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Temperature Dependence of Poly(phenylsiloxane) Fluorescence. 2. Comparison of Poly(methylphenylsiloxane) with Copolymers of Methylphenylsiloxane and Dimethylsiloxane

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ABSTRACT: Fluorescence spectra of high molecular weight poly(methylphenylsiloxane) and of oligomeric copolymers of methylphenylsiloxane with dimethylsiloxane were recorded as a function of temperature (5–60 °C), in cyclohexane dilute solution. The homopolymer and copolymers with large phenyl content present an isosbestic point between their excimer (I_E) and monomer (I_M) bands, which is attributed to excimer–monomer equilibrium in the excited state. The fluorescence ratio, when plotted as log (I_E/I_M) versus $1/T$, shows a simple linear variation, with positive or negative slope depending on the phenyl content of the copolymer. However, log I_E or log I_M, when plotted separately versus $1/T$, shows in all cases a more complex behavior, with two lines intercepting at a point which has been ascribed to a transition temperature, T_t. At $T > T_t$, the isobestic point disappears. The transition is attributed to the onset of a nonradiative mechanism involving a pair of neighboring chromophores. The high torsional and bending flexibility of the Si–O–Si structure is proposed as a factor determining the overall temperature variation of fluorescence in these siloxanes.

Introduction

In the last years, methods based in luminescence spectroscopy are being adopted (together with more traditional tools) for the study of polymers.[1] Excimer emission is one of the more fruitful of such fluorescence-based techniques. Excimers are excited-state complexes formed by a couple of chromophores placed face to face at a short distance. Excimers have red-shifted emission with respect to "monomer" or single chromophore emission. The excimer-to-monomer intensity ratio (I_E/I_M), called the fluorescence ratio, depends on intrinsic and extrinsic characteristics of the system (solvent, temperature, polymer tacticity, molecular weight, etc.).[1]

Temperature-dependent fluorescence measurements are particularly interesting in that, through steady-state experiments, they can yield information on coil dynamics. Two limits are recognized in the temperature dependence of I_E/I_M:[1,2] the high-temperature limit (HTL), in which the slope (ΔE_{EM}) of ln (I_E/I_M) versus $1/T$ is positive, and the low-temperature limit (LTL), in which the same slope is negative. Such typical behavior has been found for solutions of polymers[3-8] and bichromophoric model compounds,[9-13] whenever they were studied over a broad enough temperature range.

The interpretation in the LTL is that excimer formation is under kinetic control, and hence ΔE_{EM} can be identified with the activation energy for excimer formation.[1] In the HTL, it is generally assumed (although severely criticized) that excimer formation is under thermodynamic control, and ΔE_{EM} is associated with the excimer binding enthalpy.[1]

In the LTL, isosbestic points have been reported for some cases of polymers[3,7] and bichromophoric model compounds,[10,12] both in solution. According to the standard mechanism of Birks (Scheme I), that means that excimer dissociation is negligible and the dominant process is excimer formation. When temperature is raised, I_M decreases and I_E increases proportionally, giving rise to the isosbestic point. That is why isosbestic points, although appearing in the LTL, are associated with excited state equilibria.[12,14]

Isosbestic points have not been observed in the HTL for hydrocarbon polymers or dimeric compounds. This is not surprising, since in the HTL the rate constant for radiative plus nonradiative excimer decay (k_E in Schemes I–IV) is usually larger or about equal to the rate constant for excimer dissociation (k_{ME}).[1d] Hence, the rate of excimer decay is already larger than the rate of excimer formation when the HTL is reached, and I_E/I_M does not correspond to equilibrium in the excited state. (Under such circumstances, ΔE_{EM} should not be identified with the excimer binding enthalpy, as is usually done.)

Isosbestic points for siloxanes have been reported previously by us[2] and by others[15] in dimeric,[2] trimeric (cyclic and linear),[15] and homopolymeric[2] phenylsiloxanes.

The behavior of these siloxanes in their isosbestics is different from that of the hydrocarbons. With siloxanes, I_E decreases and I_M increases proportionally as T is being raised (the opposite to what happens in the LTL isosbestics of hydrocarbons). We propose here that the isosbestics of these siloxanes belong to the HTL and that they reflect a real excited-state equilibrium and a real thermodynamic control of excimer population.

Besides analyzing the nature of the isosbestic, we also try to get information on the dynamics of these siloxane molecules, from the temperature dependence of I_E and I_M. Fluorescence occurs in the nanosecond time scale, and it can therefore yield information on the dynamics of the fastest intramolecular motions: rotations around at least one skeleton bond,[16,17] side group rotation,[17] and cooperative backbone–side group motions,[18] etc.

We have reported before that phenylsiloxanes suffer a transition, at a given temperature, which is detected in the T variation of I_E and I_M.[2] We study here further such a transition and how it is affected by a change in chromophore concentration by using copolymers of different phenyl contents.

The systems which we study now are the homopolymer poly(methylphenylsiloxane) (PMPS) and copolymers of methylphenylsiloxane (MPS) with a photophysically inactive comonomer, dimethylsiloxane (DMS). They are studied in the temperature range 5–60 °C.

Experimental Section

The homopolymer PMPS has been fractionated and characterized by light scattering and GPC (Table I). Its tacticity has

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Table I
Characteristics of the Studied Samples: Molecular Weight (M) and Molar Fraction of MPS in the Copolymers (X_{MPS})

sample	M	X_{MPS}[c]
PMPS-3	4.2×10^5[a]	1.0
PMPS-5	1.15×10^5[a]	1.0
Co710	2.5×10^3[b]	0.663
Co8241	4.2×10^3[b]	0.543
Co8240	6.4×10^3[b]	0.095

[a] M_w by light scattering; $M_w/M_n = 1.76$ by GPC in THF. [b] M_n by vapor osmometry. [c] Spectrophotometrically determined.

Table II
Transition Temperature (T_t) and Total Activation Energy (ΔE_E),[a] at Temperatures above and below T_t, for the Homopolymer PMPS, as a Function of Molecular Weight and Concentration (c), and for the Dimeric Model Compound DS, All in Cyclohexane[b]

sample	c, M	T_t, °C	$\Delta E_E{}^{T<T_t}$	$\Delta E_E{}^{T>T_t}$
PMPS-3	7.0×10^{-2}	36	-1.40 ± 0.07	-2.7 ± 0.1
PMPS-5	5.0×10^{-3}	33	-1.6 ± 0.2	-3.1 ± 0.2
PMPS-5	2.1×10^{-3}	34	-1.59 ± 0.07	-3.5 ± 0.2
PMPS–5	4.1×10^{-4}	32	-1.64 ± 0.06	-3.5 ± 0.1
DS	4.0×10^{-4}	27	-2.4 ± 0.1	-4.6 ± 0.1

[a] ΔE_E in kilocalories/mole. [b] T_t and ΔE_E from log I_E versus $1/T$ plot.

been previously reported.[19] Fractions PMPS-3 and PMPS-5 have been selected for this work.

Three copolymers of MPS and DMS, which we call Co8240, Co8241, and Co710, have also been employed in this work.[20] Table I summarizes their characteristics.

Cyclohexane (Ch) of specific quality for fluorescence was purchased from Carlo Erba.

UV absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were run on a Perkin-Elmer LS-3 emission spectrophotometer. The maximum absorption occurs at 260 nm, but excitation wavelength was 245 nm in order to avoid the overlap of Rayleigh or Raman scattering with the monomer emission. Nitrogen bubbling increases the emission intensity by about 20% but does not modify the temperature dependence above the experimental error; therefore, air-equilibrated samples were employed. Excimer emission intensity was measured as the height of the corresponding peak at the wavelength of the maximum (325 nm in dilute Ch solution) and the same for monomer emission (285 nm). In some cases (i.e., Co8240), the spectral overlap may be very important, and corrections for overlap taken from ref 2 are applied.

Results and Discussion

Homopolymer. Fluorescence spectra of PMPS in dilute solution is mostly formed by excimer emission, but a shoulder corresponding to monomer emission can also be observed.[20] Its total fluorescence intensity always decreases on rising temperature.

In order to investigate the influence of polymer concentration and of molecular weight, we have studied log I_E versus $1/T$ for two fractions of PMPS and different concentrations, c. Table II summarizes the results of the transition temperature, T_t, and total activation energy, ΔE_E, for those experiments.[21]

Both T_t and ΔE_E, above and below T_t, are essentially independent of polymer concentration. Since c is always well below the critical value for coil overlap ($c^* = [\eta]^{-1} = 0.115$ M for PMPS-3 and 0.25 M for PMPS-5), the transition has to be ascribed, as expected, to an intramolecular process.

There is a slight dependence of ΔE_E and T_t on molecular weight (Table II). The direction of this dependence is in accordance with the observed quantitative differences between PMPS and its dimeric model compound 1,3-diphenyltetramethyldisiloxane (DS). (We use the log I versus $1/T$ results given previously for DS[2] to now obtain the T_t and ΔE values which are given in Tables II and III).

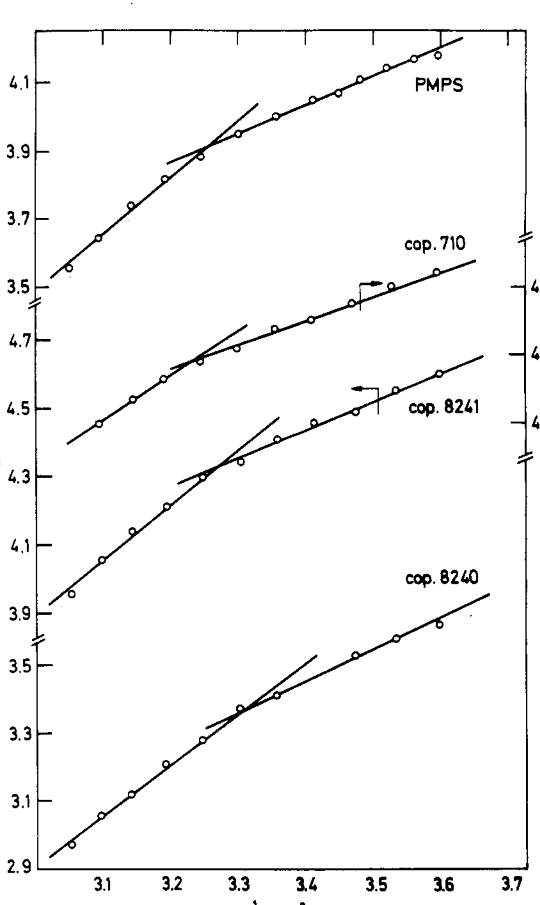


Figure 1. Arrhenius type plot of the excimer emission intensity for copolymers and the homopolymer in dilute Ch solution (4×10^{-4} M).

Copolymers. Fluorescence spectra of MPS–DMS copolymers, having around 50% MPS (Co710 and Co8241) in cyclohexane dilute solution, show a temperature dependence analogous to that of the homopolymer. In all three cases (1) Arrhenius-type plots of I_E are double linear with positive slopes (Figure 1); (2) Arrhenius-type plots of the fluorescence ratio (I_E/I_M) give single lines with positive slopes (Figure 2), which correspond to the HTL; and (3) Arrhenius-type plots of I_M show double lines with positive slope at temperatures above T_t, and negative slope at temperatures below T_t (Figure 3).

This last result concerning I_M is in accordance with the observation of an isosbestic point. The isosbestic point appears in PMPS and in the copolymers with high MPS contents (see Figure 4 for Co8241). It also appears in the dimer DS, as we reported previously.[2]

Isosbestic points reveal the existence of an excited-state equilibrium[12] between excimer and monomer. The equilibrium is such that, on increasing temperature, I_E decreases but I_M increases, because of excimer dissociation to excited-state monomer. At temperatures above T_t, the isosbestic point disappears, and the excited-state equilibrium no longer holds. Above T_t, both I_E and I_M decrease on increasing T.

Isosbestic points are not observed in polymers like PS in the HTL, because usually excimer decay through radiative and nonradiative pathways compete with excimer dissociation.[22] In such cases, excimer and monomer emissions do not correspond to equilibrium populations of excimer and excited-state monomer, and the high-temperature limit is not under thermodynamic control.

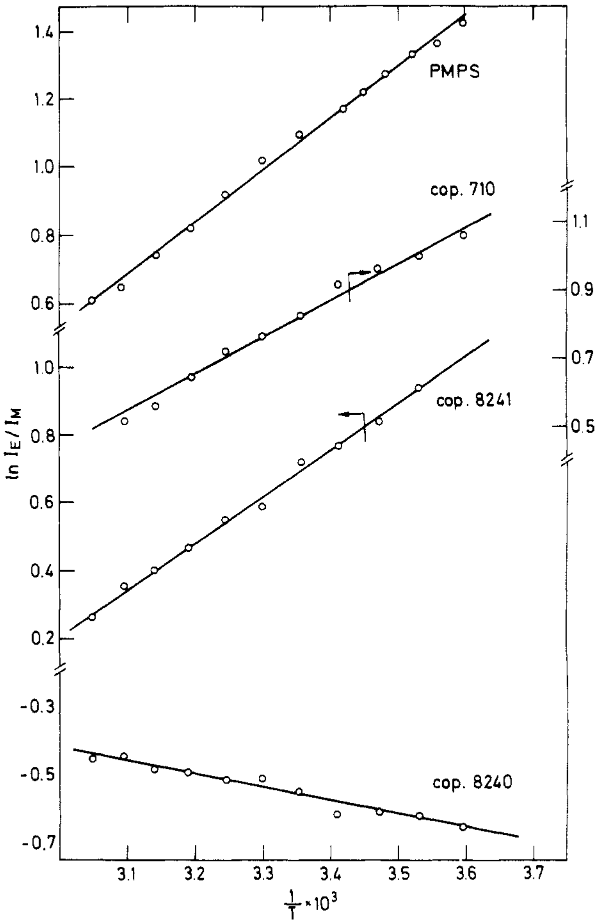
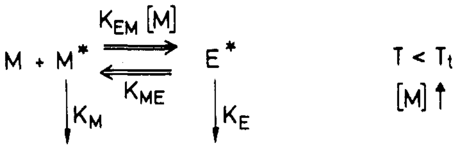


Figure 2. Arrhenius-type plot of the fluorescence ratio (I_E/I_M) for copolymers and PMPS in dilute Ch solution.

Scheme I



Disiloxanes,[2] trisiloxanes,[15] and even high molecular weight PMPS show isosbestic points. The reason can be the great dynamic flexibility of the siloxane structure. The torsional barriers for backbone rotation around Si–O bonds in siloxanes are much lower than those for rotation around C–C bonds in PS-like polymers.[23] In consequence, the formation of excimers from excited-state single monomer through rotation is faster in phenyl-containing siloxanes than it is in their vinyl counterparts (PS).[24] But, for the same reason, the siloxane excimers dissociation should also be faster than the dissociation of polystyrene-like excimers. A greater mobility in both senses, formation and dissociation of excimers, is natural for siloxanes.

Therefore, at temperatures below T_t, siloxanes are under thermodynamic equilibrium in the excited state, and the Arrhenius-type plot of the fluorescence ratio yields the excimer binding enthalpy. At temperatures above T_t, the isosbestic point disappears (Figure 4), I_M starts to decrease on raising T, and I_E continues to decrease, but at a faster rate, because of a new mechanism of decay which starts to be operative at T_t (see changes of slopes at T_t on Figures 1 and 3).[21]

It can be seen in Figure 4 (and in ref 2 and 15) that the λ_E of phenylsiloxanes becomes progressively blue-shifted as the temperature is raised above T_t. Atactic PS,[2] on the other hand, does not give such a shift with temperature (in the same conditions and with similar spectral overlap).

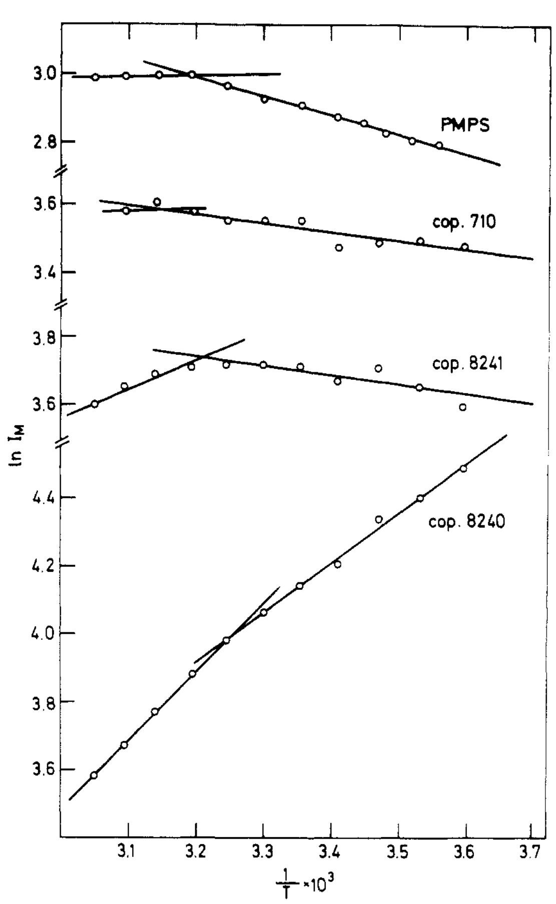
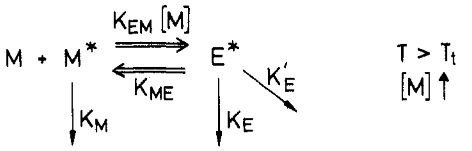
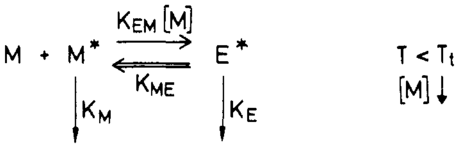


Figure 3. Arrhenius-type plot of the monomer emission intensity for copolymers and PMPS in dilute Ch solution. The breaking point for Co710 has been drawn taking into account the disappearance of the isosbestic point.

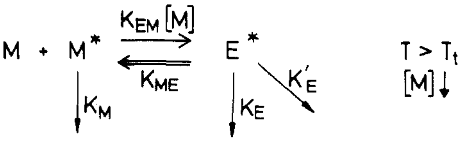
Scheme II



Scheme III



Scheme IV



Schemes I and II represent the situation (excited-state equilibrium below T_t disrupted by a new nonradiative mechanism, k_E', above T_t) for the high MPS content samples.

Co8240, with a low MPS content (9.5%, that corresponds to about eight phenyl rings per macromolecule), shows a temperature dependence more similar to that of PS than to PMPS, referring to the sign of the slopes: (1) Arrhenius-type plot of I_E is double linear with positive slopes like in the other siloxane copolymers (Figure 1). The

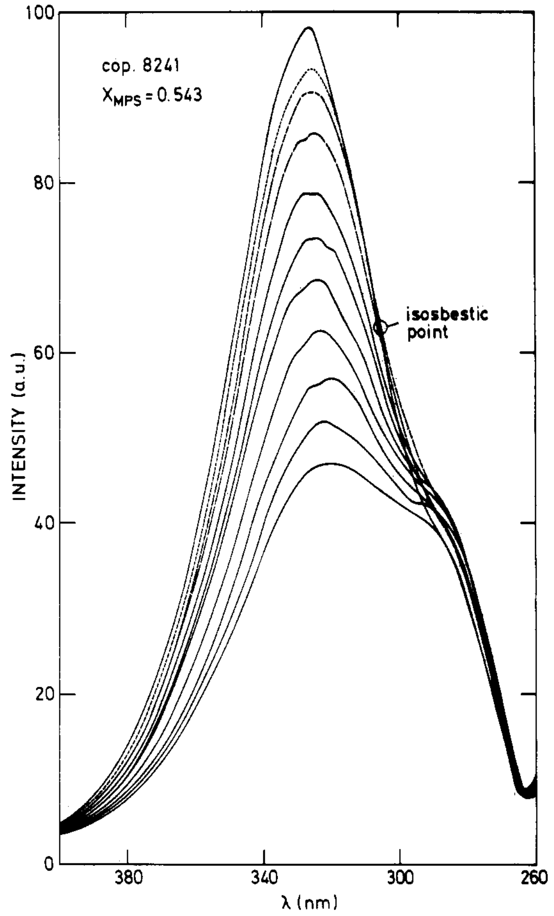


Figure 4. Temperature dependence of the emission spectrum for Co8241.

corresponding plot for PS shows a single line, but also with positive slope.[2] (2) Arrhenius-type plot for the fluorescence ratio (Figure 2) has a negative slope, like the one of PS[2] and in contrast to the other siloxanes. Both Co8240 and PS are in the LTL. (3) Arrhenius-type plot of I_M is formed by two intercepting lines, but both with positive slopes (Figure 3), contrary to the other siloxanes. The corresponding plot for PS[2] shows a single line with positive slope.

This copolymer is of very low chromophore concentration. Therefore, the bimolecular step $k_{EM}[M]$, which involves two chromophores, should be much slower and of a much smaller relative importance compared to the monomolecular decay, k_M, than it is in the other copolymers. The rate is excimer formation is so slow that the system is like it is in the LTL and I_E/I_M increases on raising T.

Since k_M is now competitive with excimer formation, I_E/I_M does not correspond to a real excited-state equilibrium even below T_t. This is in accordance with the observation of no isosbestic point for this copolymer (Figure 5). Although there is a difference with respect to the other copolymers, the transition is also observed in Co8240 (Figures 1 and 3).

The situation with this low MPS content sample is represented in Schemes III and IV for temperatures below and above T_t.

Nature of the Transition. Independently of whether a given siloxane sample is in the LTL or in the HTL, in all cases the transition is observed both in I_M and in I_E. This is a characteristic of the siloxanes. The appearance of the transition depends on the particular structure of the chain and not on the relative importance of excimer formation.

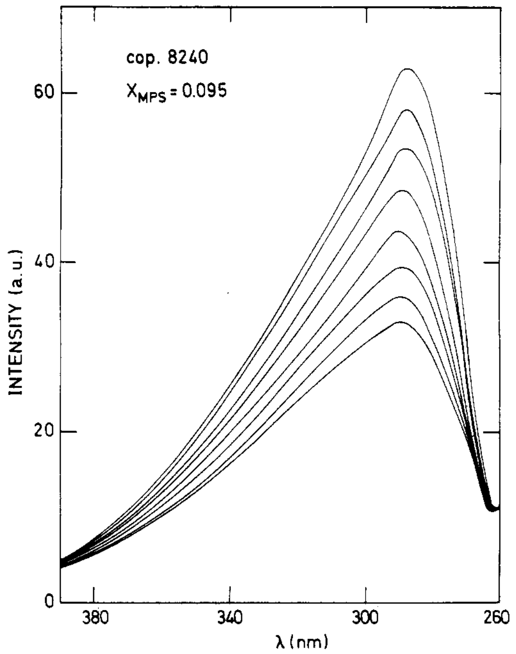


Figure 5. Temperature dependence of the emission spectrum for Co8240.

Table III
Parameters Deduced from the Arrhenius-Type Plots for the Homopolymer PMPS; the Copolymers Co710, Co8241, and Co8240; and the Dimeric and Monomeric Model Compounds DS and MS, in Cyclohexane Dilute Solution[a]

sample	ΔE_{EM}	T_t	$\Delta E_E^{T<T_t}$	$\Delta E_E^{T>T_t}$	$\Delta E_M^{T<T_t}$	$\Delta E_M^{T>T_t}$
PMPS	-3.0	32	-1.7	-3.3	1.1	-0.1
Co710	-2.2	37	-1.4	-2.6	0.5	0
Co8241	-2.8	33	-1.6	-3.2	0.5	-1.7
Co8240	0.8	30	-1.7	-3.0	-2.9	-4.0
DS	-3.4	27	-2.4	-4.6	0.9	-1.1
MS					-4.2	-4.2

[a] T_t (transition temperature) in °C; ΔE_{EM} and ΔE_E in kcal/mol. Column 2 from I_E/I_M; columns 6 and 7 from I_M.

The transition does not modify the excimer stability, as is deduced from the slopes of Figure 2. These slopes are related with the excimer binding enthalpy (ΔE_{EM} in PMPS, Co710, and Co8241) and we can see that they are not substantially modified at T_t (Table III). The transition does not modify the activation energy for excimer formation. That is the physical meaning of the slope of Figure 2 for Co8240 (ΔE_{EM} of Co8240 in Table III).

As previously mentioned, at the transition temperature, a mechanism for excimer nonradiative decay is triggered, whose rate constant modifies the temperature dependence of both I_M and I_E (in a compensating way). Such a mechanism activated at T_t should be a process involving a couple of neighboring phenyl rings, since the transition is not observed in the single-chromophore monomeric compound MS, but it is observed in the bichromophoric dimer DS as clearly as it is in the homopolymer or the copolymers.

The siloxanes are flexible with respect to torsion and with respect to bending of their Si–O–Si structure.[23] Very recently, Debolt and Mark[25] have suggested that, since the barrier for inversion in the Si–O–Si sequences is low, such inversion may be an important factor to consider in the interpretation of the temperature variation of the configurational properties of siloxane polymers. The idea is attractive, we think, not only for the configurational properties mentioned by Debolt and Mark, but also for the fluorescence spectra of excimer-forming polymers and dimers such as the ones studied here. It is reasonable to think of Si–O–Si inversion as a process by which excimer nonradiative decay may take place.

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Registry No. DS, 56-33-7.

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Monolayer, Multilayers, and Wetting Film of Poly(phenylmethylsiloxane)

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ABSTRACT: Surface pressure π has been measured as a function of surface concentration for poly(phenylmethylsiloxane) liquids, M_n = 1470, 2240, 10 560, and 19 500, spread at the water–air interface at 22.8 °C. For the two fractions of least molecular weight, the surface pressure was independent of concentration at submonolayer coverages, reflecting phase equilibria between aggregated and gaseous molecules. For these fractions π rose abruptly at a concentration consistent with estimates of full monolayer coverage and the transition was smooth to multilayers and eventually to films of macroscopic thickness. However, the two fractions of highest molecular weight did not spread. A desorption, or drying, transition appeared to occur with increasing molecular weight.

Introduction

The desire to study two-dimensional systems motivates studies of insoluble monomolecular films at the water–air interface.[1] Surface pressure π, the amount by which the liquid's surface tension is reduced by presence of film, is measured relatively easily and is analogous to the osmotic pressure characteristic of three-dimensional systems. Much interesting phase information has long been available concerning monolayers of small surfactant molecules (consisting of a polar head and a hydrocarbon tail) but less for amorphous, uncharged polymers because few synthetic polymers[2] spread to form insoluble monolayers at the water–air interface.

Original studies with polymers[3] emphasized dilute concentrations, where π depends on the density of molecules; the interest was to determine the molecular weight and the second virial coefficient. More recently, more attention was paid to a region of much higher concentrations, where surface pressure is found experimentally to rise as a power law in the surface concentration and to be independent of molecular weight; this transition region has been interpreted as a "semidilute" region of concentration in two dimensions,[4,5] although this interpretation has been questioned.[2] At high surface concentrations there begins a plateau region of relatively constant surface pressure, generally interpreted to reflect "collapse" of the monolayer to the three-dimensional state.

The study reported below concerns a polymer that has not been studied previously, poly(phenylmethylsiloxane). One purpose of the study was to obtain additional data

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