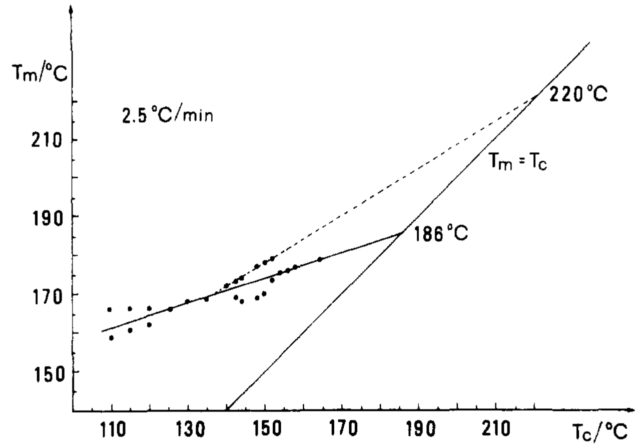

Figure 3. Plot of the peak positions of the melting endotherms (T_m), taken from the DSC scans at 2.5°C/min (Figure 1), vs. the crystallization temperatures (T_c). Two extrapolations to the line representing the relation $T_m = T_c$ are also drawn (see text).

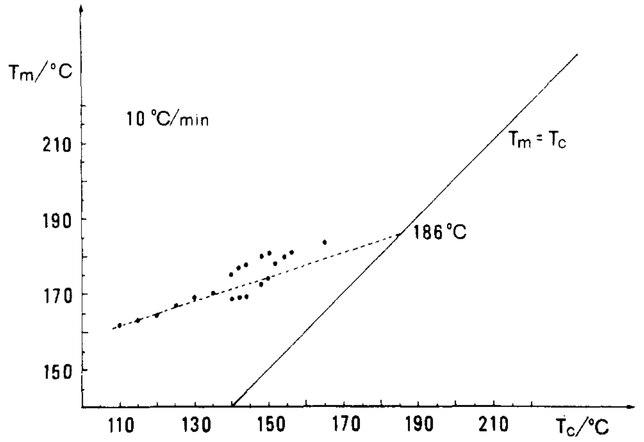

Figure 4. Plot of the peak positions of the melting endotherms (T_m), taken from the DSC scans at 10°C/min (Figure 2), vs. the crystallization temperature (T_c). The dashed line corresponds to the lower extrapolation line of Figure 3.

endotherms are obtained, both the lower and higher peak temperatures, hereafter referred to as T_m' and T_m'', are indicated.

As previously discussed,[14] all these double-peak-shape endotherms are due to the occurrence of recrystallization phenomena: the melting peak on the lower temperature side may be indeed attributed to the fusion of original crystals, its position being determined by the competition of melting and recrystallization processes; the melting peak on the higher temperature side may be attributed to the fusion of crystals generated by the recrystallization processes occurring during the scan. At least for the T_c range 135–150 °C, we have shown[14] that neither T_m' nor T_m'' are melting peak positions of species obtained at the corresponding crystallization temperature but are located below and above, respectively, the ideal melting peak which should characterize the species crystallized at T_c, in the absence of subsequent reorganization phenomena. Hence, T_m' and T_m'' values are not useful for the extrapolation procedure.

The single-peak temperature data of the DSC scans at 2.5 °C/min (Figure 3) are well fitted by a single straight line; the extrapolation of this line, to the line representing the relation $T_m = T_c$, indicates an equilibrium melting temperature equal to $\simeq$186 °C. The same extrapolation line fits well the T_m data for T_c less than 130 °C, when the heating rate is 10 °C/min (Figure 4). The single-peak melting data for the highest T_c values ($T_c > 150$ °C) are not fitted by this line owing to superheating phenomena which would characterize especially more perfect crystals.[12]

Since the T_m'' peaks are due to the melting of crystals generated by recrystallization phenomena, no theoretical argument may justify a linear extrapolation of such data to the equilibrium melting value. However, for the sake of comparison with the literature data also the linear extrapolation of the T_m'' values corresponding to the T_c range 140–150 °C, to the line representing $T_m = T_c$, have been reported in Figure 3; an extrapolation value of nearly 220 °C has been evaluated.

In our opinion, these results allow an easy interpretation of the conflicting literature results on the $T_m°$ value for i-PP: investigations in the T_c ranges below 130 °C (carried out at high heating rates (above 10 °C/min))[4,5] or above 160 °C[3] have produced $T_m° \cong 185$ °C; investigations in the T_c range 130–160 °C have produced $T_m° = 210$–220 °C, if only the end of the melting phenomenon was taken into account,[6,9] or both $T_m°$ values, when the two endothermic peaks were considered.[11]

As a final remark, we wish to point out the unusual positive slope of the line which fits the T_m'' values, reported vs. T_c, for the range 140–150 °C; generally the melting peak positions of species generated by recrystallization during the measurement scans are largely independent of the original crystallization temperature,[12] as happens also for i-PP crystallized at low T_c values (Figure 3). Further investigations on this subject are in progress.

Acknowledgment. We acknowledge Prof. B. Wunderlich of the Rensselaer Polytechnic Institute, New York, and Prof. P. Corradini of the "Università di Napoli" for useful discussions. We thank the National Research Council (CNR) "Progetto Finalizzato Chimica Fine e Secondaria" and the Ministry of Public Education (Italy) for financial support.

References and Notes

(1) J. I. Lauritzen and J. D. Hoffman, *J. Res. Natl. Bur. Stand., Sect. A* **64A**, 73 (1960).
(2) H. W. Wyckoff, J. Polym. *Sci.*, **62**, 83 (1962).
(3) F. Danusso and G. Giannotti, *Makromol. Chem.*, **80**, 1 (1964).
(4) E. Martuscelli, M. Pracella, and A. Zambelli, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 619 (1980).
(5) E. Martuscelli, M. Pracella, and L. Crispino, *Polymer*, **24**, 693 (1983).
(6) B. V. Falkai, *Makromol. Chem.*, **41**, 86 (1960).
(7) F. Rybnikar, *Collect. Czech. Chem. Commun.*, **28**, 320 (1962).
(8) W. W. Cox and A. A. Duswalt, *Polym. Eng. Sci.*, **7**, 309 (1967).
(9) J. G. Fatou, *Eur. Polym. J.*, **7**, 1057 (1971).
(10) K. Kamide and K. Yamaguchi, *Makromol. Chem.*, **162**, 205 (1972).
(11) R. J. Samuels, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1417 (1975).
(12) B. Wunderlich, "Macromolecular Physics", Vol. 3, Academic Press, New York, 1980.
(13) K. Kamide and Toyama K., *Kobunshi Kagaku*, **25**, 49 (1969).
(14) V. Petraccone, C. De Rosa, G. Guerra, and A. Tuzi, *Makromol. Chem., Rapid Commun.*, **5**, 631 (1984).

Site Isolation in Macroreticular Divinylbenzene Polymers

K. J. SHEA* and E. A. THOMPSON

Department of Chemistry, University of California, Irvine, California 92717. *Received August 14, 1984*

The question of site isolation is of concern in the interpretation of chemical phenomena involving functionality immobilized on insoluble polymer supports. It is now

0024-9297/85/2218-0814$01.50/0

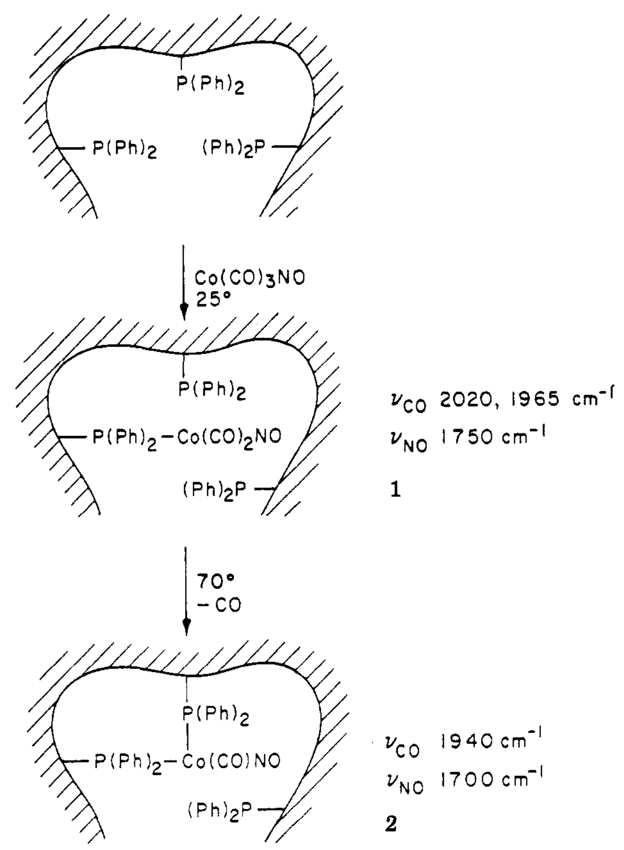

Figure 1.

recognized that many factors can influence the mobility of functionality attached to a polymer chain. A number of the more important variables are (1) degree of cross-linking, (2) method of affixing functional groups, (3) solvent, (4) length of the tether joining the functional group to the polymer backbone, (5) concentration of functionality, (6) polymer morphology, (7) diagnostic employed, and (8) homogeneity of the polymer.

As a result of the growing importance of immobilized catalysis and reagents in organic chemistry, research in the area of site isolation continues to fluorish and several reviews are now available.[1,2]

We have been involved with efforts to generate "sites" that contain multiplets of organic functional groups dispersed in a matrix of poly(divinylbenzene–ethylvinylbenzene).[3,4] Subsequent chemical reactions at these sites are interpreted within the context of events that take place as a result of preferred stereochemical arrangements of functionality at individual sites. The validity of this interpretation is dependent upon the assumption of site isolation. There are a number of studies that attest to the *mobility* of functional groups attached to styrene–divinylbenzene (DVB) copolymers.[1,2,5] We felt it was important, therefore, to compare the mobility of functionality used in our studies with materials used in these earlier reports. It was particularly important to use the same diagnostic as in the earlier studies so that a valid comparison between the two systems could be made.

Phosphine displacement on tricarbonylnitrosylcobalt ($Co(NO)(CO)_3$) has proved to be useful for determining the degree of site isolation (Figure 1). Collman reported that the bis(phosphine)–cobalt complex (**2**) results from the heating (70 °C, 24 h, diglyme) of a cross-linked (2%) resin containing the monophosphine–cobalt complex (**1**) (1.2 mmol phosphine/g, Co/P ratio 0.42).[6] Regen and Lee subsequently studied the diminution of the IR absorbance band for the monophosphine complex (**1**) (with increase in the IR absorbance for bis(phosphine) complex (**2**)) as a function of polymer swelling using a similar matrix containing the monophosphine complex (1.1 mmol of phosphine/g, Co/P ratio 0.39).[7] They observed that addition of a very small quantity of *m*-xylene (a good swelling solvent) with heating (70 °C) to a cobalt–monophosphine polymer sample resulted in a sharp decrease in the amount of monophosphine complex. Less than 20% of the monophosphine complex remained after addition of an equal weight of xylenes to the dry polymer. Addition of *n*-hexadecane (a poor swelling solvent) with heating to a dry cobalt–monophosphine-containing polymer sample had no effect.

Regen and Lee also investigated formation of the bis(phosphine)–cobalt complex on 20% cross-linked macroporous polymer.[7] After addition of xylenes to the macroreticular polymer containing monophosphine complex (0.65 mmol of phosphine/g, Co/P ratio 0.30), only 35% of the monophosphine complex remained. More recently Guyot and Bartholin systematically surveyed the relationship between resin structure and site isolation employing the same cobalt–phosphine diagnostic. Variables included in their study were degree of cross-linking, phosphine loading, and cobalt–phosphine ratio. Extensive formation of bis(phosphine)–cobalt complexes in the presence of good swelling solvents was also observed.[8] The conclusions drawn from the three investigations may be summarized as follows: site–site interactions decrease with increasing cross-linking, good swelling solvents enhance site–site interactions, and extensive site–site interactions are observed at cobalt loadings even as low as 0.1 mmol/g on macroreticular copolymers of 25% DVB and phosphine loading of 0.23 mmol/g. It should be noted, however, that the preceding studies utilized polymers that were functionalized with phosphine ligands *after* polymerization. The present study utilizes resins containing a higher degree of cross-linking than found in previous cases and employs phosphine groups that are introduced by copolymerization. As will be shown, these modifications result in a greater degree of site isolation at comparable loadings of cobalt–phosphine complexes.

Results and Discussion

A copolymer of practical-grade divinylbenzene and *p*-styryldiphenylphosphine (0.27 mmol/g, Co/P ratio 0.4) was prepared by using CH_3CN as cosolvent by bulk polymerization initiated with AIBN. Treatment with $[Co(CO)_3(NO)]$ (excess) in THF for 720 h at room temperature yielded a polymer containing the monophosphine complex (40% of available phosphine site occupation, 0.11 mmol/g). This was evidenced by the presence of the IR bands at 2020, 1970, and 1760 cm^{-1}. The bands for the bis(phosphine) complex at 1940 and 1700 cm^{-1} were absent.[9]

Portions of the polymer complex were placed in flasks under nitrogen and either xylenes or THF was added. The mixtures were heated to 70 °C for 169 h and dried, and the spectra recorded. Careful examination of the IR spectra revealed no change in the critical regions corresponding to mono- and bis(phosphine) commplex.[9]

As a control, a polymer containing monophosphine–cobalt complex (0.11 mmol/g) was treated with a xylene solution containing triphenylphosphine. The IR spectrum of the resultant polymer was examined to determine whether one of the carbonyl ligands of the complex was displaced by triphenylphosphine ligand. Bis(phosphine) complex was not observed to accumulate to any detectable extent; rather, the IR bands for the monophosphine complex diminished with time. The diminution of the absorbance bands is due to loss of cobalt displaced from the polymer by non-polymer-bound phosphine groups; less than 10% of the cobalt remained on the polymer after treatment.

The key observation from the present study is that site–site interaction could not be detected under the given experimental conditions. Several differences between the present study and earlier investigations may account for this finding. Among the more important factors are the degree of cross-linking and the method of phosphine incorporation. Increased levels of cross-linking have already been shown to *diminish* site–site interaction. What is important in the present study is that at DVB levels above 50%, effective site isolation can be achieved.

The importance of phosphine incorporation is somewhat more difficult to evaluate. Collman et al. utilized a commercially available polymer (Biobeads SX-2) derivatized by sequential bromination (Br_2, $FeBr_3$), lithiation (*n*-BuLi, THF), and treatment with Ph_2PCl.[6] This procedure can lead to nonuniform distribution of Ph_2P functionality caused either by some areas of the polymer being less accessible than others or by clustering of one of the derivatizing reagents.[8] Any nonuniform distribution would translate into areas of high local concentrations. The polymers investigated by Regen and Lee[7] were derivatized by essentially the same process.

Collman attempted to address the question of nonstatistical derivatization. He prepared a "popcorn" polymer prepared from styrene, divinylbenzene, and *p*-bromostyrene.[6] While this avoided the uncertainty in the bromination step, the polymer still required lithiation and treatment with Ph_2PCl. The lithiation sequence can result in nonuniform functionalization due to the known proclivity of lithium reagents to form clusters.[10]

A potential drawback to introducing phosphine ligands by copolymerization of *p*-styryldiphenylphosphine would be a tendency to form block copolymers. The reactivity ratios of *p*-styryldiphenylphosphine (A) and styrene (B) have been evaluated by Rabinowitz, Marcus, and Pellon, $r_A = 1.43$, $r_B = 0.52$.[11] At a monomer ratio $A/B \simeq 25$, one estimates an *initial* average mean sequence $\bar{m}(M_A) = 1.057$, and $\bar{m}(M_B) = 14$. The use of reactivity ratios (r_B) for styrene in place of ethylvinylbenzene and divinylbenzene should not *significantly* alter the conclusions—the probability of *p*-styryldiphenylphosphine next nearest neighbors should be low.[12] If the preceding analysis is correct, the average "area" of each cobalt complex, calculated from the surface area of the material (100 m^2/g), is 150 $Å^2$/Co.

Two additional factors may contribute to our results. The morphological properties of macroreticular polymers can be modified by the choice of precipitant.[8] We have shown that acetonitrile results in greater average pore size than, for example, toluene.[3] The macromolecules in the present study may differ somewhat in the microenvironment of individual phosphine residues. Our polymer preparation also differs from earlier results in that the material is mechanically ground prior to use. The influence of this step on the results is at present difficult to assess.

Although these results do not permit accurate quantification of site–site interactions, it is clear that effective isolation can be achieved by a judicious selection of parameters that influence functional group mobility.

Experimental Section

Divinylbenzene–Styryldiphenylphosphine Copolymer (0.27 mmol of Phosphine/g). A solution of *p*-styryldiphenylphosphine (2.31 g, 0.0080 mol),[13] freshly distilled divinylbenzene (26.2 g, 0.20 mol, Matheson, typical composition after purification by distillation *m*-divinylbenzene 42%, *p*-divinylbenzene 16%, *m*-ethylvinylbenzene 29%, *p*-ethylvinylbenzene 13%), acetonitrile (28 g, 0.60 mol), and AIBN (0.164 g, 1.0 mmol) was divided into two portions and placed into two medium-walled glass tubes which had constricted necks for sealing. The tubes were degassed on a vacuum line through five consecutive freeze–thaw cycles. The tubes were sealed on the line, covered with wire gauze, placed in an oil bath, and incubated at 75 °C for 12 h and then at 125 °C for 12 h. The tubes were cooled and broken open, and the white crumbly polymer was ground up with a mortar and pestle. The polymer was sized by sieving. The fraction 60–200 mesh was collected and washed in a Soxhlet extractor with methanol for 1 day. The polymer was removed and dried under vacuum: surface area (BET) 104.0 m^2/g; IR (KBr) ν_{max} 3025, 2970, 2930, 1607, 1490, 1450, 1390, 1120, 900, 830, 710 cm^{-1}. Anal. Calcd: C, 90.78; H, 8.25; P, 0.87; N, 0.10. Found: C, 90.45; H, 8.00; P, 0.87.

Dicarbonylnitrosylcobalt–Polymer-Bound Phosphine Complex. Dry polymer (2.5 g, divinylbenzene–styryldiphenylphosphine bulk copolymer, 0.27 mmol of phosphine/g) was placed in a nitrogen-purged flask and THF (100 mL freshly distilled from benzophenone–Na) was added via needle tubing. Tricarbonylnitrosylcobalt (50 μL, Alfa) was added via syringe. The flask was wrapped with aluminum foil and placed on a wrist-action shaker. After 720 h the excess tricarbonylnitrosylcobalt and the THF were removed under vacuum. The IR spectrum (KBr) of the polymer showed bands at 2030, 1980, and 1760 cm^{-1} indicative of the monophosphine (polymer-bound) dicarbonylnitrosylcobalt complex. Elemental analysis indicated that cobalt was attached to 40% of the phosphine groups. The IR bands for the bis(phosphine)–monocarbonylnitrosylcobalt complex (1940, 1700 cm^{-1}) were not detected. Anal. Calcd: C, 89.28; H, 8.00; P, 0.85; N, 0.39; O, 0.66; Co, 0.81. Found: C, 89.20; H, 8.36; P, 0.79; N, 0.12; Co, 0.32.

Treatment of Polymer Complex with Various Solvents. A portion of the polymer complex was transferred into a flask and dry solvent (100 mL of xylenes or THF or decane) was added. The flask was fitted with a reflux condenser and a nitrogen bubbler. The apparatus was wrapped with aluminum foil. The flask was purged with nitrogen and heated to 70 °C for 168 h. The solvent was then removed under vacuum and the polymer was examined by IR. The IR spectrum was identical with that of the untreated polymer. If air was purposely allowed in the reaction during heating, all three of the IR bands for the complex disappeared. The IR bands for the bis(phosphine)-bound complex (1940, 1700 cm^{-1}) could not be observed. Treatment of polymer-bound cobalt complex resulted in diminution of intensity of the IR peaks at 2030, 1980, and 1760 cm^{-1} and resulting loss of cobalt from the polymer.

Acknowledgment. We thank the National Institutes of Health for financial support of this work and for helpful comments by a referee.

References and Notes

(1) Sherrington, D. C. In "Polymer Supported Reactions in Organic Synthesis"; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; p 67.
(2) Crowley, J. I.; Rapport, H. *Acc. Chem. Res.* **1976**, *9*, 135.
(3) (a) Shea, K. J.; Thompson, E. A.; Pandey, S. D.; Beauchamp, P. S. *J. Am. Chem. Soc.* **1980**, *102*, 3149. (b) Shea, K. J.; Thompson, E. A. *J. Org. Chem.* **1978**, *43*, 4253.
(4) For related work see: (a) Wulff, G.; Schulze, I. *Isr. J. Chem.* **1978**, *17*, 291. (b) Wulff, G.; Schulze, I. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 537.
(5) See ref 1. (a) Crosby, G. A.; Weinshender, N. M.; Uh, H. S. *J. Am. Chem. Soc.* **1975**, *97*, 2232. (b) Kraus, M. A.; Patchornik, A. *J. Polym. Sci.* **1974**, *47*, 11. (c) Scott, L. T.; Rebek, J.; Ovsyanko, L.; Sims, C. L. *J. Am. Chem. Soc.* **1977**, *99*, 625.
(6) Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 1789.
(7) Regen, S. L.; Lee, D. P. *Macromolecules* **1977**, *10*, 1418.
(8) Guyot, A.; Bartholin, M. *Prog. Polym. Sci.* **1982**, *8*, 277.
(9) A conservative estimate of the limits of detection for formation of bis(phosphine) complex 2 is placed at 5%.
(10) (a) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664. (b) Waack, R.; West, P. *J. Organomet. Chem.* **1966**, *5*, 188. (c) Brown, T. L. *Adv. Organomet. Chem.* **1965**, *3*, 365. (d)

Crosby, G. A.; Kata, M. *J. Am. Chem. Soc.* **1977**, *99*, 278.
(11) Rabinowitz, R.; Marcus, R.; Pellon, J. *J. Polym. Sci., Part A* **1964**, *2*, 1241.
(12) These estimates are at best oversimplified since sequence calculations are based on homogeneous polymerizations while in the present example the cross-linked polymer is precipitated as it forms.
(13) Rabinowitz, R.; Marcus, R. *J. Org. Chem.* **1971**, *26*, 4157.

Communications to the Editor

The QELS "Slow Mode" Is a Sample-Dependent Phenomenon in Poly(methyl methacrylate) Solutions

Recent studies of the spectrum of light scattered from semidilute polymer solutions have attempted to characterize and interpret the two observed relaxation modes.[1-11] The fast relaxation has been established as being characteristic of cooperative or mutual diffusion,[12] but the origin of the slow mode is as yet unexplained. Early studies concluded that the slow mode was representative of polymer self-diffusion.[4-6,10] However, discrepancies between apparent diffusion rates from the slow mode and self-diffusion data from other techniques called this conclusion into question.[7,9] In particular, the magnitude of the slow-mode diffusion data is consistently 1 or 2 orders of magnitude lower than that of the self-diffusion data. Most recently, the formation of transient entangled macromolecular clusters has been proposed as the physical mechanism responsible for the slow-mode relaxation.[9,11] We report here the results of a comprehensive light scattering study of nine poly(methyl methacrylate) samples in solutions in methyl methacrylate. The existence of the slow mode is found to be sample dependent and not an intrinsic property of semidilute polymer solutions. Furthermore, evidence is presented to support the transient cluster hypothesis as the mechanism responsible for the slow mode in solutions where we observe it.

Experimental Section. The properties and sources of the PMMA samples studied are given in Table I. Each polymer sample was dissolved in methyl methacrylate (Aldrich Chemical Co.) to a concentration of 0.100 g/mL. Light scattering cells were rinsed repeatedly with filtered solvent to eliminate dust. The 0.100 g/mL solutions were filtered through 0.2-μm Rainin nylon filters into the clean cells. Less concentrated samples were prepared by dilution with filtered solvent. Samples of higher concentration were prepared by fitting the scattering cell with a 0.45-μm Rainin filter unit as a lid, which allowed for MMA evaporation under dust-free conditions. All concentrations were determined by weighing, and all sample cells were sealed after preparation.

An identical procedure was used to prepare sample solutions of one of the PMMA samples in chloroform.

Dynamic light scattering experiments were carried out on a Malvern Type PCS-100M spectrometer using a Lexel Model 95-2 argon ion laser and a Langley-Ford Model 1096 correlator. Total intensity light scattering measurements were made on a Sofica apparatus.

Results and Discussion. The autocorrelation functions obtained for dilute solutions of the PC and PL samples were well represented by single exponentials. Dilute solutions of the more polydisperse PI, D, and FR samples showed a broader distribution of diffusive relaxation times as determined by analysis using the CONTIN program of Provencher.[13] For all samples studied, the distribution of relaxation times in dilute solution was unimodal. At higher concentrations, however, discrepancies in the scattering behavior among the different PMMA samples were observed. The PI, PL, D, and FR samples exhibited unimodal relaxation time distributions up to the highest concentrations studied. In contrast, solutions of the PC samples of concentrations greater than ~1% polymer displayed distinctly bimodal autocorrelation functions and relaxation time distributions. The onset of this bimodal behavior with increasing concentration corresponds to the onset of molecular overlap (c^*) and the peak in the total intensity vs. concentration profile. Figure 1 shows short- and long-time correlation functions for a semidilute solution of the 179 000 molecular weight PC sample. Shown also are the diffusion coefficient distributions for the two modes (only the fast-mode distribution is shown for the short-time correlation function; the CONTIN program cannot accurately determine the slow-mode distribution from the short-time correlation function data). Both of the two diffusive modes in these solutions are seen to have quite narrow distributions. Direct comparison of these distributions shows that the distribution of relaxation times in the slow mode is comparable in breadth to that for a dilute solution of monodisperse PMMA and narrower than for a dilute solution of polydisperse PMMA. The bimodal nature of the diffusive relaxation time distribution of the PC samples in semidilute solution was unaffected by a change in solvent ($CHCl_3$), elevation of the temperature (up to 66.6 °C), and length of time in solution (up to 1 year).

Table I
Characteristics of the PMMA Samples

sample	M^a	$M_w/M_n{}^a$	source
PC-60	60 500	1.09	Pressure Chemical Co.
PC-125	125 000	1.08	Pressure Chemical Co.
PC-179	179 000	1.08	Pressure Chemical Co.
PC-240	240 000	1.09	Pressure Chemical Co.
PI-105	105 000	1.9	Polysciences, Inc.
PI-703	703 000	2.7	Polysciences, Inc.
PL-265	265 000	1.12	Polymer Laboratories, Ltd.
D-66[b]	66 000	1.4	DuPont
FR-200	~200 000	2	free radical polymerization, in situ, 40 °C

[a] M and M_w/M_n values reported by supplier except as follows: PI-105 and PI-703 values from our measurements using low-angle light scattering and GPC; FR-200 values predicted from kinetics. [b] D-66 sample was kindly provided by Dr. D. Y. Sogah of E. I. du Pont de Nemours and Co. Inc.

A careful determination was made of the characteristic diffusive relaxation times in each sample prepared. A study of the angular dependence of the relaxation rates indicated a linear dependence on q^2 (q is the scattering wavevector), affirming the diffusive nature of both the fast- and slow-mode relaxations. The fast-mode diffusion coefficients for several of the samples studied and the slow-mode diffusion coefficients for samples exhibiting this relaxation are plotted vs. concentration in Figure 2. The fast-mode diffusion coefficient is independent of molecular

0024-9297/85/2218-0817$01.50/0