# STUDIES ON THE ORGANIZED STRUCTURES IN SOLUTIONS AND GELS OF SOME SYNTHETIC MACROMOLECULES

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## ABSTRACT

This presentation reviews our work on the organized structures of some synthetic macromolecules in solutions and gels. Various techniques, such as spectroscopic, viscometric, x-ray analytic and molecular relaxation measurements were used. Emphasis is on the *concept of solvation* of macromolecules. The following subjects are included: (*i*) The intramolecular conformational structures of some *simple polymers*, such as polyethylene and polyethylene oxide, are presented. It is clearly revealed that even an isolated chain molecule in an infinitely dilute solution is subjected to both intra-polymer and polymer–solvent interactions that determine *its final structure*—organized or disorganized. (*ii*) The nature of macromolecular association is discussed in terms of polymer–polymer and detailed polymer–solvent interactions. In particular, we discuss the effect of molecular association based on stereospecific complementarity of the interacting species on the local segmental environments of chain molecules. This leads to *a deep insight* into the intricate nature of macromolecular associations in gel or in solutions. (*iii*) Interactions of solvent with macromolecules in organized and random structures are compared and significant differences are observed. It therefore suggests a *new route* to the study of macromolecular structure by examining the behaviour of the interacting solvent molecules.

## INTRODUCTION

In recent years there has been an increasing interest in studying biological principles in synthetic polymer systems. This is particularly true in the area of molecular structures and interactions. Organized structures long recognized in solutions of biopolymers may no longer be characteristic of biopolymers only. There are counterparts in synthetic polymers. In this presentation we review our work on the organized structures of some synthetic macromolecules in solutions and gels.

## STRUCTURAL STUDIES OF CHAIN MOLECULES

It is well known that the conformational structure of many biopolymers in solution is determined by the solvent in which they are dissolved. Relatively

little work has been done on synthetic polymers. Let us start with the 'simplest' polymer, polyethylene (PE). It does not contain chemical groups that interact in a specific pattern, such as the hydrogen bonding in polypeptides. Its structure in solution was, therefore, taken for granted as a typical representation of random coil[1, 2]. This concept was questioned by Liu. A high-resolution proton-magnetic resonance (p.m.r.) study of the intramolecular structure of PE in solution was then carried out[3-5].

P.M.R. spectra of various $n$-alkanes in $\alpha$-chloronaphthalene are shown in *Figure 1*. These compounds are, of course, oligomers of polyethylene. The first peak to the left (I) is due to the external reference; peaks II and III are due to the methylene and methyl protons, respectively. The complicated spectral pattern arising from the methyl protons III is caused by spin–
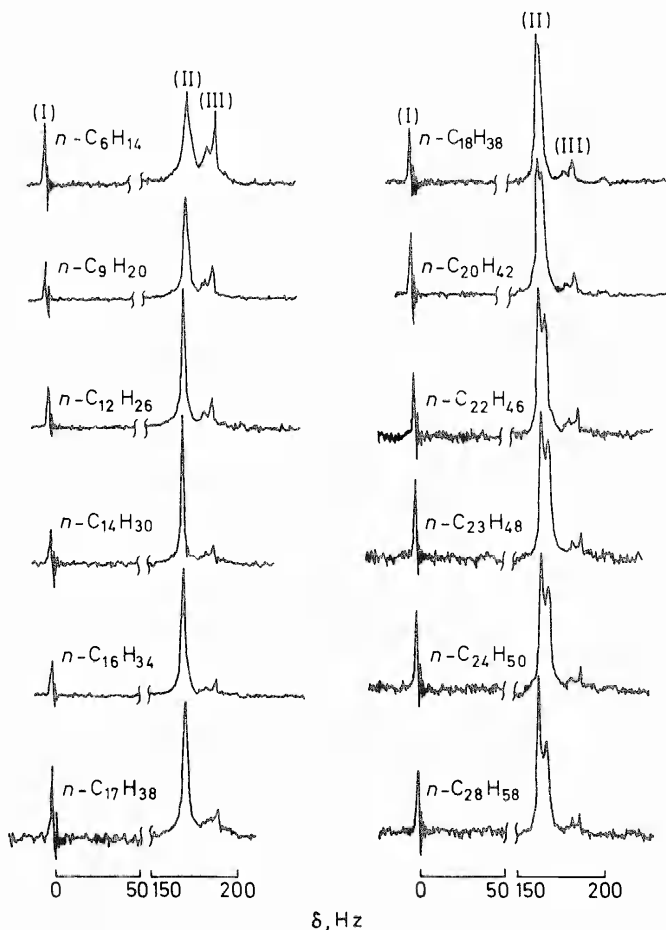


*Figure 1.* Representative p.m.r. spectra of $n$-alkanes (6 per cent) in $\alpha$-chloronaphthalene at 35°C. Peaks I, II, and III are external reference (8 per cent dioxane in carbon tetrachloride) and methylene and methyl absorption lines, respectively.

spin interactions with the adjacent methylene protons. Similar splittings should appear for the methylene protons adjacent to the methyl groups. These splittings are presumably masked in the present spectra by the internal methylene protons (IMPs) contributing to peak II.

It is noteworthy that all IMPs give rise to a single p.m.r. peak for alkanes with carbon number $n \leqslant 16$, and two partially resolved peaks (on an expanded scale) when $n \geqslant 17$. The presence of two distinct IMP resonances for the higher $n$-alkanes is a definite indication of some new structural arrangement in these compounds that is not present in the lower members of the series. Detailed analysis shows that the new peak grows in relative intensity as the number of chain units is further increased, and it can be identified with the p.m.r. peak of high-molecular-weight polyethylene.

The formation of this new structure in the higher $n$-alkanes is strongly solvent-dependent. Aromatic solvents, such as $\alpha$-chloronaphthalene and 9-chloroanthracene, were found to produce the split IMP resonance for $n \geqslant 17$. No splitting was evident on the same compounds when they were dissolved in carbon tetrachloride or in deuterated $n$-alkanes. These results do not seem to be related to 'ring current' effects in the aromatic solvents: addition of a small amount of carbon tetrachloride to a solution of $C_{24}H_{50}$ in $\alpha$-chloronaphthalene drastically modifies the new IMP resonance.

The structure of the internal methylene units responsible for the additional IMP resonance cannot be derived from p.m.r., although the explanation of the experimental results requires some ordered structural feature. A chain-folding mechanism has been proposed that is consistent with thermodynamic consideration[6]. It should be noted that whatever the structure may be, it cannot be static: the narrow p.m.r. linewidths preclude this. Rather, it must be a dynamic arrangement with fluctuating sequences of more-or-less ordered regions. As a result of this, little hydrodynamic rigidity is given to the molecules, which behave in many respects as random coils.

In addition to the observed conformational change of polyethylene in certain bulky aromatic solvents at C-17, we have also found evidence of the existence of a particular conformational change for these chain molecules in both their pure state and benzene solutions at C-9[5]. This is in agreement with the Raman results reported by Schaufele[7].

P.M.R. has been used to study the intramolecular structure of poly-(ethylene glycol), PEG[8, 9]. The spectra were measured as a function of chain length at different concentrations in various solvents. Representative spectra, obtained in benzene, are shown in *Figure 2*. In 50 per cent solutions, the PEG chains are in various states of association, and all their ether-type protons contribute to a structureless peak. In contrast, a great deal of structure is apparent in the p.m.r. spectra of the 5 per cent solutions. The internal ether-type protons contribute to a single peak for the trimer, tetramer, and pentamer but form a doublet for the hexamer. The p.m.r. spectrum of the PEG heptamer contains a new peak that is absent in lower members of the series. As the chain length is increased beyond the heptamer, this peak grows in relative intensity. Thus, it appears that a local polymeric environment is revealed in an oligomer that is seven units long. P.m.r. studies of PEG in carbon tetrachloride yield similar results, although the splitting of the various peaks is not as great in this solvent.
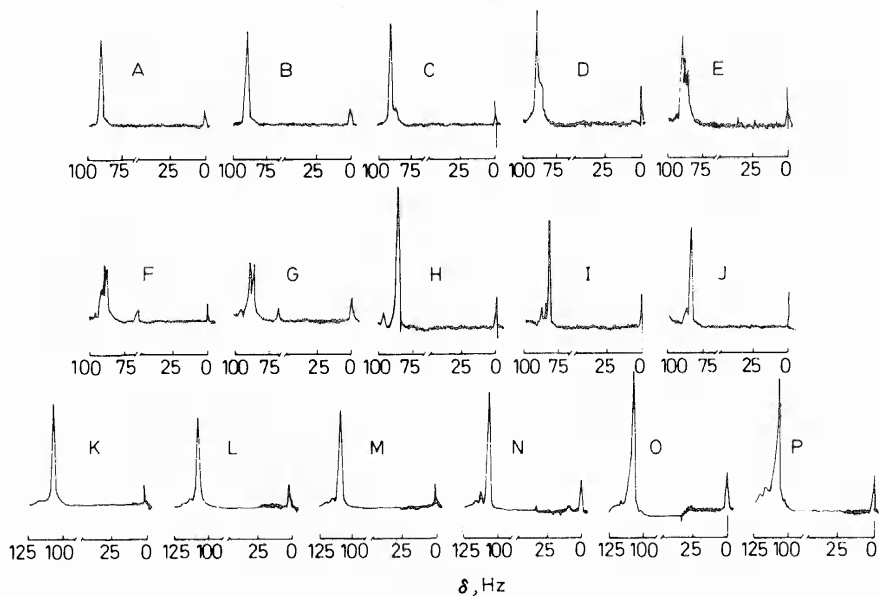
*Figure 2.* P.M.R. spectra of PEGs in benzene (A–J. 5 per cent; K–P, 50 per cent) at 35°C. (A) PEO–20 000, (B), PEO 4 000, (C) PEO–1 000, (D) PEO–600, (E) PEO–400, (F) heptamer, (G) hexamer, (H) pentamer, (I) tetramer, (J) trimer, (K) octamer, (L) heptamer, (M) hexamer, (N) pentamer, (P) trimer.
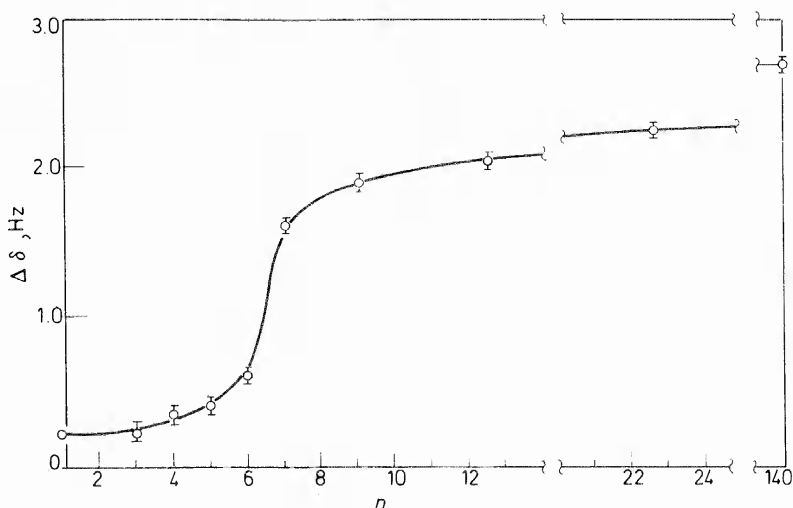


*Figure 3.* Plots of the difference of chemical shifts (with bulk magnetic susceptibility correction) of PEO (1 per cent) in methanol with and without potassium iodide (0.05 M) as a function of the chain length (*n*) at 35°C.

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Additional evidence of ordered conformations of PEG is provided by chemical-shift studies of the PEG oligomers in methanol[10]. The difference in PEG chemical shifts in methanol with and without added potassium iodide is plotted as a function of chain length in *Figure 3*. It is evident that ion–dipole interactions with the lower PEG oligomers ($n \leqslant 6$) are substantially weaker than interactions with oligomers of greater chain length[11]. The distinct transition in these chemical-shift data with chain length is consistent with a new PEG conformation in chains containing seven or more units.

We have further carried out conformational studies of PEG by p.m.r. and i.r. measurements[12]. The p.m.r. results indicate that the average segmental environment of PEG is very sensitive to water concentration up to about 50 vol % and then remains almost constant for any further addition of water. Three molecules of water are required for the hydration of each ethylene oxide unit in a PEG chain. The temperature dependence of the hydrate formation in aqueous PEG solutions is small. Without specific interaction between the polymer and the solvent, the segmental environment changes linearly with the solvent content in chloroform or benzene over the entire composition range. In concentrated chloroform or benzene solution, PEG shows strong molecular association through intermolecular hydrogen bonds. The i.r. results contribute further information about the nature of the solvent effects on the conformational structures of PEG. Significant differences were observed in the i.r. spectrum of PEG in an aqueous medium as compared with that in benzene. The conformation of PEG is believed to be in a more ordered form in an aqueous medium than in either benzene solution or in the melt, and favours the TGT conformation for the COCCOC sequence. This specific conformation change of PEG in an aqueous medium was also reflected by a number of our proton magnetic relaxation measurements[13, 14].

## ORGANIZED STRUCTURE INDUCED BY POLYMER–POLYMER INTERACTIONS

The association of stereo-regulated poly(methyl methacrylate) (PMMA) isomers is an interesting subject since the interaction is a consequence of the steric complementarity of the two interacting species, utilizing a principle similar to that which accounts for such striking specific interactions as those of an enzyme with its substrate or an antigen with its antibody[15]. Studies of this association phenomenon have been carried out by a number of investigators[16–23]. According to Liquori[19], the stereo-association between the tactic PMMAs is promoted in polar solvents through the affinity of the side methyl groups attached to the polymer backbones. Our studies on detailed molecular interactions indicate that the interaction between a nonpolar solvent benzene and the backbone of the PMMA is very weak because of steric hindrance of the polymer chain[24]. The association may therefore be expected to persist even in certain nonpolar media. Here, we report the results of our studies on these polymer–polymer interactions.

When relatively dilute benzene solutions of syndio- and iso- ($M_v = 9.32 \times 10^5$, 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
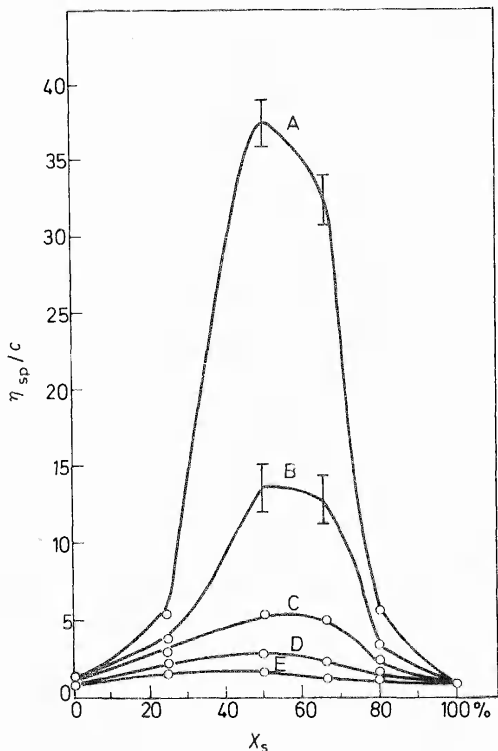
*Figure 4.* Plots of equilibrium reduced viscosity ($\eta_{sp}/c$) as a function of syndiotactic PMMA content ($x_s$) in the syndio- ($M_v = 1.1 \times 10^5$) and iso- ($M_v = 9.3 \times 10^5$) PMMA mixtures in benzene at 24°C. The total polymer concentrations are (A) 0.5 per cent, (B) 0.4 per cent, (C) 0.3 per cent, (D) 0.2 per cent and (E) 0.1 per cent.

presented in *Figure 4*. Since the association rate is slow, the reduced viscosity ($\eta_{sp}/c$) was linear in the composition of the mixed stereoregular PMMA immediately after mixing.

When the polymer concentration was less than 0.4 per cent, the maximum viscosity was found in samples containing a 1:1 syndio:iso ratio (*Figure 4*). More concentrated samples (0.4 and 0.5 per cent of PMMA in benzene) yielded values of reduced viscosity greater than 10 in some cases. The measurements were less accurate, as indicated in *Figure 4*, and it is difficult to identify precisely whether samples of PMMA of 2:1 or 1:1 syndio: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–2 ($M_v = 1.68 \times 10^5$) was used in the polymer mixtures, the maximum viscosity is definitely obtained with solutions with a 2:1 syndio:iso ratio at concentrations greater than 0.5 per cent; the maximum occurs again at 1:1 syndio:iso ratio for more dilute solutions.

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An interesting aspect of the molecular weight dependence is that the 2 : 1 syndio : iso mixture (0.5 per cent 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 ($M_v = 6.88 \times 10^4$, iso-PMMA–3), stereo-association between this iso-PMMA–3 and the syndio counterpart could hardly be detected, even in relatively concentrated samples (0.5 and 1.0 per cent of PMMA). These results clearly indicated that the effect of the stereo-association between the two tactic PMMAs on the viscosity behaviour of the polymer solution depends profoundly on molecular weight.

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 syndio : iso PMMA ratio are shown in *Figure 5*. In sample mixtures containing iso-PMMA–1, the reduced viscosity increased sharply when the PMMA concentration was above 0.3 per cent (curve A, *Figure 5*). When the
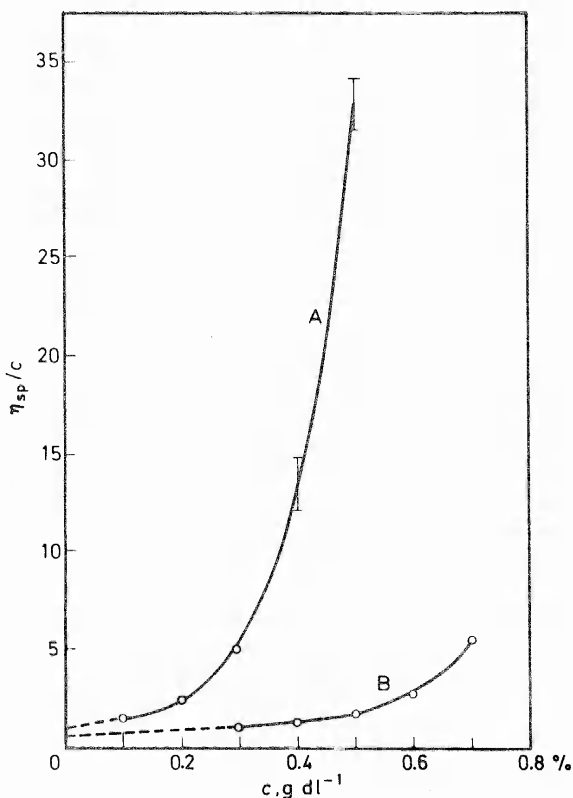


*Figure 5.* Plots of equilibrium reduced viscosity ($\eta_{sp}/c$) as a function of polymer concentration for samples containing a 2 : 1 syndio : iso PMMA ratio in benzene at 24°C; (A) syndio–iso-PMMA–1 system; (B) syndio–iso-PMMA–2 system.

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 per cent (curve B, *Figure 5*). This indicates that the effect of the polymer complexation on solution viscosity is highly dependent on polymer concentration as well as on molecular weight.

Stereochemical association between syndio- and iso-PMMAs was also observed in toluene solution, another nonpolar medium. In relatively more polar solvents, such as chlorobenzene and chloroform, molecular association between these tactic PMMAs was not detected by viscometric measurement. Plots of the reduced viscosity (at a constant polymer concentration of 0.5 per cent) as a function of the composition of these two tactic PMMAs were linear.

In solvents of higher polarity than those mentioned above, i.e. acetone and acetonitrile, phase separation of the iso–syndio-PMMA complex took place. However, viscometric measurements could be obtained in PMMA–acetone series before any sign of phase separation took place. The highest viscosity is found in the sample of a 2:1 syndio: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.

Although the stereocomplex of PMMA precipitated from acetonitrile, the complex remained in solution in a mixture of 20 per cent chloroform and 80 per cent acetonitrile. A maximum viscosity is again found in the sample of a 2:1 syndio:iso PMMA ratio. By contrast, the addition of 20 per cent chloroform to benzene seems to eliminate the formation of the stereocomplex completely. Particularly striking are the results in the benzene–acetonitrile systems. The solvent system, made of 80 per cent acetonitrile and 20 per cent benzene, led, as expected, to complex formation of the two tactic PMMAs. However, it is surprising to note that a solvent system made of 20 per cent acetonitrile and 80 per cent benzene was unexpectedly found to destroy completely the stereocomplex. Further viscometric results indicate that, although both pure solvents support complex formation, no complex exists in mixtures of the two solvents over a certain concentration range of 50 per cent to 80 per cent of benzene.

Studies on the stereo-association of these tactic PMMAs using a high-resolution p.m.r. technique yielded further information on the nature of this PMMA stereocomplex. For simplicity, only two representative sets of high-resolution p.m.r. peaks of the ester-methyl protons of PMMA (5 per cent) in chloroform and in benzene with various syndio : 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 PMMAs in benzene. This type of p.m.r. peak reduction reflects a restriction of local segmental motion when the PMMA complex is formed in benzene. On the other hand, the two tactic PMMAs independently coexist in chloroform; little reduction of the polymeric p.m.r. peak was observed in chloroform solutions. Similar results were also obtained in many other solvent systems. These p.m.r. results are in complete agreement with those obtained from viscometric determinations, regarding the presence or absence of the PMMA complex in various solutions.

It may be beneficial to mention here briefly the significance of employing

high-resolution p.m.r. spectroscopy and viscometric measurements for the detection of association between polymers. Even very slight segmental association may well be detected by viscometric determinations, while this is difficult to reveal by a high-resolution p.m.r. technique. It is known that in systems of lightly crosslinked PMMA networks, the crosslinking strongly affects the viscosity of the swollen gel, but hardly influences the segmental motion[25]. Under the present experimental conditions, the p.m.r. 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 stereo-association between the two tactic polymers.
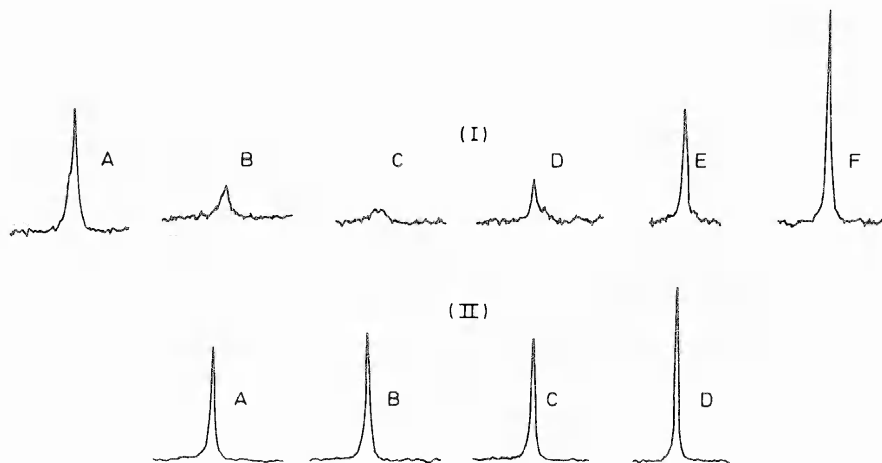


*Figure 6.* Representative high-resolution p.m.r. absorptions of the ester methyl protons of syndio- ($M_v$ 1.1 $\times$ 10$^5$) and iso- ($M_v$ 9.3 $\times$ 10$^5$) PMMAs (5 per cent) in benzene (I) and chloroform (II) at 35°C. The syndio : iso ratios are, respectively, (A) 1 : 0, (B) 4 : 1, (C) 2 : 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.

The fact that, in the present study, all the polymeric peaks almost completely disappear from the p.m.r. spectrum of the sample with a 2 : 1 syndio : iso PMMA ratio in complex-supporting solvents implies that the association between these two tactic PMMAs must be so strong as to restrict highly polymeric motion at the segmental level. There, according to the p.m.r. 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.

It is important to note that viscometric data are by themselves insufficient to characterize the degree of polymer association. According to viscometric determinations, relatively dilute samples (0.5 and 1.0 per cent) of the syndio- and iso-(iso-PMMA–3) PMMAs in benzene gave little sign of stereocomplexation. However, this does not conclusively exclude the possible presence of the stereocomplex. P.M.R. data may be used to supplement the information obtained by viscometry.

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 PMMAs should be expected to increase. This is true as illustrated in the p.m.r. spectra obtained at various high temperatures. The p.m.r. peaks gradually increase as the temperature is raised from 35 to 60°C. A sharp increase of the p.m.r. peak was seen as the temperature increased from 60 to 70°C. Melting of the PMMA complex is clearly demonstrated in these p.m.r. spectra. This agrees with what has been found from viscometric determinations.

We have further carried out x-ray diffraction measurements on samples of individual tactic PMMAs and 2:1 syndio:iso PMMA mixtures prepared under various conditions. The results can be summarized as follows: (i) All the mixed 2:1 syndio:iso PMMA solid samples prepared under various conditions (from acetone, acetonitrile and benzene solutions) give the same type III[26] x-ray diffraction pattern. (ii) A poor diffraction pattern of the PMMA mixture was obtained for the sample prepared by freeze drying the solution immediately after the mixing of the two tactic benzene solutions, while a sharp diffraction pattern was observed for the same sample obtained by freeze drying the mixed solution after a long period of standing time. (iii) The concentrated (50 per cent) 2:1 syndio:iso PMMA mixture in benzene yields the same diffraction pattern as those solid samples.

According to these x-ray results, it seems clear that the stereocomplexation of the two tactic PMMAs in benzene involves a crystallization of segments of PMMA chains, whose structure is identical with that of the solid crystal. It seems also clear that if a period of standing time is not allowed, the crystallization of the PMMA complex in dilute benzene solution is very poor, even when promoted by lowering the temperature to a dry-ice–acetone temperature. Although the growth of the organized structure cannot quantitatively be evaluated from the present x-ray measurements, it is clear that the structural organization of the PMMA complex in benzene is time-dependent. This is consistent with our previous viscosity and n.m.r. results.

## SOLVENT INTERACTIONS IN SYSTEMS OF ORGANIZED AND RANDOM POLYMERS

Synthetic polypeptides are frequently used as models for proteins since they adopt similar conformational structures in solution. Transitions among these conformations have been extensively studied by techniques such as o.r.d. and dielectric relaxation. Recently, p.m.r. has thrown further light on this interesting subject. However, the emphasis has almost always been on the p.m.r. peaks of the polymer[27-33]. Very little attention has been paid to examining the chemical shifts of helix-breaking solvents, such as trifluoro-acetic acid (TFA), in the system, although the important role of this solvent component for controlling the helix–coil transition of PBLG has been well recognized and discussed[32-38]. We therefore suggested studies of this nature[39]. This is particularly useful for polypeptides of high molecular weight and/or high polymer concentration, because no clear high-resolution

p.m r. peaks of PBLG may be observed in the helical (or even partially helical) form under these conditions.

We measured chemical shifts of the solvent peak (TFA) in various poly (γ-benzyl-L-glutamate) (PBLG) solutions. These results were compared with the corresponding values of TFA in the solvent mixtures without the presence of the polypeptide. Obviously, the difference (Δ in Hz) is due to the presence of the polypeptide. A representative plot of Δ versus TFA content in solvent mixtures (TFA–benzene) is shown in *Figure* 7. The corresponding optical activity data are also included in the same figure for comparison. Clearly, Δ changes abruptly in the range when the polypeptide converts from an organized structure to a random coil.
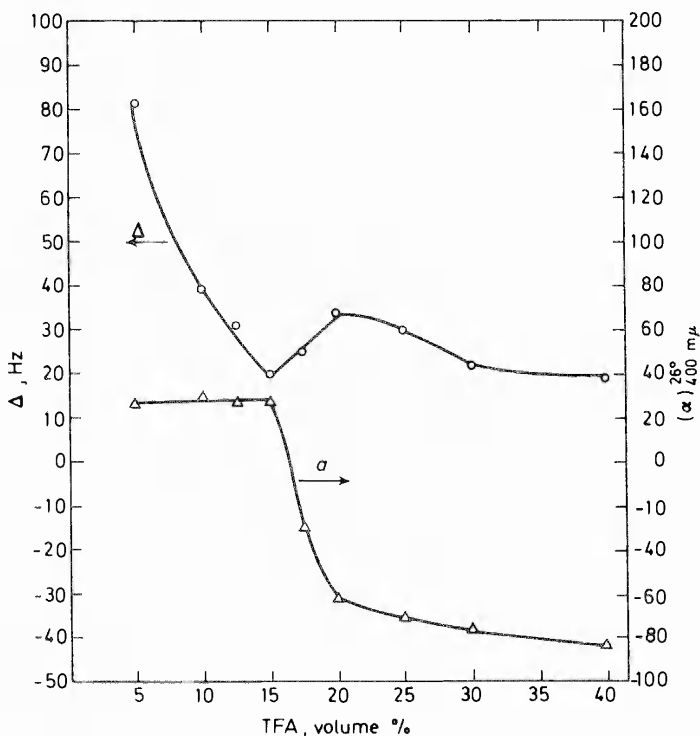


*Figure 7.* Plots of Δ and $[d]_{400\,m\mu}$ versus TFA content in benzene–TFA at 26°C in the presence of 10 per cent PBLG.

It is understandable that Δ decreases as the TFA content increases at constant polymer concentration, because the relative polymeric effect on the chemical shift of TFA decreases. This is true when the polypeptide is either in a helical form or in a random coil structure. Δ varies very differently when helical PBLG starts to transform into a random coil form; it actually increases with increasing TFA content. When the transformation has been completed, it varies normally again; it decreases with increasing TFA content.

This peculiar variation of Δ during a helix → random coil transition may be

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understood in terms of the different solvation behaviours of PBLG in the helical form and in the random coil structure. More TFA molecules are likely to be used for the solvation of PBLG in the random coil form than in the helical structure where intramolecular association prevails. Therefore, when the polypeptide starts to transform from a helix into a random coil, a certain excess amount of TFA is used, thus leading to a larger proportion of solvated TFA than is found at slightly lower TFA concentration. As a consequence, the observed relative chemical shift $\Delta$ increases rather than decreases with TFA, the latter being the normal course in the absence of the helix $\rightarrow$ random coil transition. Of course, when the transformation of PBLG from helix to random coil has been completed, the polypeptide is solvated as a random coil molecule, and further addition of TFA contributes only a normal concentration effect. This is exactly what has been experimentally observed.

Solvent interactions with organized and random macromolecules in systems other than synthetic polypeptides have also shown very interesting results. The spin–lattice relaxation time of the solvent benzene was measured as a function of tactic composition at constant total PMMA concentration. Our preliminary results indicate that the solvent relaxation time is affected more by the organized PMMA complex than the individual PMMA at the same polymer concentration.

## CONCLUSION

In this presentation, we reviewed some of our work which was stimulated by the principles existing in biological macromolecules. It is not my intention to convince all my polymer colleagues to convert to biologists, although the temptation is high. I am only trying to show how we may learn more principles from nature to guide us for the future development of synthetic polymers.

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