Effect of stereoregularity and solvent upon molecular motion and structure of stereoregular poly(methyl methacrylates) in solution. ^{13}C and ^{1}H n.m.r. relaxation study

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Spin-lattice relaxation times T_1 of ^{13}C and ^{1}H nuclei, as well as nuclear Overhauser enhancement (*NOE*) values of stereoregular poly(methyl methacrylates) (PMMA) in CD_3CN and $CDCl_3$ were measured. Analysis of these data has shown that the mobility of PMMA in solution is affected by stereoregularity of PMMA and by solvent. Comparison of ^{13}C and ^{1}H n.m.r. relaxation data has further shown that the solvent affects also the local conformational structure of stereoregular PMMA in solution; this conclusion is supported by preliminary measurements of infra-red spectra. Based on this finding, the effect of solvent upon formation of the ordered structure of the so-called stereocomplex of PMMA is discussed.

INTRODUCTION

Recently there appeared short communications concerned with measurements of spin–lattice relaxation times T_1 of ^{1}H (ref 1) and ^{13}C (refs 2 and 3) nuclei of stereoregular poly(methyl methacrylates) (PMMA) in solution. The results of these measurements indicated a number of common features of ^{13}C and ^{1}H n.m.r. relaxation: both ^{13}C and ^{1}H T_1 differ for isotactic (i) and syndiotactic (s) (PMMA); their values indicate higher flexibility of the i-PMMA chain, as well as some rotational freedom of side chain CH_3 groups, especially of OCH_3 type. The cited papers[1–3] did not include a detailed analysis of mobility and structure of i- and s-PMMA molecules in solutions.

In this paper the results are given of ^{1}H and ^{13}C T_1 measurements, as well as of nuclear Overhauser enhancement (*NOE*) values for solutions of several PMMA samples of different stereoregularity. An attempt is made of a more detailed correlation of these data with the structure and mobility of PMMA molecules. In the discussion of the results, use was made of the fact that values of ^{13}C T_1 relaxation times of polymers in solution are practically given only by dipolar interactions of ^{13}C nuclei with directly bonded protons[4–6] and are therefore not influenced by intergroup interactions. The ^{13}C T_1 values can thus yield reliable information on the mobility of various types of ^{13}C nuclei in the polymer in a relatively straightforward manner. As the ^{1}H T_1 relaxation times in polymers are determined by mutual dipolar interactions of protons, they are much more sensitive to intergroup interactions[7]. Besides the effect of stereoregularity of PMMA, also the effect of solvent upon ^{13}C and ^{1}H n.m.r. relaxation was investigated. CD_3CN and $CDCl_3$ were selected as solvents, because it is known that CD_3CN favours formation of the ordered structure of the so-called stereocomplex of PMMA[8–12], whereas in $CDCl_3$ the stereocomplex is not formed[9–11,13,14]. The reason for this solvent effect upon stereocomplex formation has not been clarified so far.

EXPERIMENTAL

^{13}C T_1 relaxation times were measured at 15 MHz by the 'inversion recovery' technique, using the pulse sequence $180–\tau–90$ with proton noise decoupling. The duration of the 90° pulse was 19 μsec, repetition time was at least five times longer than measured T_1[15]. The number of accumulations and the remaining parameters were chosen so as to fulfill the conditions of accurate ^{13}C T_1 measurement[15]. *NOE* values were measured by the gated decoupling technique by comparison of integrated ^{13}C n.m.r. band intensities measured with noise and gated decoupling. Repetition time was at least eight times longer than the longest ^{13}C T_1. ^{1}H T_1 values were measured at 60 MHz also by the application of the pulse sequence $180–\tau–90$. Duration of the 90° pulse was 40 μsec, repetition time, 3 sec, number of accumulations, 5. All data were measured on the FX-6-JEOL spectrometer. Infra-red spectra were measured on the Perkin–Elmer 621 spectrometer.

PMMA samples: i-PMMA was prepared by anionic polymerization in toluene with $LiAlH_4$ at −78°C; s-PMMA-1 was prepared by anionic polymerization in toluene at −78°C with triethylaluminium and titanium (IV) chloride. s-PMMA-2 was prepared by radical polymerization in dioxane at 30°C, initiated by dibenzoyl peroxide in the presence of [$RhCl(C_8H_{12})$ (4-methylpyridine)]. The stereoregularity of the measured samples was determined by analysis of ^{1}H n.m.r. spectra of solutions of PMMA in an equimolar mixture of tetrachloroethylene and *o*-dichlorobenzene measured at 160°C. The number-average molecular weights

$\bar{M}_n$ were determined osmometrically. The results are shown in *Table 1*.

Solutions of stereoregular PMMA samples in CD_3CN (99% deuterium) and in $CDCl_3$ (99% deuterium) were prepared directly in measuring cells using 100 or 170 mg of polymer per ml of solvent (i.e. 10% and 17% w/v solutions, respectively). The samples were not degassed, because the relaxation times of the polymer are relatively short, so that the effect of oxygen is negligible[15]. Homogeneous solutions were prepared by temperation of the sealed cells in a bath at 60°C for several days under constant stirring.

RESULTS

In *Tables 2–4* are given the values of ^{13}C T_1 relaxation times, *NOE* values, and ^1H T_1 relaxation times of stereoregular PMMA samples in CD_3CN and $CDCl_3$ at 10% w/v concentration and 27°C. The values of these parameters found for 17% w/v solutions at the same temperature were equal within the experimental error of ±10%.

From *Tables 2–4* the effect of stereoregularity of PMMA upon the values of the relaxation times ^{13}C T_1, ^1H T_1 and *NOE* is seen. From *Table 2* it is evident that the relaxation times ^{13}C T_1 of all carbons are longer for i-PMMA compared to s-PMMA, in agreement with the results of other authors[2,3]. Also the *NOE* values for solutions in CD_3CN are higher for i-PMMA, reaching the theoretical maximum *NOE* = 3. For solutions of s-PMMA in CD_3CN the *NOE* values are considerably reduced (*Table 3*). The reduction of *NOE* values indicates that in these cases the extreme narrowing condition is not fulfilled[4]. At the same time even in solutions of s-PMMA in CD_3CN the *NOE* values are roughly equal for various types of carbon atoms, similarly for solutions of i-polystyrene (PS) in *o*-dichlorobenzene[4,5]. The values of the relaxation times ^1H T_1 of CH_2 and α-CH_3 groups in a given solvent are also higher for i-PMMA than for s-PMMA; ^1H T_1 values of OCH_3 protons are comparable within experimental error for all studied solutions (*Table 4*). From *Tables 2–4* it is evident that the relaxation times ^{13}C T_1, the *NOE* values of various carbons, and the ^1H T_1 relaxation times of various proton groups are equal within experimental error for s-PMMA-1 and s-PMMA-2, i.e. syndiotactic polymer samples differing only in the distribution of syndiotactic sequences[10,11] (see Discussion).

From the results in *Table 2* also, the effect of solvent upon the relaxation times ^{13}C T_1 of s-PMMA is evident; in $CDCl_3$ the ^{13}C T_1 values of s-PMMA-2 are longer than in CD_3CN. Also the *NOE* values are higher in $CDCl_3$, almost reaching the theoretical maximum (*Table 3*). For i-PMMA-1 both the ^{13}C T_1 values, and the *NOE* values are comparable in both studied solvents. The effect of solvent upon the relaxation times ^1H T_1 of CH_2 and α-CH_3 protons is very pronounced, both in i-PMMA and in s-PMMA, as seen from *Table 4*. At the same time the effect of solvent upon the ^{13}C T_1 (and *NOE*), values, and the ^1H T_1 values of various

Table 1 Number-average molecular weights $\bar{M}_n$ and stereoregularity of poly(methyl methacrylate) samples; I, H, S: iso-, hetero- and syndiotactic triads, respectively

Polymer	$\bar{M}_n$	Content of triads (%)		
		I	H	S
i-PMMA-1	27000	97	3	0
s-PMMA-1	86000	2.5	12	85.5
s-PMMA-2	45000	3	31	66

Table 3 Nuclear Overhauser enhancement (*NOE*) of stereoregular PMMA samples in solution (10% w/v) at 27°C and 15 MHz. Error ±10%

Solvent	Polymer	*NOE*				
		C=O	CH_2	OCH_3	–C–	α-CH_3
CD_3CN	i-PMMA-1	2.9	3.0	2.8	3.0	3.0
CD_3CN	s-PMMA-1	2.15	2.15	1.9	2.0	2.4
CD_3CN	s-PMMA-2	2.2	2.2	2.0	2.0	2.3
$CDCl_3$	i-PMMA-1	[a]	2.9	3.0	2.95	2.7
$CDCl_3$	s-PMMA-1	[a]	2.9	2.9	[a]	2.85

[a] Not measured

Table 4 Spin–lattice relaxation times ^1H T_1 of stereoregular PMMA samples in solution (10% w/v) at 27°C and 60 MHz. Error ±10%

Solvent	Polymer	^1H T_1 (msec)		
		OCH_3	CH_2	α-CH_3
CD_3CN	i-PMMA-1	180	100	60
CD_3CN	s-PMMA-1	175	62	40
CD_3CN	s-PMMA-2	190	62	40
$CDCl_3$	i-PMMA-1	200	58	70
$CDCl_3$	s-PMMA-2	170	26	29

Table 2 Spin–lattice relaxation times ^{13}C T_1 of stereoregular PMMA samples in solution (10% w/v) at 27°C and 15 MHz. Error ±10%. I, H, S: iso-, hetero- and syndiotactic triads, respectively

Solvent	Polymer	^{13}C T_1 (msec)										
		C=O			CH_2	OCH_3	–C–			α-CH_3		
		I	H	S			I	H	S	I	H	S
CD_3CN	i-PMMA-1	1800	–	–	60	450	950	–	–	90	–	–
CD_3CN	s-PMMA-1	–	–	830	20	260	–	–	320	–	–	30
CD_3CN	s-PMMA-2	–	840	870	20	230	–	230	270	–	25	25
$CDCl_3$	i-PMMA-1	[a] –	–	–	60	470	[a] –	–	–	100	–	–
$CDCl_3$	s-PMMA-2	–	1020	1180	40	260	–	350	470	–	65	40

[a] Not measured

proton groups (OCH_3, CH_2, α-CH_3) is not parallel. Whereas in carbon spectra in both solvents, $^{13}C\ T_{1\alpha\text{-}CH_3} > {}^{13}C\ T_{1CH_2}$; in proton spectra $^{1}H\ T_{1\alpha\text{-}CH_3} > {}^{1}H\ T_{1CH_2}$ only in $CDCl_3$; in CD_3CN $^{1}H\ T_{1CH_2} > {}^{1}H\ T_{1\alpha\text{-}CH_3}$ both for i-PMMA and s-PMMA (*Table 4*).

DISCUSSION

In the monomer unit of PMMA, various carbon types exhibit various kinds of motion; CH_2 group carbons and the quarternary carbons are sensitive only to the segmental motion of the backbone chain, for α-CH_3, >C=O and OCH_3 group carbons, also the internal rotation of the respective groups has to be considered. In analysis of the segmental motion of the backbone chain in polymers, the isotropic motional model is often applied, with the effective correlation time τ_{eff}[2–7]. Prior to the analysis of the presented experimental data, some comments concerning the application of this model in solutions of stereoregular PMMA have to be made. As pointed out by Schaefer[4] in some cases the application of the 'effective isotropic model' leads to different τ_{eff} values as obtained from $^{13}C\ T_1$ and *NOE* data; in such cases a distribution of correlation times has to be considered. Heatley and Begum[16] have found from analysis of the temperature dependence of $^{13}C\ T_1$ and *NOE* of CH_2 and α-CH_3 carbons that for a solution of s-PMMA in *o*-dichlorobenzene the model of one correlation time of segmental motion is inadequate and that a distribution of correlation times has to be postulated. In a discussion of the origin of this distribution, Heatley and Begum have demonstrated that it is of intramolecular origin, because the width of the distribution is concentration independent. In this connection, a comparison with our own results may be interesting; we have found that in an *o*-dichlorobenzene solution of s-PMMA (of stereoregularity comparable to s-PMMA-1) at 27°C, 70–85% of monomer units are present in the form of stable associated structures[17]. The amount and character of aggregates is independent of concentration in the range 0.2–10% w/v, indicating their intramolecular origin[18,19]. Therefore it should be considered if the distribution of correlation times in the paper of Heatley and Begum is not directly connected with the formation of the associated structures; Heatley and Begum themselves admit that the distribution of correlation times may have its origin in small scale inhomogeneity of the polymer solution. However, in solutions of s-PMMA-1 and s-PMMA-2 in CD_3CN or $CDCl_3$, studied in the present paper, association of the polymer has not been detected[17]. In solutions of i-PMMA-1 in $CDCl_3$ or CD_3CN the content of associated structures is relatively low (about 5 and 20% monomer units, respectively)[10,17,20]. As in the systems presently studied, $^{13}C\ T_1$ and *NOE* data can be described by a single effective correlation time τ_{eff} (see below), we assume that in analysis of these systems a distribution of correlation times need not be considered.

For ^{13}C-^{1}H dipolar interactions, theoretical relations between $^{13}C\ T_1$ relaxation times, *NOE* values and correlation time τ_{eff} as well as their graphical representation are given in the paper by Doddrell *et al.*[21]. As for CH_2-group carbon atoms, $^{13}C\ T_{1CH_2}^{-1} = 2\,{}^{13}C\ T_{1CH}^{-1}$, τ_{eff} values of the segmental motion of PMMA in various solutions may be obtained directly from the results in ref 21. From $^{13}C\ T_{1CH_2}$ values of solutions of s-PMMA-1 or s-PMMA-2 in CD_3CN at 27°C, $\tau_{eff} = 2 \times 10^{-9}$ sec is obtained. The value obtained from *NOE* data is practically equal ($\tau_{eff} = 2.5 \times 10^{-9}$ sec). For i-PMMA-1 in CD_3CN, $^{13}C\ T_{1CH_2}$ values yield $\tau_{eff} = 2 \times 10^{-10}$ sec. In this case the extreme narrowing limit ($\omega_0\ ^{13}C + \omega_0\ ^{1}H)\tau_{eff} \ll 1$ is reached, so that the *NOE* values attain their theoretical maximum value. These results indicate that there exists an order of magnitude difference between the effective correlation times of segmental motion of i-PMMA and s-PMMA solutions in CD_3CN, the i-PMMA chain being more flexible. This fact is also confirmed by the much longer $^{13}C\ T_1$ values of quarternary carbons of i-PMMA as compared to s-PMMA.

In $CDCl_3$, the τ_{eff} value for i-PMMA is the same as in CD_3CN ($\tau_{eff} = 2 \times 10^{-10}$ sec). Contrary to this, for the solution of s-PMMA-2 in $CDCl_3$, $^{13}C\ T_{1CH_2}$ and *NOE* data indicate a $\tau_{eff} = 6 \times 10^{-10}$ sec. For s-PMMA-2 in $CDCl_3$ the velocity of segmental motion is thus about 3 times greater than in CD_3CN, whereas for i-PMMA this velocity is not affected by different solvents. This indicates that the mobility of polymer segments depends on the polymer–solvent interaction, and this interaction is stereospecific. With segmental mobility as solvent quality characteristics, $CDCl_3$ appears a better solvent for s-PMMA-2 than CD_3CN.

From a comparison of $^{13}C\ T_1$ relaxation times of carbons with directly bound protons (OCH_3,CH_2, α-CH_3) in *Table 2*, a considerable rotational freedom of ester CH_3 groups is evident, in agreement with the results of measurements of the temperature dependence of proton T_1 relaxation times for solid PMMA[22]. Some rotational freedom is also exhibited by α-CH_3 groups. If the correlation time of internal rotation τ_c of α-CH_3 groups is defined according to the original paper of Woessner[23] (motion of the CH_3 group is described by random jumps between three equilibrium positions at an average rate $3\tau_c^{-1}$), then (in extreme narrowing limit conditions) internal rotation of α-CH_3 groups can be analysed by means of the relation[7]:

$$x = \frac{1 - B}{B - 0.11} \tag{1}$$

where

$$x = \tau_{eff}/\tau_c \text{ and } B = \frac{2}{3}\frac{^{13}C\ T_{1CH_2}}{^{13}C\ T_{1\alpha\text{-}CH_3}}$$

By means of equation (1) for i-PMMA in CD_3CN and $CDCl_3$ $\tau_c = 10^{-10}$ sec is obtained, whereas for s-PMMA-2 in $CDCl_3$ $\tau_c = 10^{-9}$ sec is obtained. It is thus evident that in a given solvent ($CDCl_3$) the correlation time τ_c for i-PMMA is shorter by an order of magnitude compared to s-PMMA, and that in s-PMMA internal rotation of α-CH_3 groups is strongly hindered. This result agrees very well with the results of neutron scattering, from which much higher barriers of internal rotation are obtained for α-CH_3 groups of s-PMMA (34 kJ/mol) as compared to i-PMMA (16.7 kJ/mol)[24].

In analysis of $^{1}H\ T_1$ relaxation times, in addition to intragroup dipolar interactions, other contributions have also to be considered. $T_{1\,total}^{-1}$ for protons of a given type can generally be expressed by the relation[7]:

$$T_{1\,total}^{-1} = T_{1\,intragroup}^{-1} + T_{1\,near\ intergroup}^{-1} + T_{1\,far\ intergroup}^{-1} + T_{1\,intermol}^{-1} \tag{2}$$

The first three terms represent the contributions from intramolecular interactions. The first term refers to interactions within the given group; the second term, to interactions with

protons from other groups (e.g. α-CH_3–CH_2; CH_2–CH_2; α-CH_3–α-CH_3) in the same and in nearby monomer units (1st and 2nd neighbours) of the chain; and the third term, to intergroup interactions with monomer units farther removed in the chain. The last term represents contributions from intermolecular interactions. As it was found that in the studied systems associated structures are not present, and as in all measured PMMA solutions the ^1H T_1 values are equal for 10 and 17% w/v concentrations, the system may be considered as sufficiently dilute so that the last two terms of equation (2) can be neglected, giving:

$$T_{1\,\text{total}}^{-1} = T_{1\,\text{intragroup}}^{-1} + T_{1\,\text{near intergroup}}^{-1} \tag{3}$$

For CH_2 group protons, $T_{1\,\text{intragroup}}^{-1}$ can be expressed by means of the familiar relation[7,23,25]:

$$T_1^{-1} = \frac{9\gamma^4\hbar^2}{8}\left[J_1(\omega_0) + J_2(2\omega_0)\right] \tag{4}$$

where $J_i(\omega)$, $i = 1,2$ are the so-called spectral intensities at frequency ω, ω_0 is the proton resonance frequency and the remaining constants have their usual meaning. For an isotropic motion of a pair of protons with a correlation time τ_{eff} the $J_i(\omega)$ are of the form[7,25]:

$$J_i(\omega) = K_i \frac{2\tau_{\text{eff}}}{1 + (\omega\tau_{\text{eff}})^2} \tag{5}$$

where $K_0 = 4/(5r^6)$, $K_1 = 2/(15r^6)$, $K_2 = 8/(15r^6)$, and r is the interproton distance (for CH_2 and CH_3 groups $r = 0.1796$ nm). When $\omega_0\tau_{\text{eff}} \ll 1$, then from equations (4) and (5) it follows:

$$T_1^{-1} = \frac{3}{2}\frac{\gamma^4\hbar^2}{r^6}\tau_{\text{eff}} \tag{6}$$

In systems with more than two interacting protons, the relaxation rate T_1^{-1} of a given proton is in good approximation[7,25] given as a sum of pair interactions of this proton with all the others. For CH_3 groups, where in addition to skeletal motions also internal rotation of the group itself has to be considered, the expression for $J_i(\omega)$ is modified; explicit relations are given in refs 7 and 23.

Exact analysis of the second member in equation (3), involving in general intergroup interactions of several proton pairs with time dependent interproton distance, is very difficult. In an analysis of the special case of interaction of CH_3 groups Woessner[26] came to the conclusion that in all cases of such multispin interactions, the contribution to the relaxation rate T_1^{-1} due to intergroup interactions of proton pairs can be described by a number of terms $C_i\tau_i$ where the sum of the C_i is equal to double the mean inverse sixth power of the internuclear distance $\langle r^{-6}\rangle$. One of the τ_i is equal to τ_{eff}, the correlation time of the overall molecular motion, all the remaining τ_i's are shorter. This procedure makes possible a discussion of the effect of the geometry of macromolecules upon the ^1H T_1 relaxation times[7].

Let us first compare the results for s-PMMA-1 and s-PMMA-2 in CD_3CN. Both these polymers contain very few isotactic triads and differ only in the distribution of syndiotactic sequences. Assuming 1st order Markov statistics, s-PMMA-1 contains about 80% of monomer units in syndiotactic sequences longer than 15 monomer units, in s-PMMA-2 80% of monomer units are in sequences shorter than 15 units[10,11]. The mean syndiotactic sequence length[27] is $\bar{l}_s$ = 16 for s-PMMA-1 and $\bar{l}_s = 6$ for s-PMMA-2. Equal ^{13}C T_1 values of corresponding carbon atoms in both these polymers imply that also the correlation times of segmental motion, as well as the correlation times of internal rotation of α-CH_3, ester CH_3 and total ester groups are equal in both polymers. As even ^1H $T_{1\text{total}}$ are equal for s-PMMA-1 and s-PMMA-2 (*Table 4*), it may be assumed on the basis of equation (3) that also $T_{1\,\text{near intergroup}}^{-1}$ does not differ for these two polymers. This indicates that the geometry of short range order as well as the conformational structure of syndiotactic sequences of s-PMMA-1 and s-PMMA-2 in solution is equal.

From *Tables 2* and *4* it is evident that whereas the values of ^{13}C T_1 of OCH_3 carbons are considerably longer for i-PMMA than for s-PMMA, the values of ^1H T_1 of OCH_3 groups are equal. Based on equation (3) and the above analysis this indicates that in i-PMMA intergroup interactions of OCH_3 protons are larger than in s-PMMA. This is probably a consequence of the regular helix structure of i-PMMA.

It is interesting to compare the effect of solvent upon the ^1H T_1 relaxation times. It follows from *Table 4* that the relaxation rate T_1^{-1} of CH_2 protons (and for s-PMMA also of α-CH_3 protons) is much larger in $CDCl_3$ than in CD_3CN. At the same time the correlation times τ_{eff} and τ_c for i-PMMA are comparable in both solvents; for s-PMMA τ_{eff} and τ_c are even shorter in $CDCl_3$ than in CD_3CN (see *Table 2*). It is therefore evident that in $CDCl_3$, as compared to CD_3CN, considerable short range intergroup interactions must be operative contributing to the T_1^{-1} of CH_2 protons, and for s-PMMA also to T_1^{-1} of α-CH_3 protons. For CH_2 groups the values of $T_{1\,\text{intra}}^{-1}$ calculated by means of equations (4)–(6) (using τ_{eff} values from ^{13}C T_1), and $T_{1\,\text{near intergroup}}^{-1}$ calculated from equation (3), are shown in *Table 5*. From this Table it follows that especially for s-PMMA in $CDCl_3$ the intergroup contribution to the overall relaxation rate $T_{1\,\text{total}}^{-1}$ of CH_2 protons is considerable, whereas for the same polymer in CD_3CN it is practically zero. It follows from the above analysis that this difference must be due to different local geometry of the PMMA macromolecules in the two solvents. This implies that the conformational structure of a sequence of monomer units in i-PMMA and especially in s-PMMA is different in $CDCl_3$ and in CD_3CN.

Table 5 Comparison of intragroup and intergroup contribution to the relaxation rate ^1H T_1^{-1} of CH_2 protons for stereoregular PMMA samples in solution (10% w/v) at 27°C and 60 MHz

Polymer	Solvent	T_1^{-1}meas[a] (sec^{-1})	T_1^{-1}theor[b] intra (sec^{-1})	T_1^{-1} near intergroup[c] (sec^{-1})
i-PMMA-1	CD_3CN	10	4.9	5.1
i-PMMA-1	$CDCl_3$	17.2	4.9	12.3
s-PMMA-2	CD_3CN	16.1	16.9	~0
s-PMMA-2	$CDCl_3$	38.5	17.4	21.1

[a] T_1^{-1}meas – experimental T_1^{-1}
[b] T_1^{-1}theor intra – value calculated by means of equation (6) (for i-PMMA-1) or equations (4) and (5) (for s-PMMA-2) using τ_{eff} from ^{13}C T_1 measurement (see text)
[c] T_1^{-1}near intergroup = T_1^{-1}meas – T_1^{-1}theor intra (see equation 3)

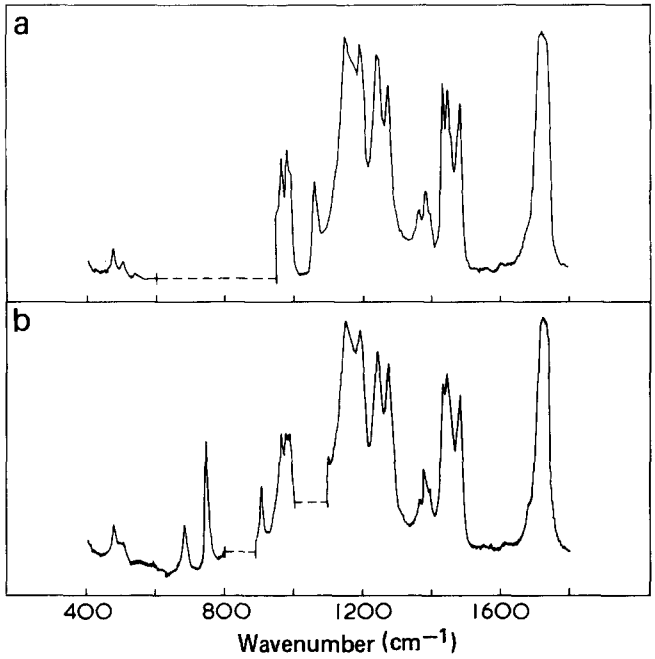

Figure 1 Infra-red spectra of s-PMMA-1 in $CDCl_3$ (a) and CD_3CN (b) at 25°C

Differences of conformational structure of a polymer are usually exhibited in its vibrational spectrum. Therefore, we measured infra-red spectra of solutions of s-PMMA-1 in $CDCl_3$ and in CD_3CN at a concentration of 17% w/v (*Figure 1*). From *Figure 1* it is seen that these spectra differ e.g. in the range of the CH_3 bending vibrations (1430–1450 cm^{-1}), and in the range of CH_3 rocking vibrations around 980 cm^{-1}. The observed differences can be explained so that the conformational equilibrium of s-PMMA in solution is affected by solvent, in agreement with the analysis of n.m.r. relaxation data. It is interesting to note that the infra-red spectrum of s-PMMA-1 in $CDCl_3$ is practically identical to the spectrum of solid PMMA measured at normal and elevated temperature[28]; the infra-red spectrum of s-PMMA-1 in CD_3CN resembles the spectrum of solid PMMA measured at −130°C and the room temperature spectrum of the stereocomplex of PMMA[28].

The results of this paper can be applied in discussing the formation of the ordered structure of stereocomplex PMMA, which takes place easily upon mixing solutions of i-PMMA and s-PMMA in CD_3CN[8–12], but which is not formed in $CDCl_3$[9–11,13,14]. There exists convincing evidence that stereocomplex formation takes place as a consequence of intermolecular interactions of sterically complementary isotactic and syndiotactic sequences[10,11]. The finding that the conformational structure of i-PMMA, and especially of s-PMMA is solvent-dependent and that it differs in CD_3CN and $CDCl_3$ indicates that in CD_3CN conformational forms of stereoregular PMMA suitable for stereocomplex formation are favoured. It might be interesting to speculate about an analogous interpretation of medium effects upon similar interactions observed in a number of biological systems[8–10,29].

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