units. This strongly supports the proposal that the long lifetime emission originates from a highly localized excitation or "self-trapped" exciton which arises due to the mixing of the ring states of one or two isolated electron-donating side groups with the backbone silicon states.

The discussion of the processes by which polarization information is lost requires consideration of the multiexponential fluorescence decay and the existence of more than one emitting species. The excitations may experience different anisotropy decay pathways, or there may only be a single decay process which is being measured on three different fluorescent lifetime scales. The hydrodynamic radii of the polymers^{37,38} prevents a reorientational process of the backbone occurring on less than a millisecond time scale. Interchain energy transfer is also considered as an unlikely depolarization pathway in such low concentration solutions. The results are entirely consistent with anisotropy decays reported in polysilanes^{10,22,32} in which the fast decay is attributed to superexchange of energy between segments to populate the longer, lower-energy chains. Planarization of the bonds in the silicon backbone in the excited state which minimizes the energy of the LUMO may occur on these short time scales and is a possible origin of the loss in anisotropy.¹⁰ The slower decay is probably due to the motion of the excitation by superexchange along a chain segment which is not quite linear. The concentration of the electron-donating side group does not affect the anisotropy decay despite altering the segment length distribution, and this may be an indication that these side groups do not greatly alter the geometry of the backbone when compared with the phenyl side groups.

Summary

Steady-state and time-resolved fluorescence studies of a novel series of polysilane copolymers with electron-donating side groups have been reported for the first time. From the steady-state emission spectra, a narrow emission at 370 nm and a much broader emission with some structure at 420 nm were identified. Timeresolved studies revealed three rigorously discrete lifetimes of about 50, 150, and 500–1000 ps. By a consideration of the timeresolved emission at detection wavelengths of 370 and 420 nm, we have been able to unambiguously identify the fast lifetime with the 370-nm emission and the longest lifetime with the 420nm species. It is possible that the middle lifetime originates from a further emission at 345 nm.

Furthermore, the fastest lifetime emission has been shown to originate from a highly delocalized excitation (in the homopolymers) which is proposed to be of the $\sigma - \sigma^*$ type probably with some π character. We have demonstrated for the first time that the coherence length of this exciton can be controlled by the degree of substitution of an electron-donating side group, and we propose that electronic perturbations due to the DMAP side group define the size of the excitations. A simple statistical model has shown strong correlation between the coherence length of the excitations and the mean length of homogeneous chain segments. There is some evidence to suggest asymmetry in the extent of delocalization on SiPhenylMe segments compared with SiD-MAPMe segments in favor of larger excitations on the SiPhenylMe chains. In future work we will explore other properties of these confined excitations such as their temperature-dependent radiative powers.39

The longest lifetime emission which is broad bandwidth and strongly Stokes shifted from the absorption peak is consistent with the "self-trapped" exciton model of Throne *et al.*,²⁷ and a calculation of the size of the excitation in the polysilanes revealed it to be highly localized to a single silicon unit at a DMAP site.

Anisotropy studies are consistent with previous results reported for polysilanes and showed a nonexponential multitime scale decay with an initial rapid loss of about half the anisotropy and then an order of magnitude slower decay in the anisotropy value. These decays are too fast to be attributed to reorientational processes and are probably due to energy transfer along the chains to the lowest-energy segments essentially prior to emission and motion of the excitation in the longer nonlinear segments on the slower time scale. The nature of the anisotropy decay appears to be independent of the concentration of DMAP side groups and the emission wavelength.

Acknowledgment. This research was supported by the NSF-DMR. The authors thank J. R. G. Throne for helpful discussions.

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