polymer communications

Comparison between the effects of temperature and cosolvency. Coil expansion, association, and phase separation of PMMA in the poor solvents acetonitrile and chlorobutane

A. Horta
Departamento de Química Física, Facultad de Ciencias, Universidad a Distancia (U.N.E.D.), Madrid 3, Spain

and M. G. Prolongo, R. M. Masegosa and I. Hernández-Fuentes
Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 3, Spain

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Introduction

Recently, we have studied the dilute solution viscosity of poly (methyl methacrylate) (PMMA) in the cosolvent mixture formed by acetonitrile (MeCN) and 1-chloro-n-butane (ClBu), at 25°C[1,2]. The cosolvent effect in this system is extremely large. Addition of MeCN to PMMA/ClBu solutions, or addition of ClBu to PMMA/MeCN solutions, produces a large increase in the hydrodynamic volume of the macromolecule in solution[1,2]. It also produces a steep depression in the critical temperature of phase separation (UCST)[3,4]. The quantitative determination of the magnitude of these effects was the object of previous work[1-4].

Here, we report on measurements of the limiting viscosity number, $[\eta]$, as a function of temperature, T, in the interval 25°–45°C, for PMMA in the single solvents MeCN and ClBu. The polymer is one of the predominantly heterotactic samples already used in the study of cosolvency. The points which we consider in the present paper are the following. First we compare the relative capacities of temperature and of cosolvent mixing on: (a) expanding the macromolecular coils; (b) disrupting the tendency of the polymer to associate in poor solvents. Second, we show that there is a connection which relates the dependencies of $[\eta]$ on temperature and solvent composition with the depression in critical temperature (UCST) caused by cosolvency. Third, we determine the θ temperatures of our predominantly heretotactic samples in MeCN and ClBu, and compare them with those for other tacticities.

Polymer

The molecular weight of the sample is $M_w = 189\,000$ determined by light scattering[2], and its tacticity: 5% iso, 51% hetero, 44% syndio (triads), determined from its ^{1}H-n.m.r. spectrum[2].

Viscosity

Details about the viscometric technique can be found in our previous report (ref 2). The results of $[\eta]$ vs. T are shown in *Figure 1*. $[\eta]$ increases with T, as is typical of polymers in poor solvents. The values of $[\eta]_\theta$ have been calculated from the unperturbed dimensions (K_θ) determined before[2] in MeCN and ClBu ($[\eta]_\theta = K_\theta M_w^{1/2}$). They are also shown in *Figure 1*.

θ-Temperatures

By interpolating $[\eta]_\theta$ in the $[\eta]$–T smooth curves of *Figure 1* we find the θ temperatures correspond to our PMMA in MeCN and ClBu. They are: $\theta_{\mathrm{MeCN}} = 48°C$; $\theta_{\mathrm{ClBu}} = 41°C$. The values reported in the literature for PMMA in MeCN and in ClBu are as follows, MeCN; $\theta = 27.5°C$ (iso)[5,6], 45°C (atactic)[7], ClBu; 26.5 (iso)[8], 35°C (atactic, syndio)[8-10].

We can summarize these results by saying that: (a) in either solvent, the iso polymer has a lower value of θ than the atactic or syndiotactic one; (b) for a given tacticity, θ is higher in MeCN than in ClBu. The results obtained here for a heterotactic-like polymer also show a θ higher in MeCN 48°C than in ClBu 41°C. In each solvent, the present values of θ is higher than the literature one for atactic PMMA, although the difference is small. A lower value of $\theta = 32°C$ has been determined in ClBu[11] for a sample of unspecified tacticity but synthesized under conditions similar to those leading to heterotactic-like polymers.

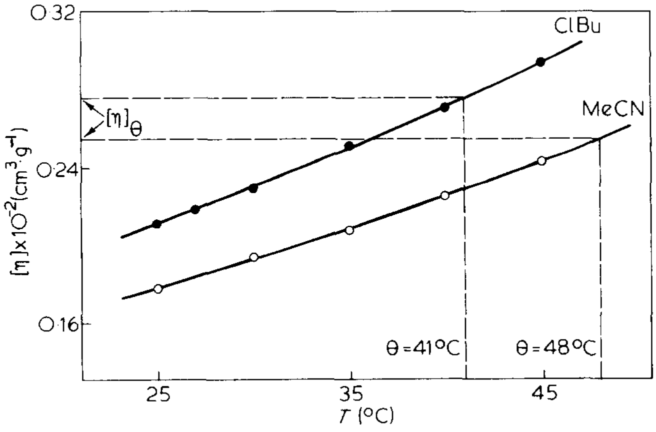

Figure 1 Limiting viscosity number as a function of temperature for heterotactic PMMA (M_w = 189 000) in acetonitrile and chlorobutane

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Coil expansion

The expansion of the hydrodynamic radius of the macromolecule (calculated as $\alpha_\eta = ([\eta]/[\eta]_\theta)^{1/3}$ is due to excluded volume. In a poor single solvent, the excluded volume is an increasing function of T. In a cosolvent mixture, at constant T, the excluded volume is a function of the mixed solvent composition and reaches a maximum value for a certain φ (φ = volume fraction in the liquid mixture). In the case of PMMA/MeCN + ClBu, the maximum in α_η is found[2] for $\varphi_{\mathrm{MeCN}} \simeq 0.42$. Thus, the coils of PMMA dissolved in either single MeCN or in single ClBu, at 25°C, can be expanded in one of these two ways: (a) by increasing T, as in *Figure 1*; (b) isothermally, by adding the other liquid (the cosolvent). Let us now compare the magnitude of the expansion produced by each one of these two ways of increasing excluded volume.

The macromolecular coils in single MeCN and in single ClBu, both at 25°C, are in a contracted state. The temperature increase, ΔT, needed to expand them up to their unperturbed states is: 23°C in McCN, and 16°C in ClBu (according to *Figure 1*). A similar expansion, leading to the unperturved state is reached, at constant 25°C, by adding ClBu to pure MeCN up to a concentration $\varphi_{\mathrm{ClBu}} = 0.088$ or by adding MeCN to pure ClBu up to $\varphi_{\mathrm{MeCN}} = 0.044$ (because the θ compositions determined in the cosolvent mixture are[2]: $\varphi_{\mathrm{MeCN}} = 0.912$ and 0.044). Therefore, $\Delta T/\Delta\varphi = 23/0.088 = 2.6 \times 10^2$ degrees, and $\Delta T/\Delta\varphi = 16/0.044 = 3.6 \times 10^2$ degrees, respectively.

These values are only rough estimates since we have ignored the cruvatures in the $[\eta]$–φ and $[\eta]$–T dependencies. Such curvatures can be taken into account by using the derivatives $\mathrm{d}[\eta]/\mathrm{d}\varphi$ at $\varphi \to 0$ and $\mathrm{d}[\eta]/\mathrm{d}T$ at $T \to 25°\mathrm{C}$. From *Figure 1* we obtain (graphically): $(\mathrm{d}[\eta]/\mathrm{d}T)_{25°\mathrm{C}} = 0.30\ \mathrm{cm^3/gK}$ in MeCN, and $0.37\ \mathrm{cm^3/g.K}$ in ClBu. From the results of reference 2 we calculate* $(\mathrm{d}[\eta]/\mathrm{d}\varphi_{\mathrm{ClBu}})_0 = 1.1 \times 10^2\ \mathrm{cm^3.g^{-1}}$ in MeCN, and $(\mathrm{d}[\eta]/\mathrm{d}\varphi_{\mathrm{MeCN}})_0 = 2.1 \times 10^2\ \mathrm{cm^3.g^{-1}}$ in ClBu. Combining these results with $(\mathrm{d}[\eta]/\mathrm{d}T)_{25\,\mathrm{C}}$ we finally get for $(\mathrm{d}[\eta]/\mathrm{d}\varphi)_0/(\mathrm{d}[\eta]/\mathrm{d}T)_{25\,\mathrm{C}} = (\mathrm{d}T/\mathrm{d}\varphi)_0$:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}\varphi_{\mathrm{ClBu}}}\right)_0 = 3.7 \times 10^2\,\mathrm{K}\ (\text{in MeCN});$$
$$\left(\frac{\mathrm{d}T}{\mathrm{d}\varphi_{\mathrm{MeCN}}}\right)_0 = 5.7 \times 10^2\,\mathrm{K}\ (\text{in ClBu}) \qquad (1)$$

In practical terms, the action of the cosolvent is much more effective in expanding the macromolecule than temperature is. We can say that the replacement of just 1% of the volume of one solvent by the other produces an increase of the hydrodynamic volume equivalent to a temperature rise of 4–6 degrees. It is interesting to note that values of a similar order of magnitude (namely, between 10^2 and 10^3 K) have been obtained in cloud point experiments[3,4] for the depression in UCST. As we shall see later, there is a fundamental reason for this similarity.

We end this section on coil expansion by giving the temperature dependence of the expansion coefficient, α, in MeCN and in ClBu. We obtain α from α_η by means of[12] $\alpha^{2.43} = \alpha_\eta^{\,3}$, and plot α^5–α^3 vs. $1 - \theta/T$ in *Figure 2*. At $T = \theta$ the slope of this plot is 4.0. According to theory[13], this slope equals $0.98\ C_M \psi_1 M_w^{\,1/2}$, where $C_M = 1.42 \times 10^{-24} (\bar{v}/V)\Phi/K_\theta$, $\bar{v}$ being partial specific volume of the polymer, V molar volume of the solvent and Φ Flory's viscosity constant: $\Phi = 2.6 \times 10^{23}\ \mathrm{mol^{-1}}$ [14]. The results thus obtained from *Figure 2* for ψ_1 are $\psi_1 = 0.121$ in MeCN and 0.259 in ClBu.

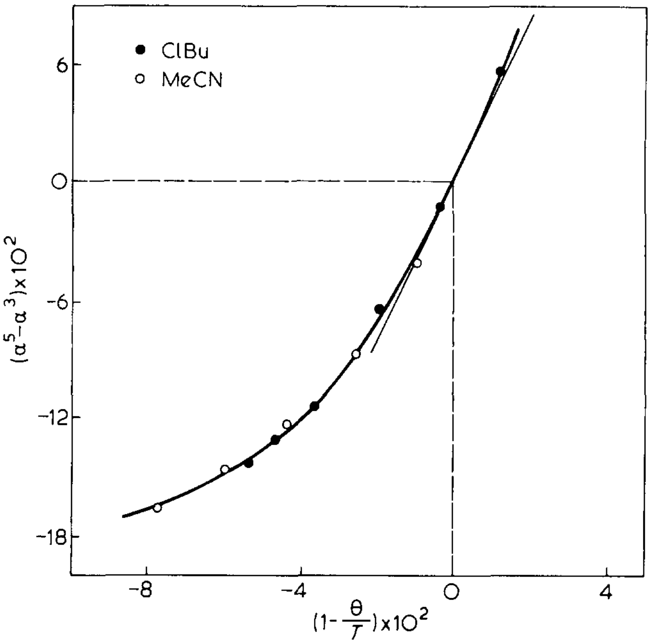

Figure 2 Expansion coefficient as a function of temperature (calculated from the data of *Figure 1*)

Association

At temperatures below θ, the interactions between polymer segments are attractive and this determines not only a contracted or deswelled configuration of the coils, but, also, a tendency of chains to associate intermolecularly. A large excluded volume effect introduced by cosolvency can disrupt this tendency to association besides expanding the coils. In the cosolvent system PMMA/MeCN + ClBu this has been detected previously by studying the variation the Huggins constant, k_H, or the Schulz–Blaschke constant, k_S, with mixed solvent composition[1,2]. At the extremes of the φ range ($\varphi \simeq 0$ and $\varphi \simeq 1$), k_s attains large values ($k_s > 1$) indicative of association. At an intermediate value of φ, k_s adopts values around 0.3 typical of isolated coils in an expanded state. We compare now this cosolvent action with the equivalent disruption of intermolecular association introduced by raising T in the single liquid solutions.

We have determined k_s in MeCN and in ClBu, as a function of T. The results are shown in *Figure 3*. As we can see, k_S decreases with increasing T, denoting that the tendency to association diminishes. However, in the 20 degree range covered by the data, the lowest values of k_S reached are $k_S \simeq 0.6$–0.9, still much higher than in the cosolvent system, *Figure 3*. Again, the action of the cosolvent in annulating the tendency to association is much more effective than the corresponding action of temperature.

It should be noted that the association of PMMA in single solvents and its temperature dependence, vary with

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* $(\mathrm{d}[\eta]/\mathrm{d}\varphi)_0$ has been calculated as follows. According to thermodynamic theory, $\Delta[\eta] \sim \varphi_1\varphi_2\chi_{12}$, where χ_{12} is the interaction parameter for the liquids (denoted as 1 and 2), and $\Delta[\eta] = [\eta] - (\varphi_1[\eta]_1 + \varphi_2[\eta]_2)$. Then, $(\Delta[\eta]/\Delta\varphi_2)_0 = \Delta[\eta]/\varphi_1\varphi_2$. If the increments $\Delta\varphi_2$ are small $(\mathrm{d}[\eta]/\mathrm{d}\varphi_2)_0 \simeq (\Delta[\eta]/\Delta\varphi_2)_0 = \Delta[\eta]/\varphi_1\varphi_2$. We have plotted the data of ref 2 in the form of $\Delta[\eta]/\varphi_1\varphi_2$ vs. φ_2 and have extrapolated to $\varphi_2 \to 0$ to obtain $(\mathrm{d}[\eta]/\mathrm{d}\varphi_2)_0$.

tacticity of the sample. N.m.r. data obtained in MeCN (deuterated) have shown that the proportion of aggregates at room temperature is higher for the iso-polymer than for the syndio-polymer[15], and that the iso-aggregates are temperature stable while the syndio-aggregates decompose completely at about 60°C[15]. Our polymer is not a pure tactic form, but it may show a greater tendency to aggregation than the syndio-polymer (and greater than the atactic polymer also). Thus, the data of Schulz *et al.* for a syndio-PMMA ($M_w = 168\,000$, close to our M_w) in ClBu[8] lead to $k_H \simeq 0.34$ at temperatures as low as 35°C, in contrast with our finding of much higher k_H's in the same solvent and temperature (k_H is even larger than k_S of *Figure 3*). Similarly, light scattering measurements from our laboratory[16] have indicated that the heterotactic-like polymers used here, show signs of aggregation at 25°C, even in good solvents such as ethyl acetate in which the same measurements carried out with atactic samples give a normal non-associating behaviour[16]. This higher tendency to association detected by light scattering in the heterotactic-like polymers has been attributed to their rather stereoregular microstructure[16]. According to a previous analysis, these polymers contain an abundance of *mrrr* sequences[17,18]. These *mrrr* sequences could possibly form associated structures of the stereocomplex type[16]. As is known, in mixtures of iso- and syndio-PMMA solutions a stereocomplex is formed. At room temperature, nearly all polymer units are associated forming the stereocomplex in solvents such as MeCN[19]. A minimum sequence length of three *r* diads has been found necessary for the formation of the stereocomplex in MeCN[19]. Since the heterotactic-like polymer is itself a hybrid of *m* and *r* and since the *mrrr* sequences fulfull the minimum length requirement of *r* diads, we can think that a kind of self-complexation could possibly develop in heterotactic chains and be responsible for their enhanced association[16].

Correlation with cloud points

In the PMMA/MeCN + ClBu cosolvent system, when a small amount of liquid 2 is added to the polymer/liquid 1 pair, the UCST, T_c, decreases linearly with x_1 at a rate characterized by the slope $(\mathrm{d}T_c\mathrm{d}x_2)_0$, x_i being the mol fraction in the liquid mixture and $(\ )_0$ denoting $\lim_{x2\to 0}$[3,4]. A theoretical expression to calculate $(\mathrm{d}T_c\mathrm{d}x_2)_0$ has been developed before[3,4]. Its derivation establishes that $(\mathrm{d}T_c\mathrm{d}x_2)_0$ is related to the interaction parameter for the ternary system, χ, in the following way[3,4]:

$$(\mathrm{d}T_c/\mathrm{d}x_2)_0 = (\partial\chi/\partial x_2)_{0,T_{c1}}/(\partial\chi/\partial T)_{0,T_{c1}} \qquad (2)$$

Here, T_{c1} is T_c for $x_2 = 0$. This expression was given a further, more explicit form by performing the derivative in the numerator with χ written in the single-liquid approximation[3,4]. The result is[3,4]:

$$(\mathrm{d}T_c/\mathrm{d}x_2)_0 = -(\chi_{23} - \chi_{13} - V_2\chi_{12}/V_1)_{T_{c1}}/(\mathrm{d}\chi_{13}/\mathrm{d}T)_{T_{c1}} \quad (3)$$

where the χ_{ij}'s are binary interaction parameters (1 and 2 = liquids; 3 = polymer), and V solvent molar volume (as before).

We can use the $[\eta]$–T dependence of *Figure 1* to obtain $(\partial\chi/\partial T)_{0,T_{c1}}$, and the $[\eta]$–φ dependence previously reported[1,2], to obtain $(\partial\chi/\partial x_2)_{0,T_{c1}}$. For the polymer sample studied here, T_c is 26.9°C, in MeCN, and 28.4°C, in ClBu[3,4], so that the use of experimental $[\eta]$–φ data obtained at 25°C is only approximate.

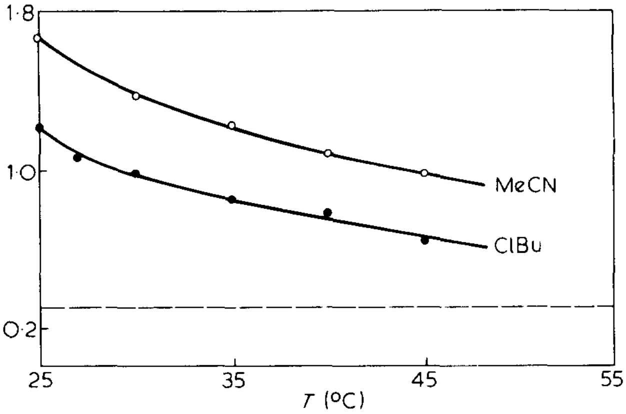

Figure 3 Schulz–Blaschke constant as a function of temperature for the same system as *Figure 1*. Broken line: $k_S = 0, 3$ attained at 25°C in the cosolvent mixtures of intermediate composition

The relationship between $[\eta]$ and χ can be written[20].

$$[\eta] = K_\theta M_w^{1/2} + (1.02 M_w \bar{v}^2 \Phi / N_A V)(1/2 - \chi) \qquad (4)$$

(N_A = Avogadro's constant). If we ignore, as a first approximation, the T and x variations of K_θ and of $\bar{v}\Phi/V$, we can write:

$$\frac{(\mathrm{d}[\eta]/\mathrm{d}x_2)_{0,T_{c1}}}{(\mathrm{d}[\eta]/\mathrm{d}T)_{0,T_{c1}}} \approx \frac{(\partial\chi/\partial x_2)_{0,T_{c1}}}{(\partial\chi/\partial T)_{0,T_{c1}}} = -\left(\frac{\mathrm{d}T_c}{\mathrm{d}x_2}\right)_0 \qquad (5)$$

The left hand side of equation (5) for the system PMMA/MeCN + ClBu can be obtained from the values of $(\mathrm{d}[\eta]/\mathrm{d}\varphi)/(\mathrm{d}[\eta]/\mathrm{d}T)$ calculated above (equation 1) and using the relation: $(\mathrm{d}/\mathrm{d}\varphi_2)_0 = (V_1/V_2)\,(\mathrm{d}/\mathrm{d}x_2)_0$. The results are:

$$-\left(\frac{\mathrm{d}T_c}{\mathrm{d}x_2}\right)_0 \approx \frac{(\mathrm{d}[\eta]/\mathrm{d}x_2)_{0,25\,\mathrm{C}}}{(\mathrm{d}[\eta]/\mathrm{d}T)_{0,25\,\mathrm{C}}} = \begin{cases} 7.4 \times 10^2\,\mathrm{K}\ (\text{in MeCN} = 1) \\ 2.9 \times 10^2\,\mathrm{K}\ (\text{in ClBu} = 1) \end{cases} \qquad (6)$$

The experimental values of $(\mathrm{d}T_c/\mathrm{d}x_2)_0$, determined from cloud point measurements, are[3,4]:

$$-\left(\frac{\mathrm{d}T_c}{\mathrm{d}x_2}\right)_0 (\text{experimental}) = \begin{cases} 9.4 \times 10^2\,\mathrm{K}\ (\text{in MeCN} = 1) \\ 3.2 \times 10^2\,\mathrm{K}\ (\text{in ClBu} = 1) \end{cases} \qquad (7)$$

We see that the predictions from $[\eta]$ (equation 6) give values comparable to the experimental values (equation 7). Differences between both can be due to the approximations used, such as assuming constancy of K_θ, $\bar{v}^2\Phi/V$, and taking $T_c \simeq 25$°C. Finer agreement could be reached presumably, by avoiding some of these approximations. However, the present agreement is remarkably good. Especially in view that large discrepancies are found, as a rule, when values of $\mathrm{d}\chi/\mathrm{d}T$ predicted from viscosity are compared with those from cloud points. The temperature dependence of the interaction parameter is given by ψ_1 through $\mathrm{d}\chi/\mathrm{d}T = \psi_1\theta/T^2$. It is well known that ψ_1 values obtained from $[\eta]$ and from T_c differ widely[21]. In general, ψ_1 values from $[\eta]$–T are 5 to 10 times lower than ψ_1

values from T_c–M_w[7]. Atactic PMMA in MeCN is one of the cases where such large discrepancies are found[7]. The agreement between the values of equations (6) and (7) is therefore an important result.

We could have used equation (3) instead of equation (2) to estimate $(dT_c dx_2)_0$ from viscosity data. If we do so, with the values of χ_{13}, χ_{23}, χ_{12} determined previously by light scattering[22], and with $(d\chi_{13}/dT)_{T_{c1}}$ obtained from $(d[\eta]/dT)_{0,25^{\circ}C}$ as:

$$(d\chi_{13}/dT)_{T_{c1}} \approx -(N_A V_1/1.02 M_w \bar{v}^2 \Phi)(d[\eta]/dT)_{0,25^{\circ}C} \quad (8)$$

then we obtain an estimate for $(dT_c/dx_2)_0$ which is an order of magnitude larger than the experimental values, namely: 7.8×10^3K, and 2.0×10^3K, for MeCN = 1 and ClBu = 1, respectively. This does not mean that equation (3) is not adequate*, but, rather, that the temperature dependence of χ_{13} determined from $[\eta]$–T is, as discussed above, not compatible with T_c measurements.

However, agreement between cloud points and viscosity is found if we use the $[\eta]$ results twice: to estimate $\partial\chi/\partial x_2$ and $\partial\chi/\partial T$ simultaneously, as we have just done using equation (2). We reach the interesting conclusion that the comparison between the temperature and solvent composition variations of $[\eta]$ allows for a correct prediction of the cosolvent depression of the UCST. The comparison between cloud points and $[\eta]$–T gives, in general, inconsistent results, but the combination of $[\eta]$–T and $[\eta]$–φ corrects or compensates such an inconsistency and establishes a valid link between T_c and $[\eta]$.

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* It has been successfully applied to predict $(dT_c/dx_2)_0$ using solubility parameters[3,4].

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Proton-decoupled ^{13}C solid state n.m.r.: A lineshape study of molecular motion in a mesomorphic aryl-aliphatic polyester

P. Sergot and F. Lauprêtre
Laboratoire de Physico-Chimie Structurale et Macromoléculaire associé au C.N.R.S., 10, *rue Vauquelin*, 75231 *Paris Cedex* 05

and C. Louis and J. Virlet
Departement de Physico-Chimie, C. E. N. Saclay, B.P. n°2, 91191 *GIF-sur-Yvette Cedex*

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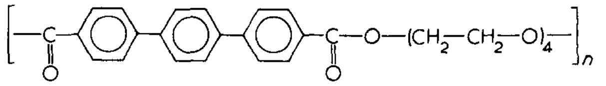
Introduction

High-power proton-decoupled ^{13}C nuclear magnetic resonance has proved to be a powerful tool for investigating molecular dynamics in solids. In this respect, attention has mainly been focused on measurements of the carbon spin-lattice relaxation times in the rotating frame $^{13}C\ T_{1\rho}$ which are used to probe the density of motion of the C–H vectors in the tens of kilohertz region[1]. Interesting information about motional modes can also be provided by proton-decoupled ^{13}C n.m.r. lineshape analysis[2]: variations of these lineshapes can indeed be interpreted in terms of molecular reorientation or conformational processes[3]. In the particular case of mesomorphic polymers, they can be considered as a means for examining the dynamics of these compounds as a function of the structure or organization of their various states.

This communication gives some preliminary results obtained on the polyester:



$$\left[-\underset{\underset{O}{\|}}{C}-C_6H_4-C_6H_4-C_6H_4-\underset{\underset{O}{\|}}{C}-O-(CH_2-CH_2-O)_4-\right]_n$$

(A)

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