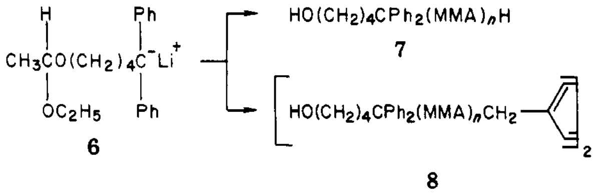
give the substituted diphenylmethyl anion **6** in quantita-



tive yield. At −78 °C, **6** initiated polymerization of MMA with 100% efficiency to produce, after acid hydrolysis, hydroxy-PMMA **7** with n from 1 to 500 and $M_w/M_n < 1.2$. Similarly, the adduct of allyllithium and 1,1-diphenylethylene in place of **6** produced polymers like **4**. Living PMMA produced from **6** was coupled in 90% yield with 1,4-bis(bromomethyl)benzene and then hydrolyzed to give α,ω-dihydroxy-PMMA (**8**).

Methacrylate polymers 100% functionalized as in **7** and **8** have not been prepared before. We have used these materials to prepare PMMA with polymerizable functionality, block copolymers of PMMA with other polymer types (both AB and ABA types), and AAAA... block copolymers by chain extension of **8**.

Details of these and other related studies will be the subject of forthcoming publications.

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Polystyrene Fluorescence: Effects of Molecular Weight in Various Solvents

Intramolecular excimer formation is observed in dilute solutions of vinyl polymers containing aromatic groups. Hirayama[2] demonstrated in his study of di- and triphenylalkanes that intramolecular excimer formation occurs exclusively in chains in which the phenyl groups are separated by three carbon atoms. This "$n = 3$" rule also applies to adenine, carbazole, and naphthalene substituents.[3-5] Because excimer formation occurs by the rotation of bonds to bring two adjacent chromophores into a coplanar arrangement, the ratio of excimer to monomer fluorescence intensity (I_E/I_M) can be used as a probe of the conformational transitions in these molecules.

Polystyrene was one of the first polymers to be studied by fluorescence techniques.[6,7] From comparisons with model bibenzyl compounds, Vala et al.[8] concluded that the polystyrene fluorescence peak at 335 nm is due to excimer emission while the peak at 280–285 nm is due to monomer emission. A dramatic feature of polystyrene fluorescence is its molecular weight dependence. Not only is I_E/I_M higher for polystyrene than for low molecular weight model compounds containing several phenyl groups,[2,9] but there is also a difference in I_E/I_M for different molecular weights of polystyrene. Ishii et al.[10] have shown that I_E/I_M for dilute solutions of polystyrene in 1,2-dichloroethane (a good solvent for polystyrene) increases up to 1.0×10^4 daltons and is constant at higher molecular weights. The molecular weight effect is not confined to polystyrene; Aspler and Guillet[11] have shown a molecular weight dependence up to 3.6×10^5 daltons for the fluorescence of dilute solutions of poly(1-naphthyl methacrylate) in dichloromethane, and other studies have shown this effect in poly(α-vinylnaphthalene)[12] and poly(2-vinylnaphthalene).[13]

Copolymer studies have determined that excimer fluorescence decreases significantly when the aromatic component in the copolymer is less than 20 mol %[7,14] and that I_E/I_M is proportional to $f_{ss}\bar{l}_s$, where f_{ss} is the fraction of aromatic pairs in the copolymer and $\bar{l}_s$ is the mean sequence length of aromatics.[15] Energy migration was suggested as a possible explanation for this effect;[15] however, there remains some uncertainty about the role of singlet energy transfer.[16] Time-resolved fluorescence studies[17,18] have shown that excimer fluorescence increases with time after pulsing and that excimer dissociation to excited monomer can be observed in poly(1-vinylnaphthalene) but is unimportant in polystyrene solutions.

Spectroscopic quality cyclohexane, 1,2-dichloroethane, and ethyl acetate were used without further purification. Reagent grade decalin was purified by silica gel filtration. The polymer samples were standard polystyrenes with narrow molecular weight distribution (Pressure Chemical Co. and Polymer Laboratories) of molecular weight 725, 830, 2.0×10^3, 2.9×10^3, 9.0×10^3, 1.75×10^4, 2.5×10^4, 3.5×10^4, 5.0×10^4, 1.0×10^5, 2.0×10^5, 2.33×10^5, 6.0×10^5, 9.0×10^5, and 1.8×10^6. The head-to-head polystyrene was synthesized and kindly supplied to us by Dr. M. Malanga and Professor O. Vogl of the Department of Polymer Science and Engineering at the University of Massachusetts. According to their measurements, $[\eta] \simeq 0.7$ dL/g in tetrahydrofuran, which corresponds to a molecular weight of approximately 1.3×10^5. The concentration of polymer solutions was maintained at 5 mmol/L (chromophore unit) unless otherwise specified. I_E/I_M was independent of concentration near 5 mmol/L.

A mercury lamp was used as an excitation source. The exciting light (253.7 mm) was isolated by a chlorine gas filter and a Beckman DU spectrophotometer. The Suprasil sample cell had a 1-cm path length. A Beckman DU spectrophotometer was also used as the analyzing monochromator and was positioned at 180° to the excitation source. The slits on both spectrophotometers were maintained at 2 mm. The analyzed light was then processed through a photomultiplier and a Keithley 610C electrometer. Absorbance corrections to the fluorescence spectrum of the ethyl acetate solutions were made with a Cary 15 spectrophotometer.

All reported I_E/I_M measurements are for air-equilibrated solutions at 24 ± 1 °C unless stated otherwise, are un-

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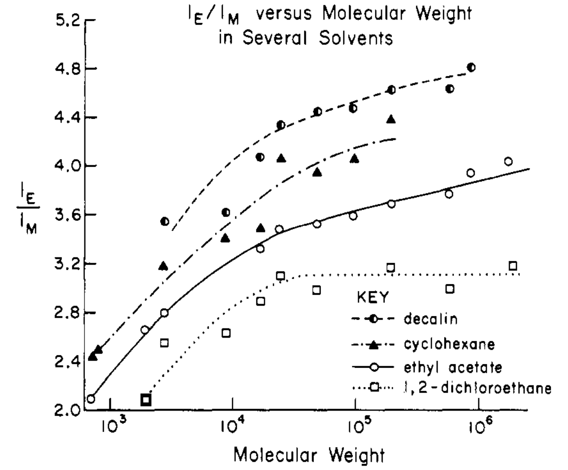


Figure 1. Molecular weight dependence of the excimer-to-monomer intensity ratio, I_E/I_M, for polystyrene in four different solvents.

Table I
Θ Temperatures of Solvents

solvent	Θ, K
1,2-dichloroethane[23]	190
ethyl acetate[24]	222
decalin[25]	293.6
cyclohexane[26]	307.6

corrected for spectral response, and are the ratios of the intensity at 335 nm to that at 283 nm. We have verified in several cases that the I_E/I_M values reported lead to the same conclusions as the ratios of quantum yields calculated from corrected spectra. Quenching measurements were made by employing reagent grade carbon tetrachloride in the concentration range 0–0.10 M as the quenching agent.

We have noticed an unusual solvent effect in studying the molecular weight dependence of the fluorescence of dilute solutions of polystyrene. All the data on I_E/I_M as a function of molecular weight in the solvents studied are given in Figure 1; the Θ temperatures for polystyrene in the four solvents are given in Table I. The I_E/I_M ratios in 1,2-dichloroethane are in general agreement with those of Ishii et al.,[10] increasing at low molecular weights but becoming independent of molecular weight above about 2.0×10^4. However, in the poorer solvents, I_E/I_M does not become independent of molecular weight over the molecular weight range we have studied; instead, there is a diminished yet persistent molecular weight effect above 2.0×10^4.

In dichloroethane, Ishii et al.[10] have shown that above $\sim 10^4$ daltons both the excimer formation and dissociation rates are independent of molecular weight, but below $\sim 10^4$ daltons the association rate declines and the dissociation rate increases. These effects are considered by them to have their origin in a tendency for adjacent phenyl rings in the higher molecular weight polymers to move in a coordinated fashion whereas a more independent motion is postulated at lower molecular weights.

As the solvent quality is reduced and the polymer coil contracts, other factors may be important in sustaining an increase in I_E/I_M at high molecular weight. (The importance of solvent can be seen in Figure 1; cyclohexane gives higher excimer-to-monomer ratios than dichloroethane at each molecular weight.) Thus, we have considered one possibility that the tighter coiling of a long chain around itself in the poorer solvents might cause nonadjacent (i.e., remote) chromophores to come into close coplanar contact, thus facilitating excimer formation. Remote excimers have

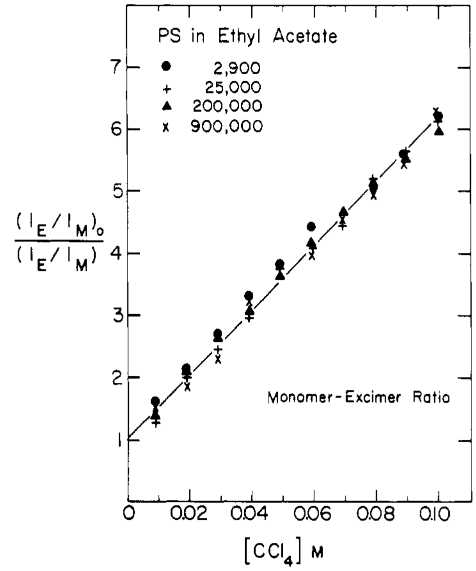
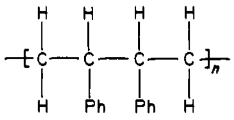


Figure 2. Stern–Volmer plots for four molecular weights of polystyrene in ethyl acetate.

been observed in special cases, as in the fluorescence spectra of α,ω-di(1-pyrenyl)alkanes.[19,20]

Several tests were made to determine if remote excimers make any contribution to the persistent molecular weight effect in poor solvents. A quenching study was done using carbon tetrachloride to quench fluorescence. Stern–Volmer plots of the excimer-to-monomer ratio are shown in Figure 2. The basis for the quenching experiment is that the dissociation entropy of a remote excimer is expected to be greater than that of a vicinal excimer. Accordingly, the lifetime of a remote excimer and therefore its sensitivity to quenching should be reduced (indeed perhaps even approaching the properties of the benzene excimer in neat liquid benzene[21]). This effect should have manifested itself in a concave-downward curvature in Figure 2 at high quencher concentration and increasingly so at the higher molecular weights. These effects were not observed.

A more direct approach for finding a contribution of remote excimers is the measurement of the fluorescence of head-to-head polystyrene:



$$-\!\left[\mathrm{CH_2-CH(Ph)-CH(Ph)-CH_2}\right]_n-$$

PS H-H

Strazielle, Benoit, and Vogl[22] have studied the properties of this molecule in various solvents and have found the Mark–Houwink parameters for solutions in THF to be not greatly different from those of "head-to-tail" polystyrene and in fact virtually identical with those of isotactic polystyrene. We would expect no nearest-neighbor excimers in PS H-H, as the phenyl groups are spaced at $n = 2$ and $n = 4$, both of which violate the "$n = 3$" rule. Figure 3 shows the emission spectrum of PS H-H at two concentrations, one approximately 20 times as concentrated as the usual 5 mmol. We see no excimer emission whatsoever. Thus, remote excimers cannot explain the high molecular weight effect on I_E/I_M in poor solvents.

Figure 4 shows the results of a temperature study of the fluorescence of polystyrene in cyclohexane. The molecular weight dependence above 2.0×10^4 decreases dramatically when the solvent quality is improved by raising the tem-

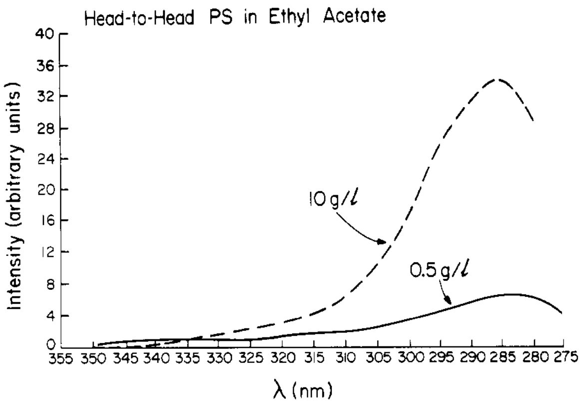


Figure 3. Fluorescence spectra of head-to-head polystyrene in ethyl acetate.

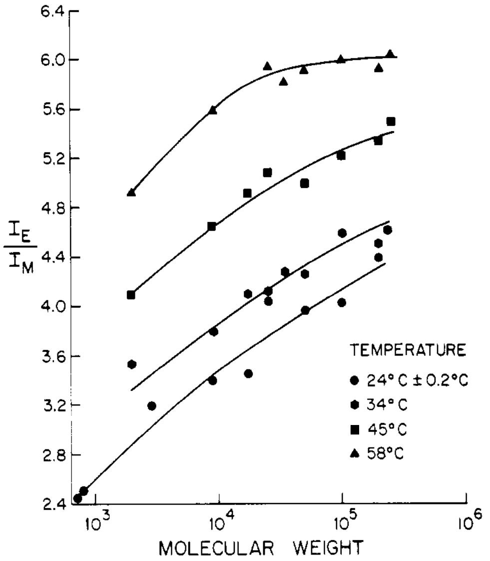


Figure 4. Effect of temperature on the molecular weight dependence of I_E/I_M for polystyrene in cyclohexane.

perature, and the data suggest a plateau I_E/I_M at high temperature, similar to that found in the room-temperature study in dichloroethane. Although we cannot yet explain the reasons for the molecular weight effect in poor solvents, we can conclude that the effect is due to solvent quality and not to other properties peculiar to a single solvent.

Finally, we note that a paper by Lindsell et al.[27] appeared during the preparation of this paper which studied the spectrum of head-to-head polystyrene more extensively. They reach the same conclusion about the dominance of nearest-neighbor excimers as we have based upon different evidence. Our present observation of the persistent molecular weight dependence of I_E/I_M remains to be explained.

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High-Performance Liquid Chromatography Analysis of Polymers. Separation of Hydroxy-Functional Poly(methyl methacrylate) by Number of Hydroxyls and Separation of Poly(methyl methacrylate) Oligomers

We have found that high-performance liquid chromatography (HPLC) is an excellent method for separation of hydroxy-functional methacrylate polymers. Narrow molecular weight distribution, hydroxy-functional poly(methyl methacrylate) (PMMA) made by anionic polymerization can be separated by HPLC into fractions based on the number of hydroxyl groups per molecule. Additionally, HPLC can be used to separate not only individual oligomers of PMMA but also different diastereomers of each oligomer.

Terminal hydroxy-functional PMMA **2** was prepared by hydrolysis of the acetal-terminal PMMA **1**.[1] Functional

$$\underset{\mathbf{1}}{\mathrm{EtOCH(CH_3)O(CH_2)_4CPh_2(MMA)_nH}} \rightarrow \underset{\mathbf{2}}{\mathrm{HO(CH_2)_4CPh_2(MMA)_nH}}$$

polymers such as **2** are typically analyzed for functionality by some sort of hydroxyl equivalent analysis.[2] Hydroxyl equivalent weights consistent with projected and measured values of M_n are judged to prove that each polymer molecule contains a hydroxyl group.

A more convincing structure proof for these methacrylate polymers follows from the chromatographic be-