As seen in Figure 3, the slopes at the inflection point of the curves increase rapidly with decreasing concentration of D, up to [D] = 1 M. Below this concentration, the slopes at the inflection point remain reasonably constant and the curves are displaced to the left. This behavior illustrates the limitations one encounters in preparing an α,ω-functionalized poly(dimethylsiloxane). If the miscibility of the α,ω-functionalized dimer or oligomer in a dimethylsiloxane medium is low, the introduction of a solvent may enhance the incorporation of D units. However, the introduction of solvent will also limit the amount which may be incorporated. Often in these cases the miscibility of the linear species will increase as its molecular weight builds. Therefore removal of the solvent as the reaction progresses will increase the conversion of cyclics to linears. Conversely, if one removes solvent during the polymerization, or before introduction of the catalyst to dry the system, careful control of the final volume must be made if a specific molecular weight is desired. As the size of the end group increases there is a natural dilution for a given [D]/[E] ratio. Particularly, when one tries to incorporate cyclic siloxane into a preformed copolymer, dilution by the end group must be considered.

In conclusion, the relationship between the concentration of end groups and repeat units charged in an equilibration mixture and the resulting composition at equilibrium has been illustrated for the range of $[D]/[E] < 50$. By use of eq 8, a close approximation of the initial conditions necessary to produce a desired equilibrium molecular weight of the linear polymer may be made for $X_n = 100$ or less.

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Poly(phenylsiloxanes) Electronic Spectra

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The photophysics of siloxane polymers containing phenyl groups as substituents has not yet been studied, as opposed to the situation with polysilanes and short-chain silanes containing aryl groups whose fluorescence and phosphorescence have been extensively studied.[1-4] The objective of this work is to examine the electronic spectra of methylphenylsiloxane polymers, namely, the homopolymer poly(methylphenylsiloxane) (PMPS) and copolymers of methylphenylsiloxane with dimethylsiloxane (MPS–DMS). The spectroscopic behavior of these polymers is compared with that of polystyrene (PS) because this is a purely organic polymer whose structure is very closely related to that of PMPS and whose photophysics is quite well-known.[5-7]

Experimental Section

The homopolymer sample PMPS was kindly provided by Dow Corning Co. It was fractionated by precipitation at 25 °C in toluene–methanol as solvent–precipitant system. One of the fractions with $M_w/M_n = 1.71$ (as determined by GPC) was selected for the present work. Its M_w measured by light scattering in cyclohexane (Ch) is 1.15×10^5 and its tacticity, determined by ^{1}H NMR, is, in diads, 51% meso and 49% racemic.[8] A description of the PMPS network is in ref 8.

We also examined a monodisperse PS sample from Pressure Chemical Co. with $M_n = 1.11 \times 10^5$ and $M_w/M_n = 1.05$ and an isotactic PS sample with $M_v = 3 \times 10^5$. They were previously purified by precipitation to eliminate monomer impurities.

Three copolymers of MPS and DMS have been employed in this work. The samples called copolymer 8240 (molar fraction of methylphenylsiloxane $x_{MP} = 0.095$) and copolymer 8241 ($x_{MP} = 0.543$) were provided by Polysciences Ltd, and sample copolymer 710 ($x_{MP} = 0.663$) was provided by Siliconas Hispania S.A. The three samples are fluid, and their molecular weights are M_n = 6400, 4200, and 2500, respectively.

Solvents used, cyclohexane (Ch) and dioxane, were from Carlo Erba and of RS quality, special for fluorescence.

Emission spectra were recorded on a Perkin-Elmer LS-3 spectrofluorometer. Front-face excitation was employed for solid samples and transmission spectra for dilute solutions. Absorption spectra were measured on a Perkin-Elmer 560 UV–vis spectrometer.

Results and Discussion

Absorption spectra of PMPS and copolymers in dilute Ch solutions resemble those of PS ($\lambda_{max} \simeq 260$ nm) and have practically the same extinction coefficient (ϵ_{PMPS} = 247 L mol^{-1} cm^{-1} vs. ϵ_{PS} = 193 L mol^{-1} cm^{-1}). A hyperchromic effect and red shift have been observed for polysilanes containing phenyl[2] and naphthyl[1] groups. They have been explained by an increased conjugative interaction between the $2p\pi$ orbital of the aromatic ring and the $3d\pi$ orbital of the silicon backbone. None of these effects are observed in our samples, which have a different electronic and geometric structure in their molecular skeleton.

Figure 1 shows the emission spectra of PMPS and copolymers in a very dilute Ch solution (chromophore concentration 5.0×10^{-3} M in all cases). It can be observed that the spectra show two bands with monomer emission centered around 285 nm and excimer emission around 325 nm. The excimer-to-monomer intensity ratio increases with the methyl phenyl content in the polymer chain as expected for intramolecular excimers. The fluorescence spectra of naphthyl polysilanes have also been shown to consist of monomer and excimer bands.[1] Emissions from a dimer state[1] stabilized at low temperatures and from a charge-transfer complex with a planar aryl–Si–Si configuration[3] have also been considered for polysilanes, but they have not been clearly established.

PMPS has a larger efficiency of excimer formation than PS: e.g., in dioxane solutions 5×10^{-3} M after N_2 bubbling, the ratio I_E/I_M is 2.3 for PS and 3.8 for PMPS. A similar result was found for poly(α-methylstyrene) (PαMS) with respect to PS.[9,10] PαMS exhibits a larger distance between

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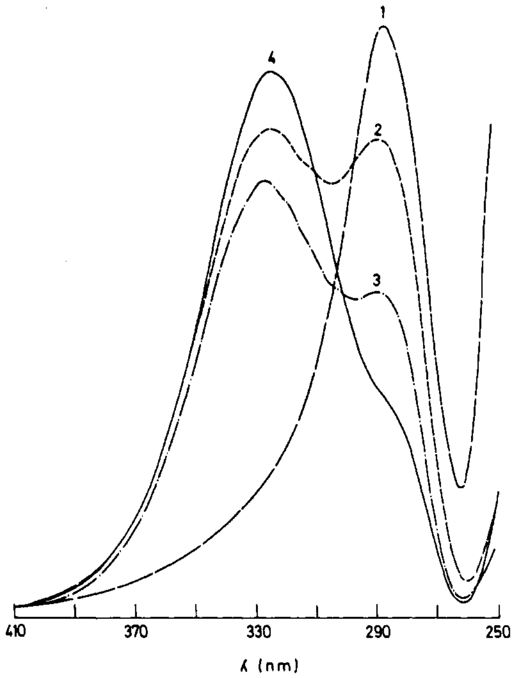
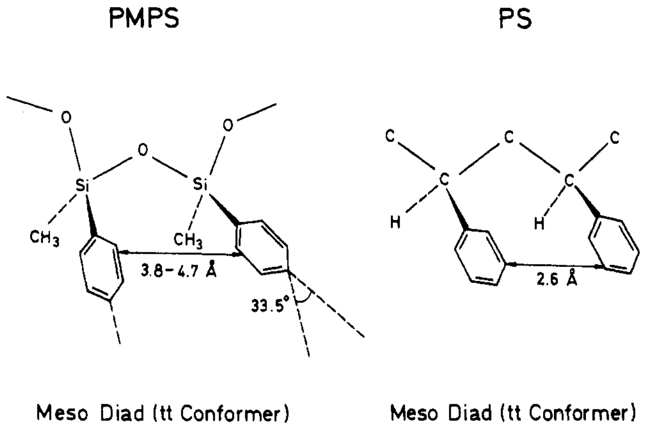


Figure 1. Fluorescence spectra of methylphenylsiloxane polymers (1) copolymer 8240, (2) copolymer 8241, (3) copolymer 710, and (4) homopolymer PMPS in dilute Ch solutions.

Scheme I



rings than does PS, and its neighbor chromophores are not parallel.[9] The same applies to PMPS.[11] Neighboring phenyl rings are farther apart in PMPS than in PS (Scheme I). Their distance is such that the interaction between contiguous phenyl rings in their ground states is attractive[11] in the case of PMPS, whereas it is repulsive in the PS case. This attraction between contiguous rings increases the concentration of potential excimer centers[12] in PMPS and, in consequence, the excimer-to-monomer intensity ratio is larger in PMPS than in PS.

The configurational differences of PS and PMPS have another effect: the excimer stability is different in both polymers. The geometry of the siloxane Si-O backbone forces the aromatic rings to be not parallel but to form an angle of 33.5° [11] (Scheme I). As a consequence, and given, too, the large distance between chromophores, the overlap between π orbitals is not very efficient, and intramolecular excimers formed between neighbor rings are less stable in PMPS than in PS. The excimer stability is related to the energy difference between the excimer and monomer excited states and that is why PMPS excimer emission is shifted to shorter wavelengths, closer to monomer emission, as compared with PS: the maximum wavelength is 325 nm in PMPS and 335 nm in PS for excimers and 285 nm for monomer emission in both polymers.

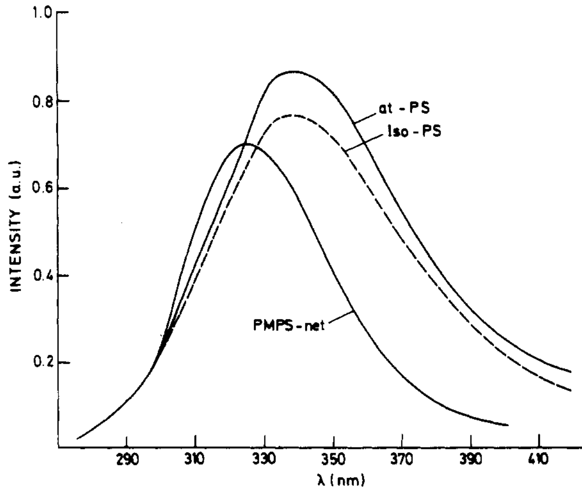


Figure 2. Fluorescence spectra with front-face excitation of atactic and isotactic PS films and a PMPS unswollen network.

PαMS excimers have also been found[9,10] to be less stable than PS excimers. The PαMS excimer emission wavelength is not clear in the literature,[9,10,13] but its dissociation begins at lower temperatures than in PS.[9] It can therefore be concluded that differences in the electronic spectra between PMPS and PS are a consequence of differences in the geometry of their respective segmental units and that the behavior of PMPS is more similar to that of PαMS.

Figure 2 shows the fluorescence spectra with front-face excitation of atactic and isotactic PS films cast from dioxane solutions, and they are compared with the emission from a PMPS network. Both polymers display only excimer emission, and as in dilute solutions the difference in the maximum emission wavelength is again evidenced. Since intermolecular excimers have no geometrical restrictions it suggests that they are not formed; otherwise, a shift of the PMPS excimer emission to 333 nm should be observed in the solid state. Copolymers in bulk with front-face excitation give an excimer-to-monomer intensity ratio larger than that in dilute solution, and again the excimer emission wavelength is about 325 nm. It seems therefore that the proximity of other coils causes the increase of excimer emission[14] but not the formation of intermolecular excimers.

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Communications to the Editor

Radiation Degradation of Poly(1-butene sulfone). Mechanistic Data from Fourier-Transform Mass Spectrometry

Poly(olefin sulfone) polymers are important positive resists for microlithography, exhibiting unusually high sensitivity to electron beam irradiation.[1,2] Previously proposed mechanisms for their high-energy degradation involve an initial carbon–sulfur bond scission to produce cationic and radical chain ends followed by rapid depolymerization to volatile monomer species.[3-5] To study further this chemistry, we have employed mass spectrometry (MS), subjecting poly(1-butene sulfone) (PBS) to high-energy radiation under the high-vacuum ($<10^{-6}$ Torr) conditions of MS instruments. This should minimize secondary reactions, providing a direct analysis of the resulting fragment ions or initial neutral products ionized close to the site of formation. Utilizing similar MS conditions, a very recent study[6] of the thermal degradation of PBS postulated initial random cleavages at weak chain links,[7] followed by depolymerization to form monomers and the stable telomers $CH_2{=}CC_2H_5(SO_2C_4H_8)_nSO_2CH{=}CHC_2H_5$.

Our initial experiments carried out with a tandem double-focusing instrument[8] utilized a beam of neutralized 10-keV xenon ions from a fast atom bombardment (FAB) gun to irradiate the polymer. Surprisingly, the spectra of PBS gave no evidence for the monomers butene and SO_2; abundances at m/z 56 and 64 were $<10^{-4}$ of those of residual solvent peaks. However, scanning for higher mass products gave very poor sensitivity and reproducibility.

To reduce these problems, pulsed radiation with multichannel recording was employed, utilizing a Fourier-transform (FT) instrument[9-13] and two other forms of high-energy radiation, 11-keV cesium ion bombardment (secondary ion MS (SIMS))[12,14] and plasma desorption (PD) induced by the 100-MeV fission products of ^{252}Cf.[15-19] Laser desorption (LD)/FTMS[13] and Cs^+ bombardment/FTMS[12,14] have been successfully used to ionize polymers of lower molecular weight (up to 7000)[13] with varying degrees of accompanying degradation. Cs^+ bombardment and ^{252}Cf PD/FTMS of PBS again show no presence of any monomeric species (m/z 56 and 64 $<0.1\%$ of total ions), contrary to the prediction of a depropagation[1-5] mechanism. The peaks observed are consistent with oligomeric products, but not those expected from a weak-link mechanism.[6,7]

Experimental Section. The Nicolet FTMS-2000 with 3-T superconducting magnet used is described elsewhere.[14,19] For Cs^+ bombardment spectra[14] 20 μL of a 10 μg/mL solution (CH_2Cl_2) of PBS (Mead Technologies) is evaporated on a gold-coated tip for the sample inlet probe. A 120-μs pulse of 20-nA, 11-keV Cs^+ ions strikes the sample, producing positive secondary ions that are trapped with a +1.3-V potential. Before detection, most of the Cs^+ and Cs_2Cl^+ (m/z 301, 303) ions are ejected from the cell; Au_n^+ ions (n = 1, 3, 5, and 7) appear at m/z 197, 591, 985, and 1379.

Samples for ^{252}Cf PD spectra[19] are prepared by electrospraying 100 μL of a 0.5 mg/mL acetone solution with a 2-μm-thick aluminized mylar foil. The ions produced from a 50-μCi ^{252}Cf source are allowed to collect in the cell for 120 s with a −5-V trapping voltage followed by a 65-ms ion detection time for each of 460 co-added measurements.

Results and Discussion. The positive ion spectrum from Cs^+ bombardment of PBS (Figure 1) shows several ion series separated by 120 daltons, corresponding to C_4H_8 (56) + SO_2 (64). This is consistent with formation of the ionized products $CH_3CH{=}CHCH_2(SO_2C_4H_8)_nSO_2H$ (I), giving the molecular ion ($M^{+\bullet}$) series at m/z (120 + 120n); quite significant peaks are observed for n = 2–7. From their mass spectra,[20] these aliphatic sulfone ions should be expected to undergo cleavage of an S–C bond to give an alkyl ion $^+CH(C_2H_5)CH_2(SO_2C_4H_8)_mSO_2H$ (IIa) and a double hydrogen rearrangement producing $CH_3CH{=}CHCH_2(SO_2C_4H_8)_mS(OH)_2^+$ (IIb); by coincidence both are consistent with the ion series m/z (121 + 120m). Unimolecular loss of H_2O from either product ion produces the most abundant series (III) in Figure 1, m/z (103 + 120m), m = 0–10. Other lower mass peaks due to alkyl ($C_nH_{2n+1}^+$) ions are also present in the spectrum.

The dominant formation of these telomers, as well as the negligible formation of monomers, would appear to rule out the depropagation mechanism, which would predict low molecular weight products containing the original chain terminus from the azobis(isobutyronitrile) (AIBN) polymerization initiator. The dominant product of thermal degradation, also thought to involve depropagation,[6] is unimportant in Figure 1 as indicated by the absence of the m/z (175 + 120n)$^+$ series. Figure 1 also gives no evidence for substructures indicative of weak chain links[6,7] as sites of initial backbone rupture.

As a possible alternative mechanism consistent with these data, the RSO_2– radical or ionic reactive sites formed by the initial carbon–sulfur bond cleavage could react further by an *inter*molecular reaction, abstraction of a secondary hydrogen on an ethyl side chain. Hydrogen abstraction reactions in sulfone decompositions have been previously described in the literature.[21,22] The new radical site formed by this hydrogen abstraction is then stabilized by cleavage of the adjacent C–S bond to cleave a second polymer chain and form a terminal olefin, regenerating a new $R'\,SO_2$–. Propagation of this *cross*-chain scission reaction then proceeds by further hydrogen abstraction, and so forth. It is even possible that the hydrogen transferred is already hydrogen-bonded in the original polymer to an oxygen on an adjacent polymer chain. Thus, radiation cleavage of a single C–S bond could cause a propagation reaction in two directions across polymer chains. A second C–S scission nearby on the chain from a second cross-chain reaction would then yield the product I.

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