These exceptionally large rate enhancements appear to be related to the "structuredness" of the solvent medium. The addition of ethanol to water has been shown to increase the structuredness of the system, and the degree of structuredness reached a maximum at an ethanol mole fraction (x_2) of 0.1 (*ca.* 27% ethanol by volume at 25°).[13,14] Beyond this maximum point the degree of the structured system decreased until the system became an ordinary binary mixture at $x_2 > 0.25$ (*ca.* 54% ethanol by volume at 25°).

Although our ethanol-water solvent systems contain additional components, it would appear that the polymeric reactivities are in part related to apolar interactions which are based on the structuredness of the solvent, especially for the catalytic rate enhancement in the region of 30% ethanol. Another factor which is apparently involved in the polymeric reaction and which is lacking in the monomeric reaction is the complexation between poly-4(5)-vinylimidazole and NDBA. Initial results of the poly-4(5)-vinylimidazole catalyzed solvolysis of NDBA in 43.7% ethanol-water have shown kinetic evidence for complex formation which could be represented by the Michaelis-Menten mechanism.[3] This saturation effect could be achieved when either the varying polymer concentration was in excess of the fixed substrate concentration or *vice versa*. The Michaelis constants (K_m) for these reactions were determined to be $(4.77 \pm 0.57) \times 10^{-4}$ M for [PVIm] > [NDBA] and $(4.53 \pm 0.64) \times 10^{-4}$ M for [NDBA] > [PVIm]. The first-order rate constants (turnover numbers) were determined to be 0.032 ± 0.004 min^{-1} for the former system and 0.088 ± 0.013 min^{-1} for the latter system. The novel similarity of these K_m values would appear to suggest that the mechanisms of complexation between poly-4(5)-vinylimidazole and NDBA involve both electrostatic and apolar interactions, a circumstance which would lead to a lowering of the free energy of activation of the solvolytic reaction. This factor in conjunction with the effect of an ordered solvent structure could be responsible for the exceptionally large esterolytic reactivities achieved with a synthetic, vinyl polymer, reactivities which approach the order of enzymic processes. These results may suggest that the high reactivity of an enzymic process could be in part related to an ordered water structure at the enzymes' active site.

Although the values of K_m determined for 43.7% ethanol-water are of the same order as those of certain enzyme-substrate reactions, the turnover numbers of this system are indicative of a rather inefficient solvolytic process. We hope to report in the near future detailed results of the rapid solvolysis of NDBA at low ethanol contents, as well as the effects of temperature, pH and ionic strength on these reactions.

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Thin Layer Chromatographic Studies on Specific Interactions between Stereoisomeric Chains of Poly(methyl methacrylate)

In our preceding papers it has been reported that thin layer chromatography (tlc) can be applied successfully to studies on the chemical structure of binary copolymers,[1] as well as on the stereoisomerism of poly(methyl methacrylate) (PMMA).[2] This short communication deals with further applications of tlc to the investigation of specific interactions between isotactic and syndiotactic PMMA chains. The problem treated here is divided into two subjects, *viz.*, stereocomplex formation in dilute solution,[3–7] and the structure of crystallizable PMMA, which was first thought to be a stereoblock PMMA.[8,9] For this first subject, stereocomplexes were formed in dilute solution in different mixing ratios of isotactic and syndiotactic PMMA, and the chromatographic behavior of the complexes was observed. For the second subject, the tlc method was utilized to separate the so-called stereoblock polymer into components without conversion to the polymeric acid, such was done by Liquori, *et al.*[10]

Fractionated samples of isotactic and syndiotactic PMMA designated iMA-3 ($M_v = 3.64 \times 10^5$) and sMA-2 ($M_v = 2.46 \times 10^5$), respectively, were used in this investigation. The preparation and the characterization of these samples have been reported in the previous paper.[2] To obtain the so-called stereoblock polymers, two different polymerization runs of MMA in toluene at −50° were made by using different catalysts, *n*-butylmagnesium chloride and diphenylmagnesium, respectively. The products were extracted with boiling acetone[4] and the insoluble portions were used for the subsequent experiments, being designated Bmc-M ($M_v = 2.66 \times 10^5$) and Dpm-M ($M_v = 2.02 \times$

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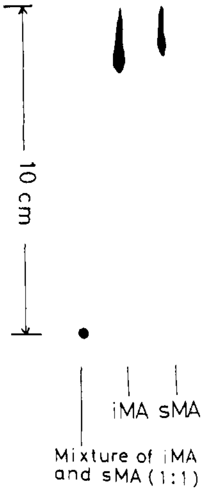

Figure 1. Tlc chromatogram obtained for isotactic and syndiotactic PMMA, and their 1:1 mixture by using acetone as developer.

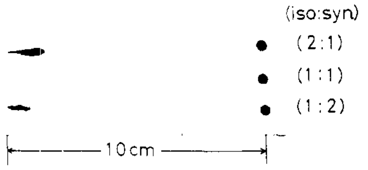

Figure 2. Tlc chromatogram obtained for the mixtures of isotactic and syndiotactic PMMA in different mixing ratios by using acetone as developer.

10^5) according to the former and the latter catalyst used, respectively.

The experimental procedure of tlc has been described in detail in previous publications.[1,2] Silica was used as the stationary phase. Stock solutions for tlc tests were prepared by dissolving each sample in chloroform and the concentrations were adjusted to 0.40 g/dl. Stereocomplex formation was achieved by admixing the stock solutions of the two stereoregular polymers, iMA-3 and sMA-2, in three different ratios (isotactic/syndiotactic), namely 2:1, 1:1, and 1:2. Upon admixture of the two solutions no visible change in transparency of the resultant solution was observed, differing from the case where the two species were mixed in acetone.

It has been well established in our previous work[2] that when ethyl acetate is used as developing agent, isotactic PMMA remains on the starting line, while syndiotactic PMMA (and atactic PMMA) reach the neighborhood of the solvent front. However, for the present purpose, acetone was used, which could develop both species to the proximity of the solvent front, as shown in Figure 1. This chromatogram indicates also that the 1:1 mixture could not be separated into components at all. In this connection it is of interest to note that to obtain such a chromatogram, the spot formed on the thin layer from the mixture in chloroform had to be moistened with a drop of acetone in advance of the development; nevertheless, a slight ascendance of the spot lying on the starting line was unavoidable in every case. This feature may be related to the conclusion that the stereocomplex formation is promoted much more in polar solvent,[6] and also to our observation made upon admixture of the two species in chloroform.

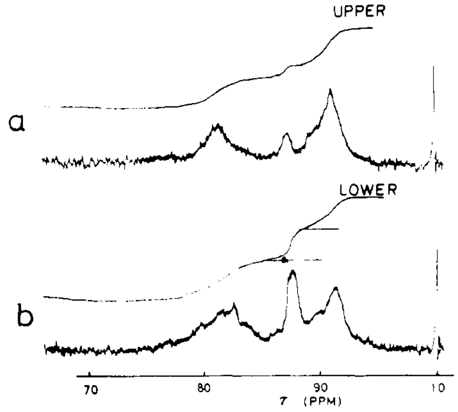

Figure 3. Nmr spectra, obtained in 10% CDCl$_3$ solutions at 60 MHz and at 30°, of polymers involved in the upper and the lower spot in the chromatogram obtained by development of the 1:2 (isotactic/syndiotactic) mixture with acetone.

The next experiment was made on the mixtures with different compositions. The chromatogram is shown in Figure 2. From the figure it is seen that the mixtures, except that of the 1:1 ratio, yield a lower and an upper spot, which appear at the starting line and in the vicinity of the solvent front, respectively. To collect the polymer species involved in each spot in order to assign the steric structure, the same development was carried out for the mixtures of 1:2 and 2:1 (isotactic/syndiotactic) ratios with a layer of 1 mm thickness. The adsorbed species were recovered by extraction with hot acetone.

The stereoregularity of these extracts was assessed on the basis of nmr spectra. Figures 3a and 3b illustrate the 60-MHz nmr spectra of the upper and the lower portion, respectively, originating from the 1:2 mixture. The nmr data permit us to confirm that the upper spot contained highly syndiotactic species, while the species in the lower spot could be identified with that of the 1:1 mixture. For the 2:1 mixture the species involved in the lower spot was assigned by nmr to the same stereoisomeric composition as the 1:1 mixture. This means, in turn, that the upper spot should contain the isotactic species, though its analysis was not made. These observations thus suggest that this type of aggregation phenomenon may occur stoichiometrically at a unique composition between equivalent portions of isotactic and syndiotactic PMMA. Our preliminary result obtained by ultracentrifugation of the mixtures appears to reveal, however, that the 1:2 (isotactic/syndiotactic) complex also might be formed as the result of further aggregation between the 1:1 complex and the syndiotactic polymer. We may conclude that two different structures for the stereocomplexes are possible depending on the ratio of syndiotactic to isotactic PMMA.[3-7] The details of this study will be published elsewhere.

In an attempt to investigate the steric structure of the so-called stereoblock PMMA, we have applied tlc technique to samples Bmc-M and Dpm-M using ethyl acetate as developing agent. Figure 4 shows the

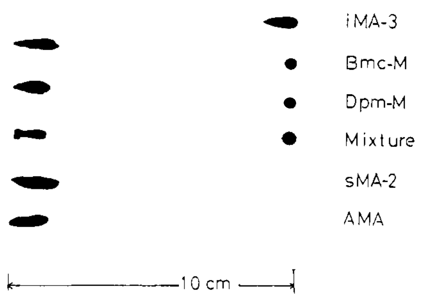

Figure 4. Tlc chromatogram obtained by development of different stereoisomeric types of PMMA with ethyl acetate, *viz.*, isotactic (iMA-3), stereoblock (Bmc-M and Dpm-M), the 1:2 mixture, syndiotactic (sMA-2), and atactic (AMA) PMMA, in order from top to bottom.

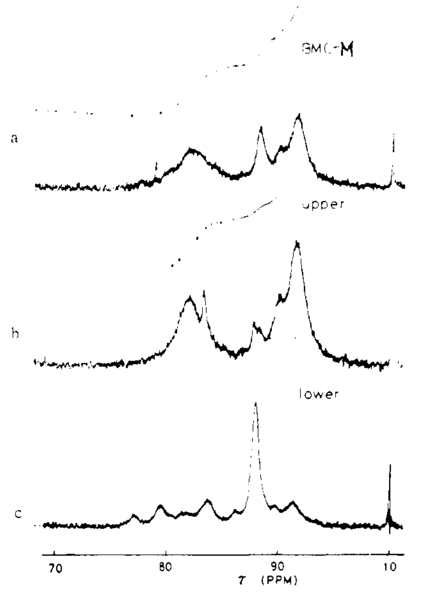

Figure 5. Nmr spectra, obtained in 10% $CDCl_3$ solutions at 60 MHz and at 30°, of original stereoblock polymer Bmc-M, the species contained in the upper and the lower portion separated from Bmc-M with ethyl acetate as developer.

chromatogram thus obtained, in which the two species, the 1:2 mixture, and an atactic PMMA (AMA) prepared with an anionic polymerization technique[11] were developed simultaneously for comparison. This result indicates that the samples Bmc-M and Dpm-M are distinctly separated into an upper and a lower spot.

By using the same procedure employed for the stereoisomeric mixtures the polymer species involved in each spot were recovered and subjected to the nmr analysis. In connection with the extraction of polymer from the thin layer it should be noted that the species thus separated were no longer insoluble in acetone in contrast to the original solubility of the samples in this solvent. Figure 5a shows the nmr spectrum for Bmc-M; Figures 5b and 5c show those for the species contained in the upper and the lower spot, respectively. The spectrum for the upper spot indicates the dominant α-methyl peak at τ 9.13 and the single β-hydrogen peak;[12] for the lower spot the dominant α-methyl peak at τ 8.80 is accompanied by four peaks for the β-hydrogens. In addition, a peak appears in both species at τ 8.98, which may be assigned to heterotactic sequences. On the basis of the nmr data we may conclude that the main components involved in the upper and the lower spot are syndiotactic and the isotactic PMMA, respectively, although these polymers contain considerable amounts of heterotactic sequences.

The relative amount of the two components separated from Dpm-M was determined by a photometric procedure established previously.[2] The chromatogram was developed with a solution of iodine in methanol. The area and blackness of each spot were measured using a photographic negative of the chromatogram. The total blackness was then converted to the amount of polymer by using a factor 1.32 to correct for the difference in the blackness of the isotactic and syndiotactic PMMA spots; iodine molecules have an affinity for the isotactic polymer which is higher by a factor of 1.32 than that for the syndiotactic polymer. The final estimation of the relative amount yielded 0.71 and 0.29 for the syndiotactic and the isotactic portion, respectively, and this is fairly in good agreement with that reported by Liquori, *et al.*[10]

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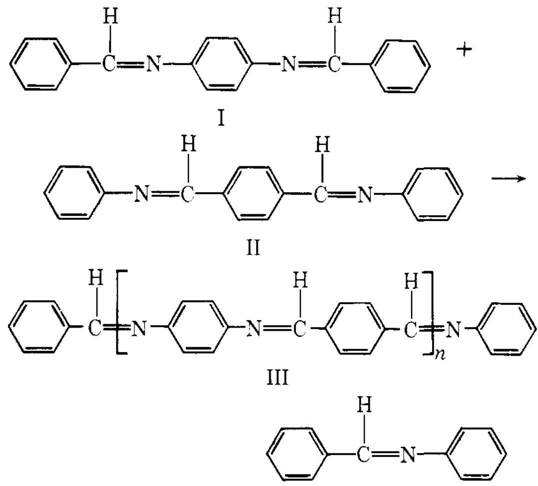
Polymeric Schiff Bases

A considerable amount of work has been carried out in recent years in an effort to obtain high molecular weight conjugated Schiff base polymers.[1,2] However, the insolubility of the growing polymer chains in any inert solvent has precluded this. Recently D'Alelio and coworkers[3] claimed to have produced high molecular weight, highly conjugated Schiff base polymers by a bis-Schiff base exchange reaction, using molten reagents at high temperatures. The exchange reaction is shown in eq 1. The reported infrared spectra of the black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