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Conformation of stereoregular PMMA in solutions during the temperature induced conformational transition

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Abstract

The temperature induced conformational transition of stereoregular PMMA in diluted or semi-diluted solution was studied by viscometry, NMR and FT-IR. The conformational energies of polymer chains were calculated from infrared spectral subtraction by following the method described by O'Reilly and Mosher [O'Reilly JM, Mosher RA. Macromolecules, 14 (1981) 602; O'Reilly JM, Teegarden DM, Mosher RA. Macromolecules, 14 (1981) 1693]. The fraction of sequences containing *gauche* conformation that can be deduced shows a large increase during the conformational transition. This increase in the probability of *gauche* conformations accounts for an increase in the chain flexibility deduced from the decrease of the calculated characteristic ratio. The increment in the hydrodynamic volume of the chain in chloroform that occurs at the transition temperature can be correlated with an increase in the density of the polymer–solvent specific interactions. The range of temperatures of the conformational transition, namely, 20–40°C, was found to be independent of the quality of the solvent (theta or athermic solvent). However, the cooperativity of the conformational changes σ is shown to depend on the solvent for the *i*-PMMA. Further, the aggregating character of the solvent (*o*-dichlorobenzene) shifts the observed transition for the *i*-PMMA solution towards higher temperatures which is ascribed to the disassociation of the aggregated structures.

Keywords: Poly(methyl methacrylate) (PMMA); Conformational transition; Polymer–solvent interactions

1. Introduction

Much interest has been devoted in the past to the temperature induced conformational transition phenomenon that arise on polymer chains in diluted solution [1–4]. It has been pointed out that many polymers such as poly(methyl methacrylate) (PMMA), poly(vinyl pyridine) or polystyrene exhibit this particular behaviour in several solvents. Conformational transition also takes place in solvent mixtures when gradually changing the quality of the solvent [5–7]. Although the real driving force that promotes these conformational transition is still unclear, several assumptions have been made to explain the observed discontinuity in the polymer chain characteristics. According to most of the workers [1–7], such transitions are ascribed to the competition between intra- and intermolecular interactions which leads to an increase in the probability of *gauche* conformation. The Stockmayer–Fixman relation has often been used from viscometric studies to decompose the effects of the recorded transition, on the one hand, on the unperturbed dimensions (K_θ) which depend on the short range and steric interactions and on the other hand, on the solvent quality (B) which depends on the polymer–solvent interactions. Thus, the overall chain undergoes changes within the transition range, namely, a decrease of its unperturbed dimensions, an increase of its flexibility [2]. The assumption of a transition from a more ordered to a less ordered conformation of the chain has also been envisaged [4].

Otherwise, conformational energies have been calculated for bulk PMMA stereoisomers by Fourier transform-infrared spectroscopy (FT-IR) [8,9] and these results have been successfully compared with rotational isomeric state (RIS) calculations [10]. Although, the infrared technique has been shown to be relevant for the study of the polymer conformation it has never been applied for quantification of the conformation of the polymer in solution. In our study, the conformational energy of stereoregular PMMA were calculated in different solvents within the range of temperature of the conformational transition. According to the RIS theory, the calculated conformational energies were used to determine the unperturbed dimensions of the polymer chains during the conformational transition.

In addition, some solvents are known to favour the formation of associated structures of PMMA through

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Table 1
Characteristics of the PMMA used in that study. I: represents the polydispersity index

PMMA	Tacticity (%)[a] *i*:*h*:*s*	M_n (10^{-3} g/mol)	I	T_g (°C)
i-PMMA	97:03:0	37	1.21	60.6
s-PMMA	0:20:80	33	1.05	130.8

[a] Tacticity is determined by ^{1}H NMR in $CDCl_3$ at 60°C.

self-aggregation [11–14]. These organised structures result in a conformational order that can be broken by an increase in the temperature [11,12]. In the present article we will compare the conformation of polymer chain as calculated from infrared spectra in solvent with aggregating or non-aggregating character.

2. Experimental

2.1. Materials

The PMMAs used in the present study are listed in Table 1. Stereoregular and atactic samples were purchased from Polymer Source Inc. The tacticity of each sample was determined by ^{1}H NMR spectroscopy in $CDCl_3$ solutions, at 333 K and 200 MHz, using a Varian XL-200 instrument. The same instrument was used to carry out the NMR temperature dependent experiments. Molecular weights were determined by size exclusion chromatography using a Waters chromatograph calibrated with PMMA standards. Mettler DSC-30 apparatus was used for bulk T_g measurements. The solvents used were Spectronorm grades purchased from Aldrich Chemicals.

The intrinsic viscosity was measured using an Ubbelhodde viscosimeter at temperatures ranging from 23 to 45°C. Each temperature was controlled at $T \pm 0.5$°C. The concentrations of the PMMA solutions studied were 0.5, 1, 1.5, 2 and 2.5 g/l. The solutions were filtered before use in order to remove the dust particles. The recorded time for the solution flow in the Ubbelhodde tube were always lower than 200 s.

2.2. Infrared spectroscopy

FT-IR spectroscopy was performed using a Bruker IFS-66 equipped with a mercury–cadmium–telluride (MCT) detector. 100 scans were recorded for good signal to noise ratio. The liquid cell was equipped with a heating device working in the temperature range of −100 to 160°C. Temperature was controlled to $T \pm 1$°C. Curve-fitting and spectral subtraction have been performed using Peaksolve [15] software.

The calculations of the conformational energies are made as described by O'Reilly and Mosher [8]. The raw spectrum, recorded at room temperature for the PMMA solution, will be named *term spectrum* and used in the following relation:

$$\text{Result spectrum} = \text{sample spectrum} - (\text{k} \times \text{term spectrum}) \qquad (1)$$

where *sample spectrum* is a spectrum recorded at a temperature above 25°C and *k* is a constant equal to unity, for our calculations. The *result spectra* are the difference spectra obtained at different temperatures. The peaks obtained from

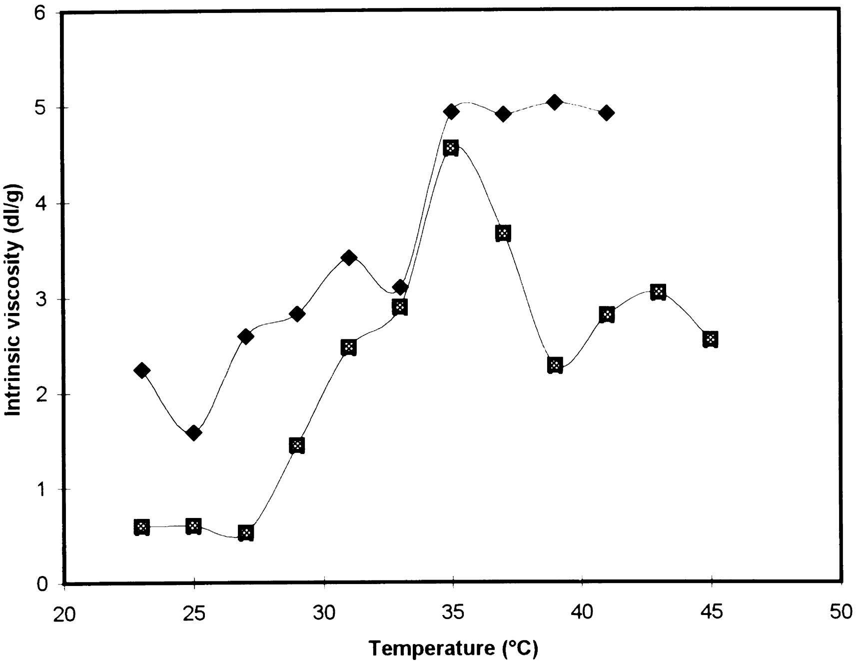


Fig. 1. Intrinsic viscosity [η] of stereoregular PMMA measured in $CHCl_3$ as a function of temperature. ◆ represents the *i*-PMMA solutions and ■ represents the *s*-PMMA solutions.

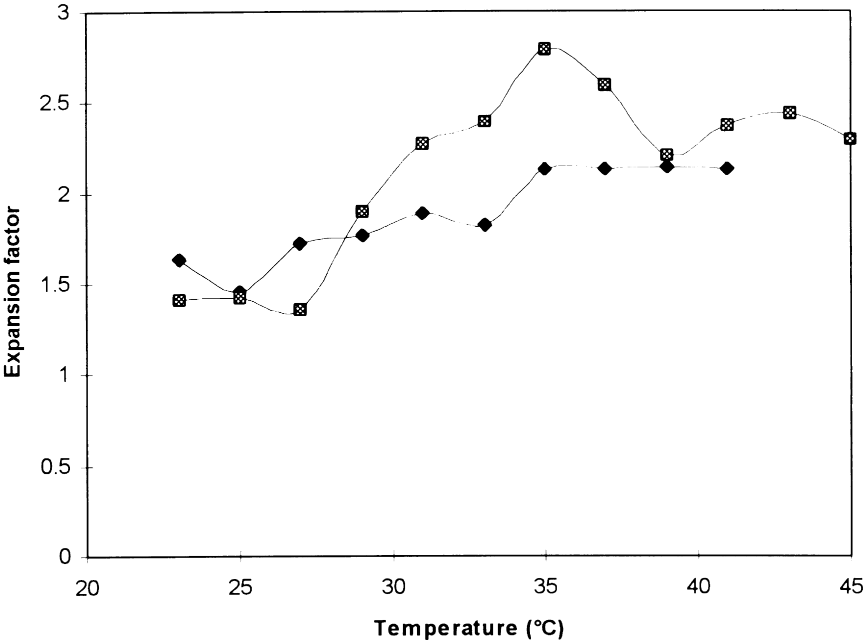


Fig. 2. Expansion factor α_η of stereoregular PMMA calculated from intrinsic viscosity $[\eta]$ measured in $CHCl_3$ as a function of temperature and $[\eta]_\theta$ obtained from acetonitrile at the θ temperature of each isomer. ◆ represents the *i*-PMMA solutions and ■ represents the *s*-PMMA solutions.

that method are both increasing and decreasing bands and their heights will be named $A_+(\nu)$ and A_- (ν), respectively. Thus, the van't Hoff energy ΔE, henceforward named conformational energy, can be calculated from these peaks intensity through the relations:

$$\Delta E = -\mathrm{R}\delta[\ln\{A_+(v)/A_-(v)\}]/\delta(1/T) \qquad (2)$$

where R is the ideal gas constant and T the temperature.

In the present article we will focus on the carbonyl band which becomes after spectral subtraction the 1748/1724 cm^{-1} doublet and also on the 1190/1170 cm^{-1} doublet. These bands are convenient because they were never merged with absorption bands of the solvents used. However, the doublet resulting from the spectral subtraction of the carbonyl peak can be more sensitive to the chemical environment in the case of solvents leading to acid–base bonding ($CHCl_3$) or aggregation (*o*-dichlorobenzene). Therefore, we preferred the 1190/1170 cm^{-1} doublet especially when the *s*-PMMA is studied in these two particular solvents.

Van't Hoff energy derived from this set of bands is assumed to represent the conformational energy of the backbone (model II) or the conformational energy of the backbone minus those of the side-chain (model I) [8]. For the need of the RIS calculations we have considered the calculated conformational energies $\Delta E_\mathrm{T} = E_\mathrm{tg} - E_\mathrm{tt}$ as the conformational energy of the backbone at a given temperature T. The statistical weights u_jk of the stereoregular PMMA were calculated at different temperatures for a jk bond pair in a simple two states scheme:

$$u_\mathrm{jk} = A_\mathrm{jk}\mathrm{e}^{-\Delta E_\mathrm{T}/RT}$$

where A_jk is a prefactor that is omitted for the sake of simplicity and T the temperature. Using Biosym [16] software, the RIS calculations were performed to evaluate the unperturbed dimensions (phantom chain) of the polymer chain within the range of the conformational transition.

3. Results and discussion

3.1. Viscometric measurements

The intrinsic viscosity $[\eta]$ of stereoregular PMMA has been measured from room temperature to 45°C in chloroform as plotted in Fig. 1. It is known that practically there is no self-aggregation of both *i*-PMMA and *s*-PMMA in this solvent [11,13]. The increase of temperature for the two isomers leads to an increase of $[\eta]$. A sharp increase of the intrinsic viscosity can be observed between 30 and 35°C which indicates a change in the hydrodynamic volume of the polymer chain that can be ascribed to a conformational transition [1]. Katime et al. [2] observed generally in solvents such as *o*-dicholorobenzene, acetone, cyclohexane or ethyl acetate, a decrease of the intrinsic viscosity at the temperature of conformational transition. Moreover, Dondos et al. [3] evidenced that PMMA solutions in benzene or acetone can increase their viscosity at the transition temperature when very diluted solutions are used.

Although, according to the PMMA tacticity, the transition occurs approximately in the same range of temperature, the overall behaviour of the PMMA isomers with temperature looks rather different. Indeed, below 35°C the intrinsic viscosity of *i*-PMMA is higher than the corresponding value

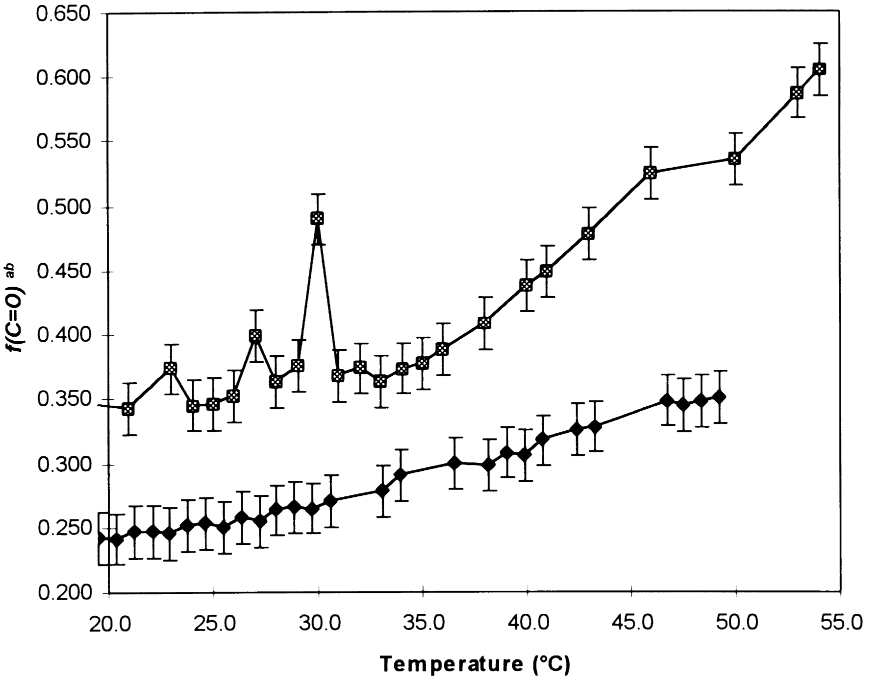


Fig. 3. Fraction of acid–base bonded carbonyls $f^{ab}_{(C=O)}$, calculated from the infrared carbonyl peak as a function of temperature, in CHCl$_3$. ◆ represents the *i*-PMMA solutions and ■ represents the *s*-PMMA solutions.

for *s*-PMMA, as already pointed out by Kamijo et al. [17,18]. During conformational transition, the values of the intrinsic viscosity become identical and above 35°C the intrinsic viscosity of *i*-PMMA seems to stabilise whereas those of *s*-PMMA decreases. These results can be interpreted in terms of expansion of the chain which increases by improving the quality of the solvent with temperature. Knowing the intrinsic viscosity of the polymers in θ conditions $[\eta]_\theta$, the expansion factor α_η can be calculated:

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \qquad (3)$$

$[\eta]_\theta$ was measured in acetonitrile at theta temperature for both the PMMA isomers and the values obtained are 0.25 and 0.51 dl/g for *s*- and *i*-PMMA, respectively. These values are consistent with RIS calculations made by Vacatello et al. [19] but also with experimental results [17] which converge to demonstrate a higher chain stiffness of the *i*-PMMA in theta conditions which leads to higher radius of gyration and consequently to higher intrinsic viscosity for that isomer as compared to the *s*-PMMA. Fig. 2 shows the evolution of the expansion factor with temperature for the two tactic PMMA. It can be noticed that below 30°C and above 38°C the expansion factor of the *i*- and *s*-PMMA are roughly identical namely, ranging from 1.5 to 2. These values higher than unity are consistent with the well known good solvent character of the chloroform on PMMA which tend to increase the excluded volume and expend the chain dimensions. Within the 30–38°C range of temperature, the expansion of *s*-PMMA exceed the expansion of *i*-PMMA by reaching values higher than 2.5. However, above 35°C the expansion factor of *s*-PMMA decreases to reach the values observed for *i*-PMMA at 40°C.

Kamijo et al. [17], have already pointed out differences in the expansion factor according to the PMMA tacticity by carrying out viscometric and light scattering experiments at a temperature of 25°C in good solvents such as acetone or chloroform. At this temperature, the difference in the expansion factor becomes noticeable only for relatively high molecular weights, namely, above 20 000 to 30 000 g/mol. This result supports our conclusion of a rather similar expansion factor of PMMA isomers, with molecular weight in the range of 30 000 g/mol, at a temperature of 25°C. The rate of increase of α_η with molecular weight found by Kamijo, which is higher for *s*-PMMA than for *i*-PMMA, can be compared to the ability of *s*-PMMA to expand faster with temperature than *i*-PMMA.

The differences in the expansion behaviour of stereoregular PMMA in solution can be explained by the balance between the two well known opposite effects, namely, the repulsive interaction between chain segments and the elastic free energy of the chain that occurs during the chain expansion [20]. Indeed, the free energy of the chain (A_{tot}) can be decomposed in, at least, two terms:

$$A_{\text{tot}} = A_{\text{rep}} + A_{\text{el}} \qquad (4)$$

where A_{rep} is the free energy of repulsion which decreases as the expansion of the chain increases, whereas the elastic free energy (A_{el}) decreases as a result of the limited number of available conformation when the chain is expanded. The strong specific interactions that take place between the

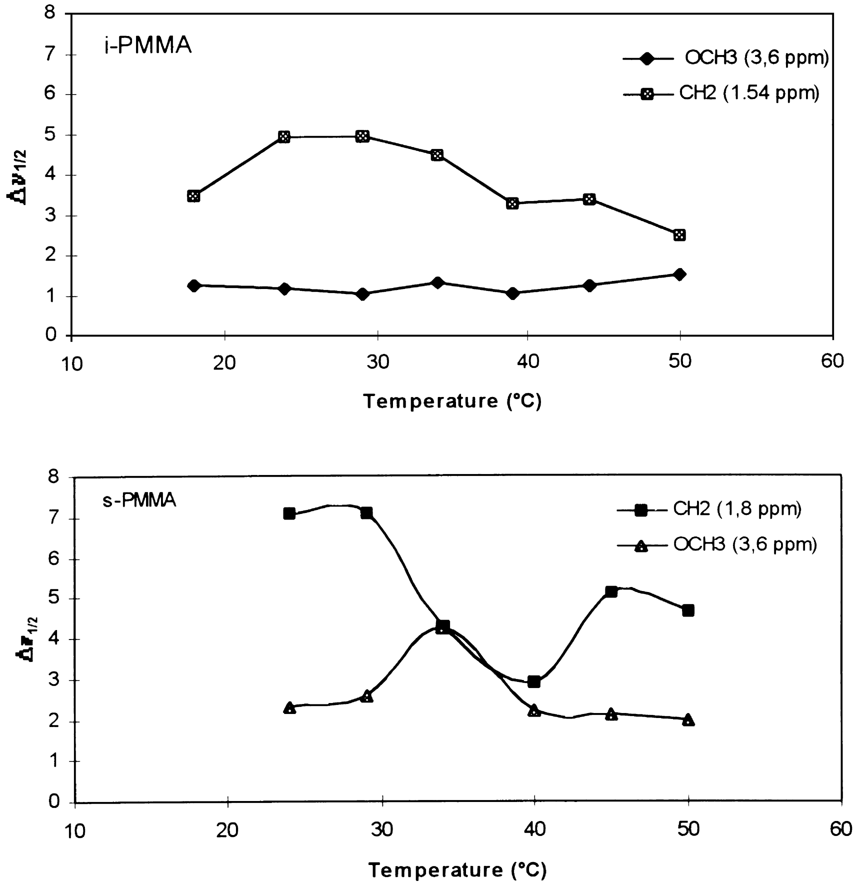


Fig. 4. Width at half height $\Delta\nu_{1/2}$, calculated from ^{1}H NMR spectra in $CDCl_3$, as a function of temperature. ◆ represents the peak of the $-CH_2-$ and ● the $-OCH_3$ groups of *i*-PMMA and ■ represents the peak of the $-CH_2-$ and ▲ the $-OCH_3$ of *s*-PMMA.

studied polymer and the solvent (which will be discussed later) can also add a specific contribution to the decrease of A_{rep} as solvation of chain segments are assumed to hinder repulsion between the beads. Moreover, Kamijo et al. [17] found evidence that the excluded volume interaction between polymer segments is independent of the stereochemical structure of the PMMA chain. We can then assume from the study that A_{rep} does not depend much on tacticity. In the interplay between the two factors mentioned above, both *i*-PMMA and *s*-PMMA are assumed to pay less entropic cost (A_{el}) to expansion, up to 35°C, as compared to the gained repulsive free energy, A_{rep}. However, above 35°C, the two factors seem to balance for *i*-PMMA as α_η remains stable. In contrast, *s*-PMMA in chloroform which expands faster with temperature, than *i*-PMMA up to 35°C, is assumed to see its elastic free energy increased so much with temperature that the syndiotactic chain tend to shrink. Therefore, the isotactic chain in solution can be viewed, up to 35°C, as an elastic coil with a higher modulus than the syndiotactic coil. Above 35°C, a balance between entropic elastic forces and enthalpic forces is likely to be reached by the coil of *i*-PMMA whereas the size of the *s*-PMMA chain is assumed to be at this stage predominantly entropically driven. This latter polymer, can be envisaged as a physically crosslinked polymer (with hard and soft segments) exhibiting the well known entropy driven retraction effect with temperature.

From this work, *i*-PMMA chains are viewed as having a relatively homogenous expansion during the conformational transition. As the coil expands each segment is expected to gain more available free volume (also free for solvent molecules) in its surrounding. We can assume that within the temperature range of the conformational transition, the local conformational rearrangements that occur in *i*-PMMA tend to be more cooperative than for the *s*-PMMA, thus leading to a more gradual expansion of the chain. The *s*-PMMA chain expansion is likely to affect first the chain segments, namely, the so-called soft segments, which are probably not in organised structures formed by helicoidal structures, namely, hard segments. Therefore the increase of the chain dimensions is supposed to concern, at first, the disordered segments of the chain but leaving the structure of the helicoidal parts rather unchanged. The conformational transition would then result in a lost of the locally organised structure and in a rearrangement of the overall coil leading to smaller dimensions at temperatures above 40°C. Additional support for these assumptions can be given by the study of the specific PMMA/$CHCl_3$ interaction with the temperature. Indeed, Fig. 3 shows that the fraction of acid–base bonded carbonyl $f^{ab}_{(C=O)}$ can be obtained from

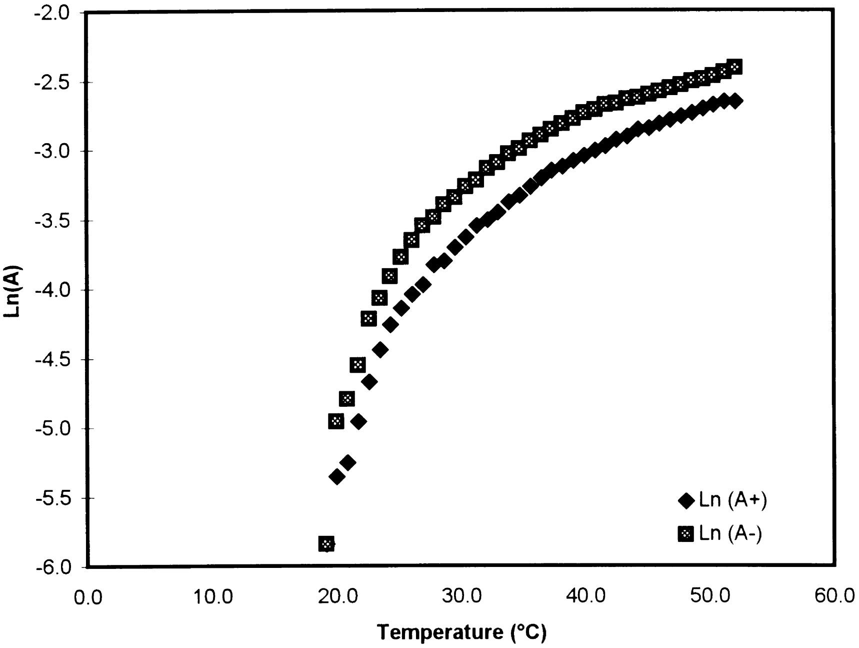


Fig. 5. Logarithm of the residual infrared absorbances A_+ (◆) and A_- (■) as a function of temperature for *i*-PMMA solution at concentration 4 g/l in $CDCl_3$.

the curve-fitting of the carbonyl peak. The free carbonyl vibration located at $1732\ \mathrm{cm}^{-1}$ and the bonded carbonyls at $1714\ \mathrm{cm}^{-1}$ are consistent with the wavenumbers given by Fowkes et al. [21]. The fraction of bonded carbonyl is given by

$$f_{(C=O)^{ab}} = \frac{A_{C=O^{ab}}}{A_{C=O^{ab}} + \dfrac{\varepsilon_{C=O^{ab}}}{\varepsilon_{C=O^{f}}} A_{C=O^{f}}} \qquad (5)$$

where $A^{ab}_{C=O}$ and $A^{f}_{C=O}$ are the absorbances of the bonded and free carbonyls, respectively. The ratio of the molar absorption coefficients $\varepsilon^{ab}_{C=O}/\varepsilon^{f}_{C=O}$ is taken as unity for a sake of simplicity. It should be noticed from Fig. 3 that $f^{ab}_{(C=O)}$ is higher for *s*-PMMA than for *i*-PMMA indicating that more syndiotactic chain segments are swollen than for isotactic chains. This observation made not only at room temperature but also at higher temperatures can be interpreted in terms of solvent permeability of the coil. Thus, *i*-PMMA is assumed to be an homogenous coil with polymer–solvent contacts predominantly taking place in the external part of the coil whereas *s*-PMMA chain is likely to be constituted of dense chain segments (helicoidal structure) and disordered parts leading to a density heterogeneous coil more easily swollen by chloroform. Therefore, an increase in the temperature increases linearly $f^{ab}_{(C=O)}$ for the *i*-PMMA by a gradual expansion of the coil which allows more polymer–solvent contacts. *s*-PMMA chains maintain their $f^{ab}_{(C=O)}$ value at approximately 0.35 up to 35°C and then the density of acid–base interactions raises sharply. It is assumed that the disordered segments of syndiotactic isomer are totally swollen even at room temperature, while the chain segments involved in helicoidal intramolecular structures require to reach the temperature of conformational transition to reorganise themselves by taking into account the surrounding solvent molecules. The acid–base interactions are expected to be an influent factor in the expansion process because of their negative sign contribution to the total free energy. However, the relative importance of the specific interactions may depend on the polymer tacticity. Thus, if the interactions can be considered as one of the prevailing driving force for the chain expansion for *i*-PMMA during the temperature induced conformational transition, the behaviour of *s*-PMMA is more likely to be dictated by entropic considerations such as local chain conformation or the energy of rotation barriers between two conformational states of the chain backbone.

3.2. ^{1}H NMR measurements

^{1}H NMR measurements were carried out on PMMA in $CDCl_3$ at different temperatures. The width at half height $\Delta\upsilon_{1/2}$ (in Hz) is characteristic of the reciprocal spin–spin relaxation time T_2 as

$$T_2 = 1/\pi\Delta\upsilon_{1/2} \qquad (6)$$

Fig. 4 shows that there are some events in the plot of $\Delta\upsilon_{1/2}$ versus temperature in the range of temperature of the conformational transition, principally for the side-chain methoxy group (3.6 ppm) and for the backbone methylene group (1.8 or 1.54 ppm for *s*- and *i*-PMMA, respectively). The $-CH_2-$ peak is broader for the *s*-PMMA than for the *i*-PMMA at room temperature, however, above 30°C things becomes inverted because of the sharp decrease of $\Delta\upsilon_{1/2}$ for the syndiotactic isomer. This change in the width at half height corresponds to an unusually rapid increase in the

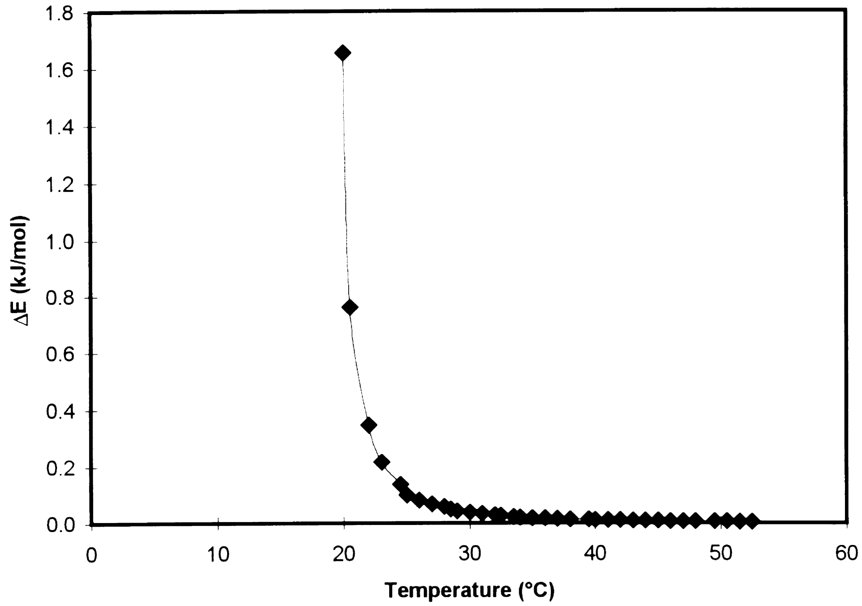


Fig. 6. Conformational energies ΔE, calculated from the residual absorbances given in Fig. 5, as a function of temperature for *i*-PMMA solution at concentration 4 g/l in $CDCl_3$.

mobility of the backbone methylene protons [22]. This can be associated to a conformational transition, from chain sequences containing only *trans* conformations to chain sequences with some *gauche* states, of the backbone which is more sensitive for the *s*-PMMA (change of $\Delta\nu_{1/2}$ equal to 4 Hz) than for the *i*-PMMA (change of $\Delta\nu_{1/2}$ equal to 2 Hz). This difference in the restriction of mobility between PMMA isomers can be correlated to the fact that *s*-PMMA is known from RIS calculations [19] to allow more *trans* states than *i*-PMMA at room temperature. Therefore, the number of *trans* to *gauche* conformational changes with temperature are likely to be enhanced for the syndiotactic polymer.

The NMR peak, assigned to the methoxy protons, exhibit a broadening at 35°C for both PMMA isomers. This effect is ascribed to a reduced mobility of that group at the midpoint of the transition. Once more, this effect is markedly higher in the *s*-PMMA (2 Hz) as compared to the isotactic polymer (0.4 Hz). As $-OCH_3$ belongs to the side-chain, it is assumed that during the conformational transition, from *trans* to *gauche* states of the backbone, some freezing of the side-chain motions is required. To our knowledge, no relevant

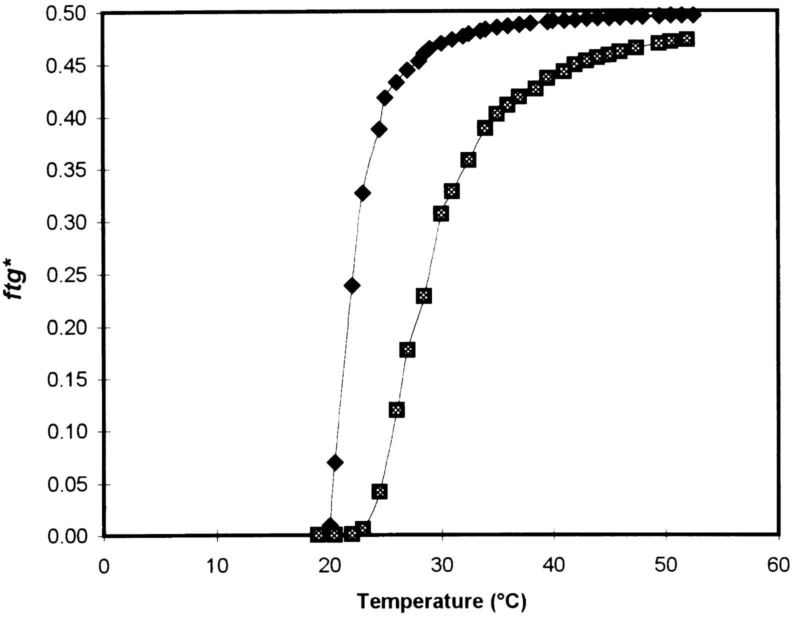


Fig. 7. Fraction of sequences containing *gauche* bonds f_{tg*} as a function of temperature for stereoregular PMMA solutions at concentration 4 g/l in $CDCl_3$. ◆ represents the *i*-PMMA solutions and ■ represents the *s*-PMMA solutions.

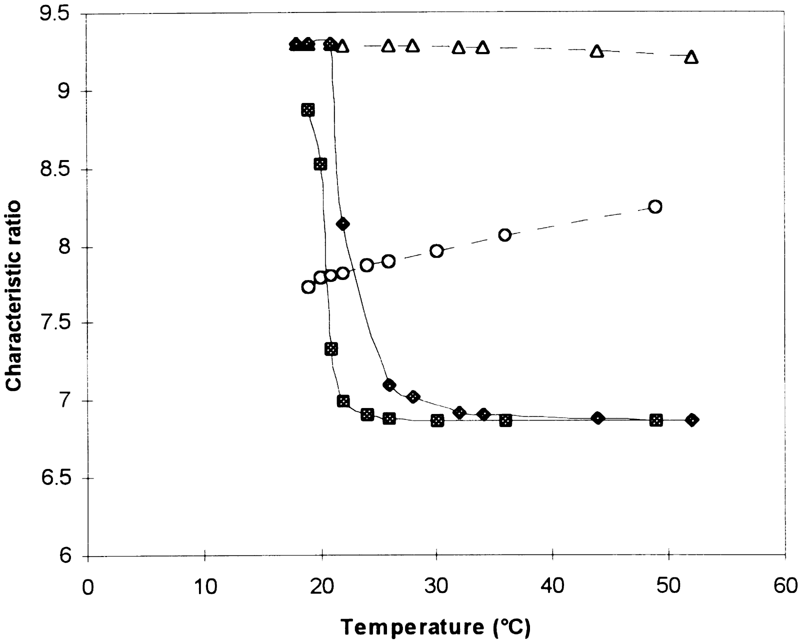


Fig. 8. Characteristic ratio C_∞ calculated from the R.I.S. theory as a function of temperature for stereoregular PMMA solutions at concentration 4 g/l in $CDCl_3$. ◆ represents the *i*-PMMA and ■ represents the *s*-PMMA characteristic ratio calculated from experimental statistical weights. ○ represents the *i*-PMMA and Δ the *s*-PMMA characteristic ratio calculated from theoretical statistical weights [19].

experimental investigations were carried out on that topic. The fact that the broadening of the methoxy peak of the *s*-PMMA is more pronounced than for the isotactic isomer can be ascribed to a lower local cooperativity during the conformational rearrangement in the chain of syndiotactic isomer as suggested previously.

3.3. FT-IR determination of the conformational energy

As shown in Fig. 5, the logarithm of the residual absorbance A_+ and A_- obtained from spectral subtraction and plotted as a function of temperature do not increase linearly as it was found by O'Reilly and Mosher [8] for bulk polymers. Therefore, the calculations of the conformational energy (ΔE) requires to fit mathematically the $\ln(A_\pm) = f(1/T)$ curve and to derive it with respect to the temperature. ΔE is then found to be temperature dependent as shown in Fig. 6 for *i*-PMMA in $CDCl_3$. These results are interpreted in terms of equilibrium between tt and tg conformational states of the polymer chain segments at different temperatures. Thus, the fraction of sequences containing *gauche* conformations, f_{tg*}, can be calculated with the help of the relation:

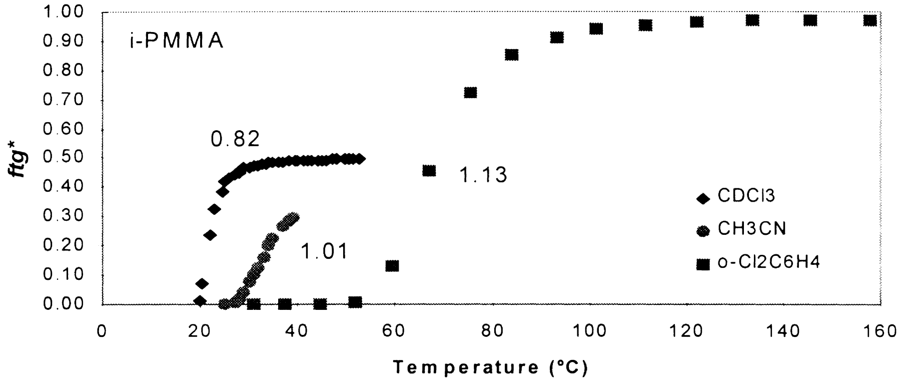
$$f_{tg*} = \frac{N_{tg*}}{N_{tg*} + N_{tt*}} = \frac{e^{(-\Delta E/RT)}}{1 + e^{(-\Delta E/RT)}} \tag{7}$$

where N_{tg*} and N_{tt*} are the number of conformational sequences containing *gauche* conformations and all *trans* conformations, respectively, ΔE the conformational energy, R the ideal gas constant and T the temperature. In Fig. 7 we have plotted the evolution of f_{tg*} as a function of temperature for the *i*-PMMA and the *s*-PMMA in $CDCl_3$. In contrast to the observations made by O'Reilly and Mosher for bulk polymers, the conformational energy changes gradually in solution with temperature within the range of the conformational transition. Indeed, the chemical environment of polymer chains in solution, even in a so-called θ solvent, such as acetonitrile, is likely to evolve with temperature in opposition to what happens in the bulk polymer where the chemical structure of the neighbouring molecules is almost independent of the temperature. Therefore, for PMMA solutions, where the solvation of the chain segments can evolve with temperature, each temperature corresponds to another conformational energy which can be calculated.

Fig. 7 shows that at a given temperature, the fraction of the sequences containing the high energy *trans–gauche* conformers increases. This observation is consistent with the assumptions made by several workers [1–5] of a decrease in the rigidity of the polymer chain during the conformational transition in solution. We evidenced this trend here for the PMMA chains by giving quantitative information of the conformational rearrangements that occurs. By using the conformational energies, ΔE calculated here, and placing it in the RIS theory through statistical weights, we can obtain the evolution of the chain rigidity, described by the characteristic ratio C_∞, as a function of temperature. This value defines the dimensions of the so called phantom chain through a direct relation which exist between the radius of gyration R_g and C_∞

$$R_g = C_\infty l^2 N/6^{1/2} \tag{8}$$

where N is the number of bonds in the chain and l the bond length. The radius of gyration of the phantom chain is only



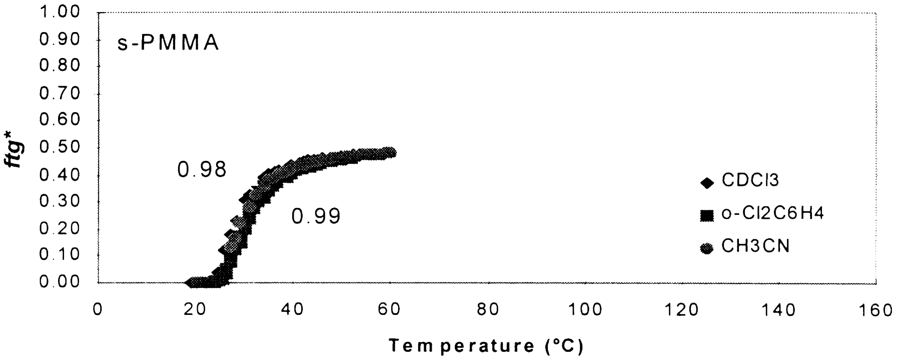


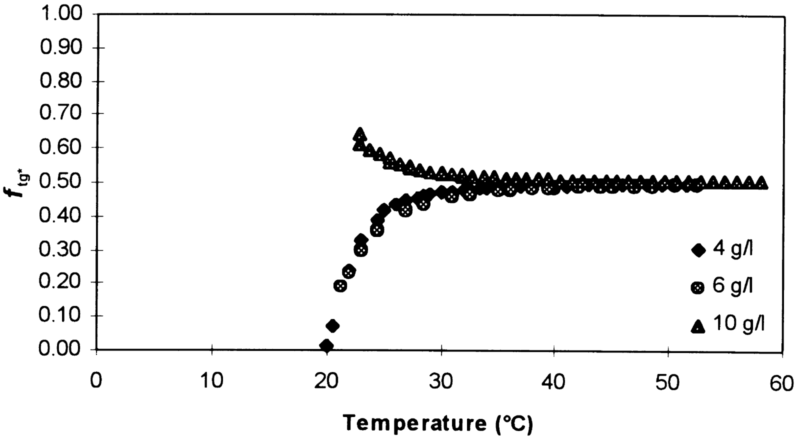
Fig. 9. Fraction of sequences containing *gauche* bonds f_{tg*} as a function of temperature for stereoregular PMMA solutions at concentration 4 g/l in various solvents. ◆ represents *i*-PMMA (upper curve) and *s*-PMMA (lower curve) in $CDCl_3$, ● represents *i*-PMMA (upper curve) and *s*-PMMA (lower curve) in CH_3CN and ■ represents *i*-PMMA (upper curve) and *s*-PMMA (lower curve) in *o*-dichlorobenzene (this latter curve is obtained from spectral subtraction made on the infrared peak at 1190 cm^{-1}).

governed by the short range van der Walls or steric interactions taking no care of the excluded volume interactions. Fig. 8 shows that C_∞ decreases sharply, indicating a lowering in the steric hindrance in the polymer chain, at the temperature of conformational transition whatever the tacticity of the PMMA. If we compare these results with the conclusions drawn from the viscosimetric measurements, it should be pointed out that during the real chain expansion in chloroform, the phantom chain dimension decreases. Therefore, if an expansion factor α_f is defined as the ratio between the real chain radius of gyration and the phantom chain radius of gyration, and compared to the calculated values of α_η these later look underestimated by about 25%. This is a complementary evidence of the dominating character of the excluded volume interactions at the conformational transition. Indeed, the high perturbation of the chain statistics of the coil, at the temperature of conformational transition, does not lead to the decrease of the chain dimensions but to an increment of the hydrodynamic volume occupied by the real chain in the solution.

Differences can be observed in Fig. 7 in the thermal behaviour of PMMA solutions according to the stereochemical composition of the dissolved polymer. Indeed, the conformational transition of *i*-PMMA occurs at lower temperature, namely, at 20°C and end sooner, namely at 28°C than the transition of *s*-PMMA which begins at 24°C and end at roughly 40°C. The temperature range of the transition is about twice for the *s*-PMMA than for the *i*-PMMA which accounts for the existence of cooperativity during the conformational transition. Conformational changes in macromolecules are known to be a cooperative process [23] as each conformation must be influenced by the conformation of the neighbouring bonds. It is then possible to define an equilibrium constant K for each individual conformational transition. The fraction of *gauche* containing sequences is defined by Teramoto et al. [24] as

$$f_g = 0.5\left(1 + \frac{K-1}{[(K-1)^2+4\sigma K]^{0.5}}\right) \quad (9)$$

where the cooperativeness of the transition is measured by a constant named σ which can be $\sigma < 1$ and indicates positive cooperativity or $\sigma = 1$ for totally independent conformational changes. Therefore, the sharpness of the transition increases with decreasing σ. Because we do not know precisely the amplitude of the conformational transition along the backbone and as direct neighbours of a *gauche* bond cannot adopt a *gauche* conformation [19] the



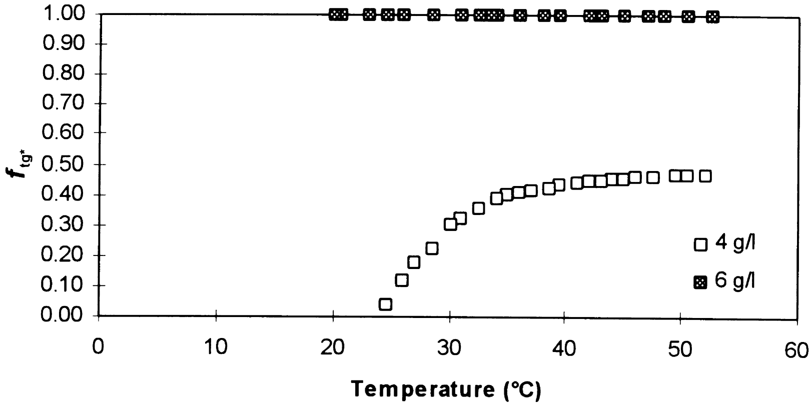


Fig. 10. Fraction of sequences containing gauche bonds f_{tg*} as a function of temperature for stereoregular PMMA solutions at varying concentrations in $CDCl_3$. ■, ● and ▲ represents the *i*-PMMA solutions at concentrations 4, 6, 10 g/l, respectively. □ and ■ represents the *s*-PMMA solutions at concentrations of 4 and 6 g/l, respectively.

calculated σ values are higher than the values found for polyamino-acids and polynucleotides [24]. Actually, the values shown in Fig. 9 according to the solvent and the stereoregularity of the PMMA solution under study, have only to be considered as good indicators of the cooperativeness of the transition. It is noticeable, from Fig. 9, that the cooperativity in the *i*-PMMA transitions strongly depends on the nature of the solvent whereas the transition in *s*-PMMA does not seem to be influenced by the surrounding medium. Starting from nearly theta conditions in CH_3CN, *i*-PMMA and *s*-PMMA with rather similar σ values of 1 and 0.98, show no differences in the cooperativity of their conformational transition. Indeed, no cooperativity is expected with these σ values equal or near unity. In contrast, in a good solvent such as $CDCl_3$, a value of 0.82 is found for *i*-PMMA which indicates a more cooperative process of the conformational rearrangement than for *s*-PMMA. We can assume that cooperativeness occurs easily when the level of excluded volume interactions is sufficient to hinder, at least partially, the short range interactions such as van der Walls or steric interactions. The cooperativity of *i*-PMMA evidenced here, supports the assumptions made earlier of a more homogenous volume expansion of the isotactic polymer coil and also the linear increase of the solvated chain segments with temperature. The poor cooperativity in *s*-PMMA, which is independent of the nature of the solvent, is assumed to be relevant to the prevailing short range interactions, even in good solvents, during the conformational transition. These results account, once more, for a transition mainly based on helix to coil segmental rearrangement occurring in the syndiotactic isomer.

O-dichlorobenzene is known to be an aggregating solvent [11,13–14] whatever the PMMA tacticity. Nevertheless, Spevacek et al. [11] noticed that the aggregates formed in solutions of *s*-PMMA were not very stable and decompose at temperatures lower than the associated structures formed in solutions of *i*-PMMA. From Fig. 9 we can observe that the conformational transition in *o*-dichlorobenzene begins roughly at 26°C for *s*-PMMA whereas *i*-PMMA exhibit a transition at higher temperatures, namely 55–70°C. The associated structures found in solutions of *s*-PMMA are assumed to decompose during the conformational transition that occurs in the same range of temperature as in the non aggregating solvents. Therefore, the aggregates are likely to require very regular *trans–trans* sequences to be formed [11] and do not resist to or do not hinder the increase of *gauche* conformation at the temperature of conformational transition. On the contrary, no transition occurs in the usual 20–40°C range of temperature for the *i*-PMMA solution in *o*-dichlorobenzene. The very stable associated structures formed with that isomer are assumed to be able to hinder the conformational transition up to higher temperatures where the aggregates are supposed to decompose [11,13].

The influence of the concentration of the polymer in the solution on the conformational transition has also been investigated in $CDCl_3$. The solution used, until now, with a concentration of 4 g/l, was considered as diluted but the question that remains is: do the PMMA solutions exhibit the same behaviour with temperature in the semi-diluted regime? Fig. 10 shows that at a given concentration, namely, 10 and 6 g/l for *i*-PMMA and *s*-PMMA, f_{tg*} at room temperature is higher than for less concentrated solutions. The compression of the polymer coil dimensions that occurs above the overlap concentration ϕ_{ov} [25] is assumed to result in the observed increase of the probability of *gauche* conformation. The overlap concentration is estimated as being in the range of 0.005–0.01 meaning that for our PMMA 10 and 6 g/l are likely to be above ϕ_{ov} according the PMMA tacticity.

Moreover, surprisingly, we observe a decrease in the fraction of sequences containing high energy tg conformers roughly at 25–35°C which is the same temperature which is recorded for the increase of f_{tg*} for less concentrated solutions. The decrease in the probability of *gauche* conformation with temperature in the semi-diluted regime may be due to a complex interplay between the intra, inter-molecular (coil–coil interactions) short and long-range interactions and entropic factors which is difficult to discuss in detail here. We will try to investigate the conformational transition in the semi-diluted regime in a future work in light of the De Gennes' scaling theory [26].

4. Conclusion

FT-IR has been shown to be a powerful tool for the study of PMMA conformational transition in solution. We evidenced and quantified the increase in the probability of *gauche* states in the chain backbone during the temperature induced transition which was already assumed by many authors [1–7].

Solutions of stereoregular PMMA exhibit a conformational transition in a range of temperature which does not depend much on the polymer tacticity. Nevertheless, the expansion of the PMMA coil with temperature differs according to the stereochemical structure of the chain. Indeed, a more homogeneous expansion of the hydrodynamic volume *i*-PMMA chain is suggested to result from a more cooperative process in the local *trans–trans* to *trans–gauche* conformational rearrangement. These conformational changes are assumed to increase the polymer–solvent specific interactions with temperature in a more linear way when cooperativity exist. The lack of cooperativity suggested in *s*-PMMA may result in the strong changes in the molecular mobility as detected by NMR. The transition observed in *s*-PMMA solutions is ascribed to conformational rearrangement more localised along the chain and relatively independent, namely, changes from helix to more coiled structures.

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