Stereochemical Interaction between Isotactic and Syndiotactic Poly(methyl methacrylates) in Polar and Nonpolar Solvents[1a]

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ABSTRACT: The nature of the stereocomplex formed from isotactic and syndiotactic poly(methyl methacrylates) was extensively studied in nonpolar solvents, polar solvents, and mixed solvents, using viscometric and high resolution nmr techniques. The stereospecific complementarity of these two tactic poly(methyl methacrylates) was found to be a slow process in many cases. Complex formation does not occur in polar solvents only, as previously believed. Most strikingly, the complex forms in both the nonpolar benzene and the polar acetonitrile, but not in certain mixtures of these two solvents. The changes in the nmr spectra accompanying complex formation suggest a highly restricted motion of the polymer chains and imply that the complex involves the interaction of long segments of the polymer.

Macromolecular association based on stereospecific complementarity of the interacting species is of interest to polymer chemists and to biochemists who engage in studies of stereoregular complexation of synthetic polymers as models of biological systems. Examples of such biological systems are the structurce and function of nucleohistones and in the specific affinity between antigen and antibody.

Watanabe and his coworkers[2a] found that the mixing of dilute solutions of isotactic and syndiotactic poly(methyl methacrylates) (PMMA) in dimethylformamide resulted in instantaneous gelation. Liquori, *et al.*,[2b] studied the nature of steric association between these two tactic polymers, and proposed that this stereocomplex was formed by the fitting of extended syndiotactic (synd) PMMA chains into the grooves of helices of the isotactic (iso) molecules. This model bears a remarkable similarity to a previously proposed structure for nucleohistone in the gel state.[3] According to Liquori, the stereoassociation between iso- and synd-PMMA's is promoted in polar solvents through the affinity of the side methyl groups attached to the polymer backbones. A stoichiometric ratio of 2:1 (synd/iso) for the complex was reported.[2,4] Chiang, *et al.*,[5] concluded that the stoichiometry for the formation of a stereocomplex between these two tactic PMMA's was not as critical as reported by Liquori.[2b] It is important, however, to realize that Chiang's conclusion was drawn from a mixture of 2:1 (iso/synd) ratio which is the reverse ratio to that employed by Liquori. All these previous studies on the stereocomplex of PMMA's were carried out in polar solvents.

In order to analyze the interaction between polymers, it is beneficial to recognize the importance of interactions between solvent molecules and various chemical groups of the polymer. It is known that the interaction between benzene and the backbone of the PMMA molecule is very weak because of steric hindrance of the polymer chain.[6] Therefore the affinity of the backbone methyl groups of the two tactic PMMA's as suggested by Liquori might not be disrupted by solvent molecules in benzene solution, and stereoassociation might also be expected to occur in benzene, a nonpolar solvent.

TABLE I

Isotactic PMMA	Molecular weight (M_v)
Iso-PMMA-1	9.32×10^5
Iso-PMMA-2	1.68×10^5
Iso-PMMA-3	6.88×10^4

We have studied by viscometry and nmr spectroscopy the complex formation between these two tactic PMMA's in certain nonpolar and polar solvents, and in mixed systems containing various proportions of polar and nonpolar solvents. The data were used to interpret the phenomenon of stereochemical complementarity.

Experimental Section

The isotactic poly(methyl methacrylates) employed in this study were synthesized, fractionated, and characterized as described previously.[7] They were polymerized in toluene solution at 0° using phenylmagnesium bromide as initiator. Three fractions of different molecular weight PMMA were adopted for this investigation. Molecular weights (M_v) of these iso-PMMA's are listed in Table I. Only one sample of synd-PMMA (M_v 1.1×10^5) was used throughout this study. It was obtained through the kindness of Dr. W. Goode of the Rohm and Haas Co., Philadelphia, Pa. The polymers were examined according to the nmr method of Bovey and Tiers.[8] The tacticity of the iso-PMMA was essentially 100%; that of the syndiotactic polymer, at least 90%. All solvents were purified in accordance with established procedure.

Stock solutions of both tactic PMMA's were prepared. From these stock solutions, series of samples were made by mixing, systemically, various portions of iso- and synd-PMMA's.

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(1) (a) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) New York State University College. (c) Ford Motor Co.

(2) (a) W. H. Watanabe, C. F. Ryan, P. C. Fleisher, and B. S. Garrett, *J. Phys. Chem.*, **65**, 896 (1961); A. M. Liquori, G. Anzuino, V. M. Coiro, M. D'Alagni, P. DeSantis, and M. Savino, *Nature*, **206**, 358 (1965).

(3) G. Zubay, "The Nucleohistones," Holden-Day, Inc., San Francisco, Calif., 1964.

(4) A. M. Liquori, M. DeSantis Savino, and M. D'Alagni, *Polymer Lett.*, **4**, 945 (1966).

(5) R. Chiang, J. J. Burke, J. O. Threlkeld, and T. A. Orofino, *J. Phys. Chem.*, **70**, 3591 (1966).

(6) K-J. Liu, *J. Polym. Sci., Part A-2*, **5**, 1199 (1967).

(7) K-J. Liu, *ibid., Part A-2*, **5**, 697 (1967).

(8) F. A. Bovey and G. V. D. Tiers, *ibid.*, **44**, 173 (1960).

TABLE II

REDUCED VISCOSITY, η_{sp}/c, OF PMMA MIXTURES IN VARIOUS SOLVENTS AT 24°

Tactic composition (synd-iso)	Iso-PMMA component	Solvent	η_{sp}/c (c = polymer concn, g/100 ml)				
1:0	Iso-PMMA-2	Benzene	0.38 (0.7%)	0.37 (0.6%)	0.36 (0.5%)	0.355 (0.4%)	0.345 (0.3%)
4:1	Iso-PMMA-2	Benzene	1.20 (0.7%)	1.00 (0.6%)	0.80 (0.5%)	0.70 (0.4%)	0.60 (0.3%)
2:1	Iso-PMMA-2	Benzene	5.45 (0.7%)	2.70 (0.6%)	1.80 (0.5%)	1.20 (0.4%)	0.90 (0.3%)
1:1	Iso-PMMA-2	Benzene	4.65 (0.7%)	2.50 (0.6%)	1.80 (0.5%)	1.25 (0.4%)	1.00 (0.3%)
1:2	Iso-PMMA-2	Benzene	2.40 (0.7%)	1.35 (0.6%)	1.15 (0.5%)	0.95 (0.4%)	0.85 (0.3%)
1:4	Iso-PMMA-2	Benzene	1.05 (0.7%)	0.95 (0.6%)	0.85 (0.5%)	0.80 (0.4%)	0.75 (0.3%)
0:1	Iso-PMMA-2	Benzene	0.57 (0.7%)	0.56 (0.6%)	0.55 (0.5%)	0.545 (0.4%)	0.535 (0.3%)
1:0	Iso-PMMA-3	Benzene	0.40 (1.0%)	0.36 (0.5%)			
4:1	Iso-PMMA-3	Benzene	0.50 (1.0%)	0.42 (0.5%)			
2:1	Iso-PMMA-3	Benzene	0.60 (1.0%)	0.39 (0.5%)			
1:1	Iso-PMMA-3	Benzene	0.50 (1.0%)	0.35 (0.5%)			
1:3	Iso-PMMA-3	Benzene	0.30 (1.0%)	0.25 (0.5%)			
0:1	Iso-PMMA-3	Benzene	0.22 (1.0%)	0.19 (0.5%)			
1:0	Iso-PMMA-1 and 3[a]	Benzene	0.36 (0.5%)				
4:1	Iso-PMMA-1 and 3[a]	Benzene	0.80 (0.5%)				
2:1	Iso-PMMA-1 and 3[a]	Benzene	1.40 (0.5%)				
1:1	Iso-PMMA-1 and 3[a]	Benzene	1.80 (0.5%)				
1:3	Iso-PMMA-1 and 3[a]	Benzene	1.30 (0.5%)				
0:1	Iso-PMMA-1 and 3[a]	Benzene	0.55 (0.5%)				
1:0	Iso-PMMA-1	Toluene	0.35 (0.4%)				
4:1	Iso-PMMA-1	Toluene	3.70 (0.4%)				
2:1	Iso-PMMA-1	Toluene	14.20 (0.4%)				
1:1	Iso-PMMA-1	Toluene	13.60 (0.4%)				
1:3	Iso-PMMA-1	Toluene	3.60 (0.4%)				
0:1	Iso-PMMA-1	Toluene	1.20 (0.4%)				
1:0	Iso-PMMA-1	Chlorobenzene	0.40 (0.5%)				
4:1	Iso-PMMA-1	Chlorobenzene	0.65 (0.5%)				
2:1	Iso-PMMA-1	Chlorobenzene	0.80 (0.5%)				
1:1	Iso-PMMA-1	Chlorobenzene	1.00 (0.5%)				
1:3	Iso-PMMA-1	Chlorobenzene	1.20 (0.5%)				
0:1	Iso-PMMA-1	Chlorobenzene	1.30 (0.5%)				
1:0	Iso-PMMA-1	Chloroform	0.50 (0.5%)				
3:1	Iso-PMMA-1	Chloroform	0.75 (0.5%)				
1:1	Iso-PMMA-1	Chloroform	1.05 (0.5%)				
1:3	Iso-PMMA-1	Chloroform	1.35 (0.5%)				
0:1	Iso-PMMA-1	Chloroform	1.70 (0.5%)				
1:0	Iso-PMMA-2	Chloroform	0.50 (0.5%)				
3:1	Iso-PMMA-2	Chloroform	0.55 (0.5%)				
1:1	Iso-PMMA-2	Chloroform	0.60 (0.5%)				
1:3	Iso-PMMA-2	Chloroform	0.65 (0.5%)				
0:1	Iso-PMMA-2	Chloroform	0.70 (0.5%)				

[a] Equivalent to iso-PMMA-2.

Viscosities were measured on sample solutions with concentrations ranging from 0.1 to 1.0%, using an Ubbelohde viscometer. For high-resolution nmr studies, more concentrated solutions (5 and 20%) were prepared in nmr sample tubes, degassed, and sealed *in vacuo* or under a He atmosphere. Nmr spectra of these samples were obtained using a Varian A-60 spectrometer with temperature control attachments (Varian Associates, Palo Alto, Calif.).

All measurements were taken at various time intervals. Aging for 1 month was required to obtain data which were no longer time dependent. Viscosities obtained after such aging are designated "equilibrium" viscosities.

Results and Discussion

When relatively dilute benzene solutions of synd- and iso- (M_v 9.32 × 10^5, iso-PMMA-1) PMMA were mixed, changes in solution viscosity occurred, which varied as a function of constituent polymer composition at constant total concentration. Results, obtained at equilibrium, are presented in Figure 1. Since the association rate is slow, the reduced viscosity (η_{sp}/c) was linear in the composition of the mixed stereoregular PMMA immediately after mixing.

When the polymer concentration was less than 0.4%, the maximum viscosity was found in samples containing a 1:1 (synd/iso) ratio (Figure 1). More concentrated samples (0.4 and 0.5% of PMMA in benzene) yielded values of reduced viscosity greater than 10 in some cases. The measurements were less accurate as indicated in Figure 1 and it is difficult to identify precisely whether samples of PMMA of 2:1 or 1:1 (synd/iso) ratio had the highest viscosity. Nevertheless, the enhancement of the reduced viscosity in the more concentrated samples is so overwhelming that the association phenomenon is easily apparent.

When a lower molecular weight iso-PMMA (M_v 1.68 × 10^5) was used in the polymer mixtures, the maximum viscosity is definitely obtained with solutions with a 2:1 synd/iso ratio at concentrations greater than

0.5%; the maximum occurs again at 1:1 synd/iso ratio for more dilute solutions (see Table II).

An interesting aspect of the molecular weight dependence is that the 2:1 synd/iso mixture (0.5% polymer) with iso-PMMA-1 had a viscosity on initial preparation about double that obtained with the corresponding mixture containing iso-PMMA-2; on equilibration the viscosity ratio was greater than 20.

When a still lower molecular weight iso component was used (M_v 6.88 × 10^4, iso-PMMA-3), stereoassociation between this iso-PMMA-3 and the synd counterpart could hardly be detected, even in relatively concentrated samples (0.5 and 1.0% of PMMA) as shown also in Table II. These results clearly indicate that the effect of the stereoassociation between the two tactic PMMA's on the viscosity behavior of the polymer solution depends profoundly on molecular weight.

These findings suggested that a distribution of molecular weights of PMMA's in a sample should also affect the result of stereoassociation between these tactic isomers. This was indeed found to be the case. At constant total polymer concentration, a mixture of iso-PMMA-1 and iso-PMMA-3, with viscosity equivalent to that of iso-PMMA-2, was used as the iso component to form a complex with the synd-PMMA in benzene. Results were compared with the corresponding values for the synd–iso-PMMA-2 system (see Table II). Plots of the reduced viscosity of the polymer mixture against concentration were characterized by a strong upward curvature. Such plots at a constant 2:1 synd/iso-PMMA ratio are shown in Figure 2. In sample mixtures containing iso-PMMA-1, the reduced viscosity increased sharply when the PMMA concentration was above 0.3% (curve A, Figure 2). When the lower molecular weight iso-PMMA-2 was used in the mixtures, the reduced viscosity did not rise appreciably until the PMMA concentration was above 0.6% (curve B, Figure 2). This indicates that the effect of the polymer complexation on solution viscosity is highly dependent on polymer concentration as well as on molecular weight. Similar effects were also observed by Bailey, *et al.*, in the poly(ethylene oxide)–poly(acrylic acid) system.[9]

It is important to note that viscometric data are by themselves insufficient to characterize the degree of polymer association. We shall see later how nmr data may be used to supplement the information obtained by viscometry.

Stereochemical association between synd- and iso-PMMA's was also observed in toluene solution, another nonpolar medium. Results are presented in Table II. In relatively more polar solvents, such as chlorobenzene and chloroform, molecular association between these tactic PMMA's was not detected by viscometric measurement (see Table II). Plots of the reduced viscosity (at a constant polymer concentration of 0.5%) as a function of the composition of these two tactic PMMA's were linear.

In solvents of higher polarity than those mentioned above, *i.e.*, acetone and acetonitrile, *phase separation* of the iso–synd-PMMA complex took place. However, viscometric measurements could be obtained before any sign of phase separation took place in some of these samples. Figure 3 shows the data obtained over a period of 12 hr on samples in acetone. The highest viscosity is found in the sample of a 2:1 synd/iso-PMMA ratio. It was interesting to note that this same sample was also the one which showed the earliest phase separation in this series.

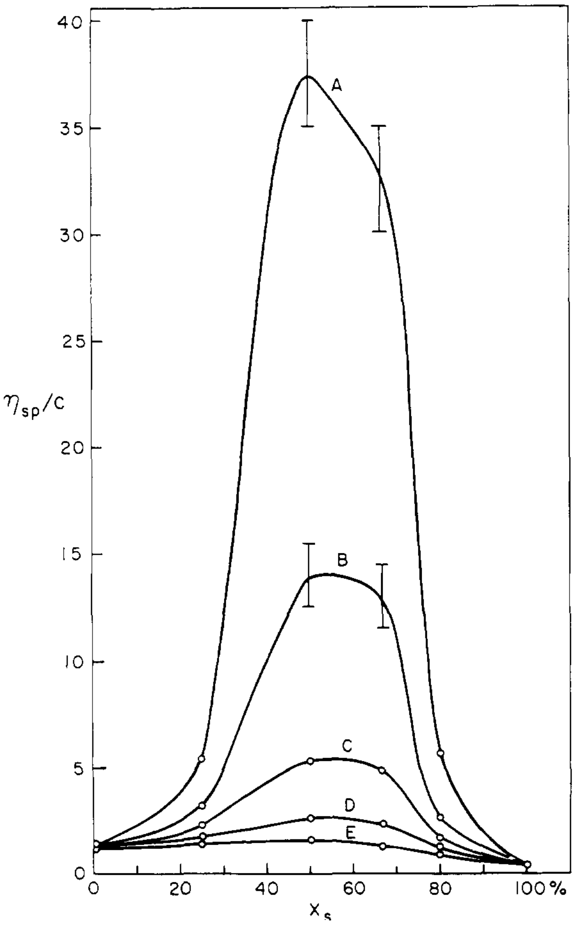

Figure 1. Plots of equilibrium reduced viscosity (η_{sp}/c) as a function of syndiotactic PMMA content (x_s) in the synd- (M_v 1.1 × 10^5) and iso- (M_v 9.3 × 10^5) PMMA's mixtures in benzene at 24°. The total polymer concentrations are (A) 0.5%, (B) 0.4%, (C) 0.3%, (D) 0.2%, and (E) 0.1%.

Although the stereocomplex of PMMA precipitated from acetonitrile, the complex remained in solution in a mixture of 20% chloroform and 80% acetonitrile. The results of measurements in this medium after 16 days of aging are shown in Table III. A maximum viscosity is again found in the sample of a 2:1 synd/iso-PMMA ratio. By contrast, the addition of 20% chloroform to benzene seems to eliminate the formation of the stereocomplex (Table III) completely. Particularly striking are the results in the benzene–acetonitrile systems. The solvent system, made of 80% acetonitrile and 20% benzene, led, as expected, to complex formation of the two tactic PMMA's. However, it is surprising to note that a solvent system made of 20% acetonitrile and 80% benzene was unexpectedly found to destroy completely the stereocomplex (Table III). Further viscometric results indicate that, although both pure solvents support complex formation, no complex

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(9) F. E. Bailey, Jr., R. D. Lundberg, and R. W. Callard, *J. Polym. Sci., Part A-2*, 845 (1964).

Table III
Reduced Viscosity, η_{sp}/c, of Synd- and Iso-PMMA-1 Mixtures (0.4%) in Various Mixed Solvent Systems at 24° [a]

Tactic composition (synd/iso)	Solvent composition, vol %			
	Acetonitrile	Benzene	Chloroform	η_{sp}/c
1:0	80	...	20	0.30
4:1	80	...	20	1.35
2:1	80	...	20	5.50
1:1	80	...	20	4.85
1:3	80	...	20	1.40
0:1	80	...	20	0.95
1:0	...	80	20	0.40
4:1	...	80	20	0.55
2:1	...	80	20	0.70
1:1	...	80	20	0.85
1:3	...	80	20	1.05
0:1	...	80	20	1.30
1:0	80	20	...	0.30
4:1	80	20	...	1.30
2:1	80	20	...	5.95
1:1	80	20	...	5.00
1:3	80	20	...	1.60
0:1	80	20	...	0.95
1:0	20	80	...	0.40
4:1	20	80	...	0.55
2:1	20	80	...	0.70
1:1	20	80	...	0.85
1:3	20	80	...	1.05
0:1	20	80	...	1.30

[a] Measurements were taken after sample solutions were equilibrated for 16 days.

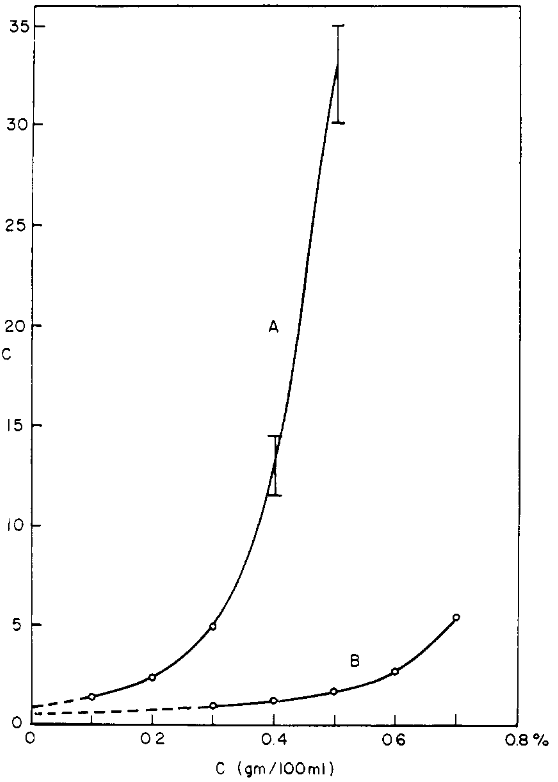

Figure 2. Plots of equilibrium reduced viscosity (η_{sp}/c) as a function of polymer concentration for samples containing a 2:1 synd/iso-PMMA ratio in benzene at 24°: (A) synd-iso-PMMA-1 system; (B) synd-iso-PMMA-2 system.

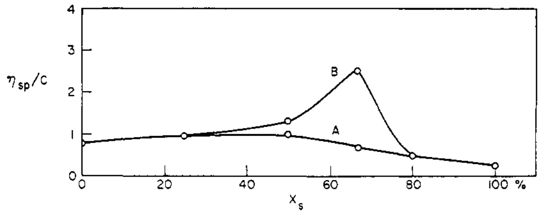

Figure 3. Plots of reduced viscosity (η_{sp}/c) as a function of synd-PMMA content (χ_s) in the synd- (M_v 1.1 × 10^6) and iso- (M_v 9.3 × 10^5) PMMA's mixtures (0.4%) in acetone at 24°. Measurements were taken after sample solutions were equilibrated for (A) 20 min, (B) 12 hr.

exists in mixtures of the two solvents over a certain concentration range (curve B, Figure 4). The benzene–toluene system behaved as expected with the stereocomplex stable over the entire concentration range of the mixed solvents (curve A, Figure 4).

The PMMA stereocomplex in benzene dissociates when the temperature is raised. The results obtained at various temperatures are shown in Figure 5. Curve A in Figure 5 represents the viscosity measurements obtained after 20 min of thermal equilibria at various temperatures, ranging from 24 to 65°. Curve B represents those equilibrium data obtained within 24 hr. These two curves illustrate an important feature of the dissociation of PMMA complex at higher temperatures. Below the temperature of complete melting (~65°), the dissociation of PMMA complex is a slow process, requiring many hours. However, complete dissociation of the PMMA complex was observed within 1 hr at approximately 65°. When a melted sample was immediately cooled to 24°, reassociation between these two tactic PMMA's occurred, but this was a very slow process.

Studies on the stereoassociation of these tactic PMMA's using a high-resolution nmr technique yielded further information on the nature of this PMMA stereocomplex. For simplicity, only two representative sets of high-resolution nmr peaks of the ester–methyl protons of PMMA (5%) in chloroform and in benzene with various synd/iso ratios are shown in Figure 6. The polymeric peak was significantly reduced in the PMMA complex, and was affected by the composition of tactic PMMA's in benzene. This type of nmr peak reduction reflects a restriction of local segmental motion when the PMMA complex is formed in benzene. On the other hand, the two tactic PMMA's independently coexist in chloroform; little reduction of the polymeric nmr peak was observed in chloroform solutions. Similar results obtained in many other solvent systems are tabulated in Table IV. These nmr results are in complete agreement with those obtained from viscometric determinations, regarding the presence or absence of the PMMA complex in various solutions. All the polymeric nmr peaks of the complex in benzene are reduced further in a high molecular weight system (synd-PMMA/iso-PMMA-1) than in a low molecular weight system (synd-PMMA/iso-PMMA-3).

It may be beneficial to mention here briefly the significance of employing high-resolution nmr spectroscopy and viscometric measurements for the detection of association between polymers. Even very slight seg-

TABLE IV
A SUMMARY OF THE NMR RESULTS ON THE DETECTION OF THE STEREOASSOCIATION OF THE SYNDIOTACTIC AND ISOTACTIC PMMA'S IN VARIOUS SOLVENT SYSTEMS AT 35°

Polymers	Concn, %	Solvents	Result on the detection of the association of the tactic PMMA's
Synd-PMMA/iso-PMMA-1	20	Benzene	Yes
Synd-PMMA/iso-PMMA-1	5	Benzene	Yes
Synd-PMMA/iso-PMMA-2	5	Benzene	Yes
Synd-PMMA/iso-PMMA-3	5	Benzene	Yes
Synd-PMMA/iso-PMMA-1	5	Chloroform	No
Synd-PMMA/iso-PMMA-3	5	Chloroform	No
Synd-PMMA/iso-PMMA-1	5	Benzene-Acetonitrile (50:50)	No
Synd-PMMA/iso-PMMA-3	5	Benzene-Acetonitrile (50:50)	No
Synd-PMMA/iso-PMMA-3	5	Benzene-Acetonitrile (80:20)	No
Synd-PMMA/iso-PMMA-3	5	Benzene-Chloroform (80:20)	No
Synd-PMMA/iso-PMMA-3	5	Acetonitrile-Chloroform (80:20)	Yes

mental association may well be detected by viscometric determinations, while this is difficult to reveal by a high-resolution nmr technique. It is known that in systems of lightly cross-linked PMMA networks, the cross-linking strongly affects the viscosity of the swollen gel, but hardly influences the segmental motion at all.[10] Under the present experimental conditions, the nmr technique appears to be more effective than viscometric determinations, only when the association involves a large number of polymer segments. Therefore, results obtained by these two techniques complement each other in a useful way to help to elucidate the intricate nature of the stereoassociation between the two tactic polymers.

The fact that, in the present study, all the polymeric peaks almost completely disappear from the nmr spectrum of the sample with a 2:1 synd/iso-PMMA ratio in complex-supporting solvents implies that the association between these two tactic PMMA's must be so strong as to restrict highly polymeric motion at the segmental level. Therefore, according to the nmr results, the formation of this PMMA stereocomplex probably involves the association of blocks of the polymer segments rather than certain isolated entanglements at a few points along the polymer chains.

When results obtained from both nmr and viscometric measurements are combined, we may assess the dependence of complex formation on polymer concentration. According to viscometric determinations, relatively dilute samples (0.5 and 1.0%) of the synd- and iso- (iso-PMMA-3) PMMA's in benzene gave little sign of stereocomplexation (Table II). However, in concentrated samples (5%) of the same PMMA mixtures, the nmr results indicated a strong association between the constituent PMMA's (Table IV). This observation of stereocomplexation by the nmr measurements clearly demonstrates that the enhancement of viscosity at higher concentration reflects also increased complex formation.

It is also interesting to note that, according to the nmr results, whenever the formation of stereocomplex is permissible, the PMMA mixture with a composition of 2:1 synd/iso ratio always shows the highest de-

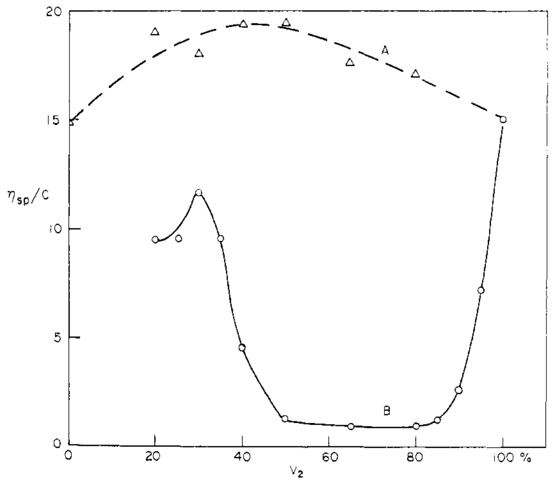

Figure 4. Plots of equilibrium reduced viscosity (η_{sp}/c) of PMMA mixture (0.4%) with a 2:1 synd (M_v 1.1 × 10^5)/iso (M_v 9.3 × 10^5) ratio as a function of benzene content (V_2) in cosolvent systems with (A) toluene and (B) acetonitrile.

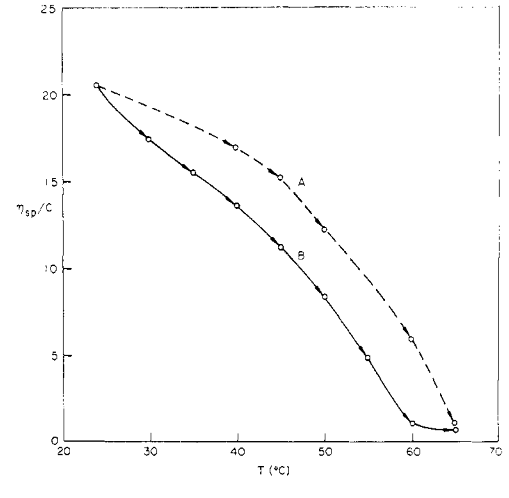

Figure 5. Plots of reduced viscosity (η_{sp}/c) of PMMA mixture (0.4%) with a 2:1 synd (M_v 1.1 × 10^5)/iso (M_v 9.3 × 10^5) ratio after equilibrium at 24° as a function of temperature: (A) data obtained after 20 min of thermal equilibrium; (B) equilibrium results.

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(10) K-J. Liu and W. Burlant, *J. Polym. Sci., Part A-1*, 5, 1407 (1967).

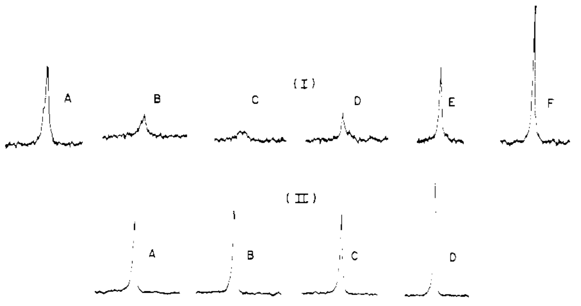

Figure 6. Representative high-resolution nmr absorptions of the ester methyl protons of synd- (M_v 1.1 × 10^5) and iso- (M_v 9.3 × 10^5) PMMA's (5%) in benzene (I) and chloroform (II) at 35°. The synd/iso ratios are, respectively, (A) 1:0, (B) 4:1, (C) 2:1, (D) 1:1, (E) 1:3, and (F) 0:1 in series I; (A) 1:0, (B) 2:1, (C) 1:1, and (D) 0:1 in series II.

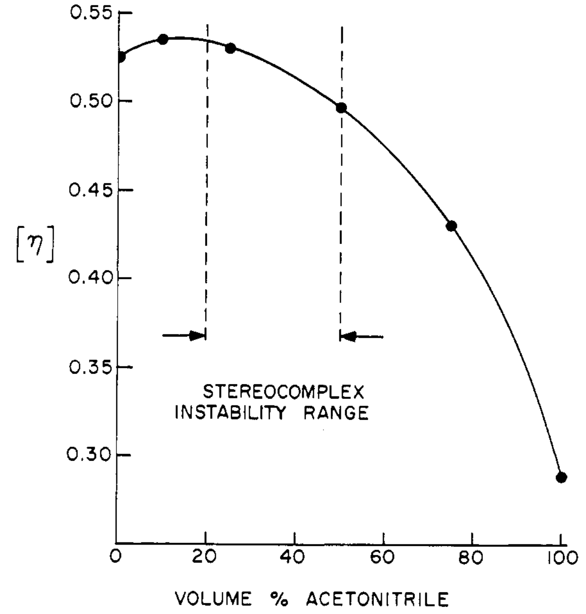

Figure 7. Intrinsic viscosities of iso-PMMA (M_v 1.68 × 10^5) in the benzene-acetonitrile system at 25°.

gree of association between the two tactic isomers as compared with samples of other compositions. This is again in complete agreement with results obtained from viscometric measurements on solutions containing more than 0.5% polymer.

It has been shown that when the ambient temperature is raised, the PMMA complex begins to dissociate; consequently, the segmental motion of the constituent tactic PMMA's should be expected to increase. This is true as illustrated in the nmr spectra obtained at various high temperatures. The nmr peaks gradually increase as the temperature is raised from 35 to 60°. A sharp increase of the nmr peak was seen as the temperature increased from 60 to 70°. Melting of the PMMA complex is clearly demonstrated in these nmr spectra. This agrees with what has been found from viscometric determinations.

The present data support Liquori's contention that the stereocomplex is stoichiometric. The implication of the nmr data is also strong support for the assumption that a large number of chain segments participate in complex formation. The interpretation of this phenomenon in terms of steric complementarity is very tempting. However, the earlier notions on the conditions favoring complex stability have to be modified in some respects. We have shown that the complex may form in nonpolar media, so that the key role of a polar solvent in promoting the mutual interaction of the nonpolar methyl groups attached to the polymer backbones may not be as important as previously believed. The fact that the complex becomes unstable in mixtures of benzene and acetonitrile, although it is stable in either of the two solvents, is reminiscent of the well-known phenomenon that a mixture of nonsolvents may provide a solvent medium for a given polymer. Gee[11] has shown that such a situation may occur when the two solvents have cohesive energy densities much higher and much lower than the polymer, so that the CED of the polymer may be matched by mixing these solvents in suitable proportions. To check whether this is the proper interpretation for the observed dependence of stereocomplex stability on the composition of benzene-acetonitrile mixtures, we determined the intrinsic viscosity of iso-PMMA in the two pure solvents and their mixtures. The results, plotted in Figure 7, show that addition of small amounts of acetonitrile raises, in fact, the intrinsic viscosity of PMMA above the value observed in pure benzene; *i.e.*, it increases the solvation of the polymer. However, the intrinsic viscosity does not give a quantitative measure of the ability of the medium to dissociate the stereocomplex; for instance, pure benzene, in which the complex is stable, solvates PMMA more strongly than a mixture of equal volumes of benzene and acetonitrile, in which the complex dissociates.

The extreme slowness with which dilute solutions of mixtures of iso- and synd-PMMA attain properties which do not change further with time in stereocomplex-supporting media is typical of polymer association phenomena.[12,13] It is explicable in terms of a rearrangement of locally associated chain segments to more stable forms with long-range order. Apparently, only such long-range interaction confers on the complex sufficient stability to render it detectable by an increase in the solution viscosity.

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