^{1}H NMR Relaxation Study of the Gelation of Syndiotactic Poly(methyl methacrylate) in Toluene

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ABSTRACT: The temperature-induced helix-to-coil conformational transition accompanying the thermoreversible gelation of syndiotactic poly(methyl methacrylate) in toluene was studied by rheology and FTIR and ^{1}H NMR spectroscopy. Both rheological and FTIR measurements, carried out dynamically as a function of temperature, revealed a marked hysteresis between the heating and the cooling cycles. It was not possible to assess a quantitative difference between the values of the temperature of onset of the physical variations between the rheological and the spectroscopic experiments. It is then possible to conclude that a conformational change of the backbone (from the evolution of the band at 860 cm^{-1}) is the molecular basis of the macroscopic formation of the gel. Spin−spin relaxation time, or T_2, measurements were used in the ^{1}H NMR study. The data obtained from the relaxation behavior of the α-methyl group, indicated a fraction of 0.28 for the chain repeating units incorporated in highly cooperative helical stretches, which are the junctions of the physical gel. The analysis of the relaxation behavior of the methoxy group led to a fraction of 0.24 for the same species. From the study of the ^{1}H-relaxation behavior of the latter group, one also can conclude that an equilibrium exists between two populations of chain repeating units, different as to their mobility. The former group is characterized by a low mobility, which is ascribed to polymer−polymer interactions. Specific interactions with the solvent are proposed as the cause of the high mobility of the latter group of ester residues.

Introduction

Syndiotactic poly(methyl methacrylate) (sPMMA) is able to form gels in many solvents and such a gelation process has been studied by several techniques.[1−5] The occurrence of a two-step gelation mechanism has been clearly demonstrated through the combination of FTIR, NMR, and rheological observations.[5] The first step of the gelation is a coil-to-single helix transition, followed by the association of helices into larger multichain association units. The coil-to-helix transition is a true equilibrium process that can be detected separately through kinetic trapping. The conformational transition is largely affected also by a complicated interplay of polymer−polymer and polymer−solvent interactions.

A powerful technique for the study of such conformational processes is ^{1}H NMR spin−spin (T_2) relaxation. Conformational changes in polymer chains are strongly correlated with appreciable changes in mobility of the chain backbone and the chain side groups. This will lead to important changes in the T_2 relaxation times. The technique is very selective so that the behavior of the different groups in the polymer chains can be studied separately.

The purpose of this paper is to assess the fundamental role played by the conformational transition in the gelation process. Information obtained from rheology and FTIR analysis will be combined with that derived from the T_2 relaxation measurements. This investigation will also allow to get information on the cooperativity of the conformational changes of these polymer chains in solution.

Table 1. Structural Characteristics of the PMMA Samples

			triads		
polymer	$\overline{M}_n$, kg/mol	$\overline{M}_w$, kg/mol	% rr	% rm	% mm
sPMMA	108	195	88.0	12.0	0.0
aPMMA	91	149	58.0	37.0	5.0

Experimental Section

Materials. Polymer Synthesis. sPMMA was polymerized in toluene using aluminum triethyl and titanium(IV) chloride as the catalyst at −78 °C. The atactic isomer (aPMMA) was supplied by ICI under the trade name of Diakon. The tacticity of the different polymers was evaluated through ^{13}C NMR spectra in CDCl$_3$ and was based on the intensities of the α-Me triads.[6] The molecular mass was determined by GPC at room temperature in tetrahydrofuran. The characteristics of the polymers are reported in Table 1.

Solvents. Toluene (Aldrich Reagent p.a.) was used for the FTIR spectra.

The solvents used for the relaxation measurements were deuterated toluene-d_8 (Acros, 100.0% atom D) and CDCl$_3$ (>99.5% atom D).

Experimental Techniques. FTIR Observations. FTIR experiments were performed with a Perkin-Elmer FTIR-2000 spectrophotometer, following both the 860 cm^{-1} band and that at 1742 cm^{-1}. A sealed liquid MIR-ATR cell was used, and the

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temperature was controlled by means of a thermostatized circulating liquid. Dynamic observations were made at a scanning rate of 0.7 °C/min. This means that the temperature of the cell is continuously increased or decreased, process during which spectra are accumulated over a period of about 1 min. The spectrum of the pure solvent has not been subtracted because shifts in the solvent peaks can occur as a consequence of possible interactions of the solvent with the polymer. No internal standard was needed, as the concentration in all the FTIR measurements was kept constant.

High-Resolution NMR. High-resolution NMR experiments were performed with a Varian Inova 400 spectrometer equipped with a dedicated 5 mm proton probe. The proton spin−spin relaxation times (T_2) were measured using the CPMG pulse sequence $(\pi/2)_x-(t_D-(\pi_y-t_D)_n-$acquisition with $t_D = 0.2$ ms and $4nt_D$ the total time for T_2 relaxation.[7,8] The latter is an array of 35 values varying from 0.8 ms to 0.8 s. Every experiment consists of 8 scans, a preparation delay of 5 s, an acquisition time of 2.2 s, and a $\pi/2$ pulse width of 4.85 μs while the temperature was controlled with an accuracy of 0.1 °C.

The measurements were performed as a function of increasing temperature. Each measurement was started after a thermostatization period of least 20 min at the temperature at which the experiment was carried out. A typical standard deviation of about 3% was obtained from T_2 measurements (in 4-fold) at 21, 45, and 70 °C. These measurements were done on the same sample but with an equilibration period of at least several days between consecutive sessions.

Nonlinear least-squares multiexponential analysis of all relaxation data were accomplished on a Macintosh computer using the program KaleidaGraph 3.0 (Marquardt−Levenberg algorithm).

In the figures representing the temperature and concentration dependence of the T_2 relaxation times and fractions of the contributing units, the 95% confidence interval is indicated by error bars.

Preparation of Solutions and Gels. The polymer concentration is expressed as polymer mass fraction, w_2. For most of the experiments, $w_2 = 0.10$. The use of different concentrations will be explicitly indicated in the text.

Homogeneous solutions of sPMMA were prepared by heating the solvent and the polymer in a vacuum-sealed glass tubes up to temperatures close to the boiling point of the solvent. The homogenized solutions were then transferred into the MIR-ATR for the FTIR measurements and into 5 mm NMR tubes. The NMR tubes were sealed under vacuum. This preparation procedure prevents the formation of air bubbles in the gel that could disturb the relaxation measurements.

Results

FTIR Observations. As in previous papers, the change in molecular conformation was followed through the change in intensity of the absorption band at 860 cm^{-1}, characteristic for the close-to-all-trans conformation of the chain backbone. The conformational change is also reflected in the frequency domain of the C=O stretching vibration through the appearance of a new absorption band at 1742 cm^{-1} in addition to the band at 1735 cm^{-1}.[9,10] The band at the higher wavenumber corresponds to the polymer in the helical conformation as it appears on cooling and disappears on heating. At high temperature, the C=O stretching band is symmetric. On cooling, this absorption band becomes asymmetric because the appearance of the band at 1742 cm^{-1}. All FTIR experiments were performed dynamically as described in the experimental part. The covered temperature range is situated between 10 and 80 °C. The temperature dependence of the intensity of absorption bands characteristic for the helix conformation is completely similar for both frequencies. This behavior is illustrated in Figure 1a for the absorption at 860 cm^{-1}. The hysteresis between the cooling and the heating cycles and the value of temperature at the end of the melting process (about 55 °C) are in good agreement with previously reported data[5] obtained by use of calorimetric and rheological techniques.

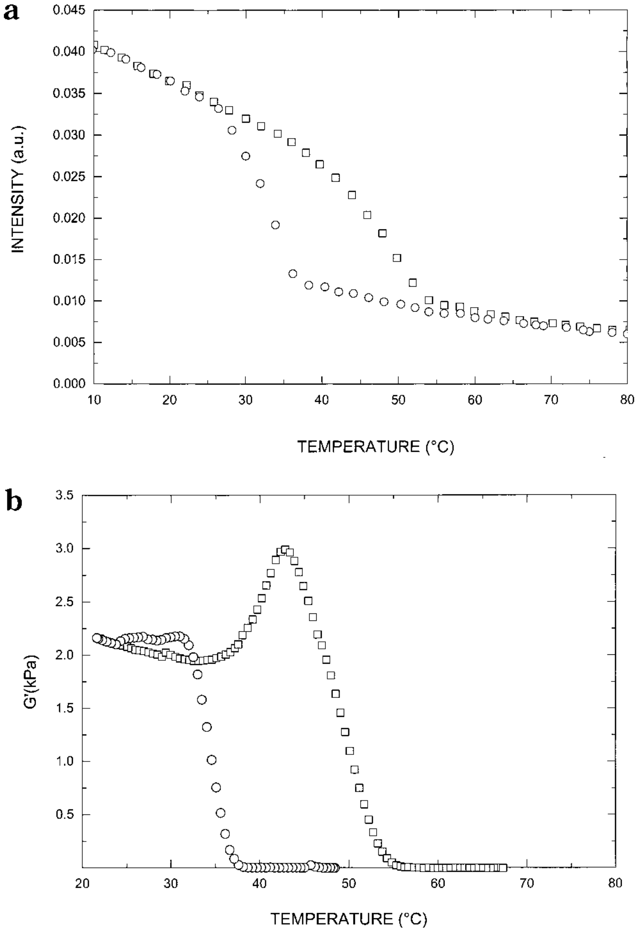

Figure 1. (a) Temperature dependence of the intensity of the CH_2 stretching band at 860 cm^{-1} of a solution of sPMMA in toluene; $w_2 = 0.10$: (○) cooling; (□) heating. (b) Temperature dependence of the elastic part of the modulus, G', of a solution of sPMMA in toluene; $w_2 = 0.10$: (○) cooling; (□) heating.

Rheological Observations. The thermal evolution of the modulus of rigidity, G', during a cooling-and-heating cycle of a 10% solution of sPMMA in toluene is reported in Figure 1c. The curves are identical to those already reported for a similar system.[5] The development of significant values of G' on cooling—corresponding to macroscopic gel formation—takes place in a T range very close to (possibly slightly lower than) that of the onset of both backbone and side-group conformational changes (see Figure 1, parts a and b, respectively). Also $G'(T)$ shows a marked hysteresis like the IR bands. Upon heating, G' values indicate complete gel melting at about the same value of T at which in a parallel cycle the spectroscopic evidence show that the conformational transition is over. A bump appears in the heating mode, in the same range of T in which a shoulder is observed in the heating profile of the intensity of the 1742 cm^{-1} band (see Figure 1b). It can be reasonably ascribed to annealing, leading to conformational and rheological reorganization of ordered chain stretches, likely of different sizes.

NMR Observations. Spin−spin relaxation times for the two different groups (i.e. the α-methyl and the ester methyl) in the monomer repeating unit were measured in order get a more quantitative insight into the changes in molecular mobility depending on the experimental conditions. The intensity−time relationship can vary from simple monoexponential to a three-exponential behavior, as clearly revealed by logarithmic plots of intensity vs time (not reported). Such a multiexponential treatment for these solutions and gels is fully justified as the resulting relaxation times differ considerably. To each relaxation time corresponds an acceptable degree of population. The temperature dependence of the T_2 relaxation time was investigated for the α-methyl group and the methoxy of both aPMMA and sPMMA. The data were obtained in equilibrium conditions, slowly heating the sample between isothermal experiments, starting at room temperature.

I. α-Methyl Group. aPMMA. A monoexponential behavior of the integrated intensity vs time is observed for the α-Me group, independent of temperature. This corresponds to a single T_2 decay. Figure 2a shows a plot of this relaxation time vs temperature (∇). The continuous increase of T_2 reflects the increase in molecular mobility with temperature, mainly caused by the decrease of the viscosity of the solution. Similar results were obtained upon analyzing the *rr* and *mr* triad resonance signals of the α-methyl group separately (data not shown).

sPMMA. The situation is more complex with this isomer. The T_2-evolution time could be fitted only by a biexponential approach for temperatures up to 50 °C, as illustrated in Figure 2a (○, long T_2 or T_2^{l}; △, short T_2 or T_2^{s}). At 21 °C, this leads to a fraction of repeating units of 0.28 with a short T_2-relaxation time, by NMR, (very low molecular mobility) and a fraction of 0.72 with a long T_2-relaxation time, T_2^{l}, (high molecular mobility). The temperature dependence of these fractions is represented in Figure 2b. They are almost constant up to 38 °C. A further increase of temperature increases the fraction with high molecular mobility at the expense of the fraction with very low molecular mobility.

At $T > 50$ °C the data can be analyzed using a single T_2-relaxation time (figure 2a). The temperature dependence of the long T_2, T_2^{l}, is quite similar to that of the monoexponential T_2 relaxation time of the α-methyl group of aPMMA (figure 2a).

II. Methoxy Group, Observations in Toluene. aPMMA. The experimental data obtained with OCH_3 can only be analyzed using a biexponential fitting. The temperature dependence of the T_2 values is reported in Figure 3a. A quasi-sigmoidal variation in the temperature dependence sets in around 48 to about 60 °C. Figure 3b represents the fractional distribution of the methoxy groups over the two relaxation times. At 21 °C, the ratio of distribution values of {mobile, long T_2, or T_2^{l}}/{less mobile, medium T_2, or T_2^{m}}, is $[T_2^{l}]/[T_2^{m}] = 0.30/0.70 = 0.43$. This ratio increases slightly with increasing temperature up to 48 °C, and it then decreases to $0.20/0.80 = 0.25$ at 75 °C. Comparable results are obtained by analyzing the two main methoxy resonance signals separately.

sPMMA. In the temperature range between 21 and 50 °C a three exponential fit is needed and three relaxation times have to be taken into account: T_2^{l} and T_2^{m}, as observed with aPMMA, and a third, very short relaxation time, T_2^{s}, that corresponds to methoxy groups with a very low mobility. The temperature dependence of these relaxation times and the corresponding fractions are represented in Figure 4, parts a and b. The values and the temperature dependence of both T_2^{l} and T_2^{m} are very similar to what is observed with aPMMA. On the contrary, the values of T_2^{s} are much shorter, pointing to the presence of a fraction of methoxy groups with very low mobility. At 21 °C, this fraction is around 0.24, a value very close to the fraction of chain repeating units with very low molecular mobility as deduced from the T_2 analysis of the α-CH_3 group (Figure 2b). This fraction with very low mobility has completely disappeared around 55 °C, i.e., at the temperature at which both *G′* and FTIR band intensities level off in the heating mode. These observations allow us to conclude that the methoxy groups with very low mobility belong to the chain repeating units incorporated in the helical junctions. At 21 °C, $[T_2^{l}]/[T_2^{m}] = 0.24/0.52 = 0.46$, i.e., very close to the ratio observed with aPMMA (0.43). This fraction has decreased to about 0.20/0.80 at 75 °C, like in the aPMMA case.

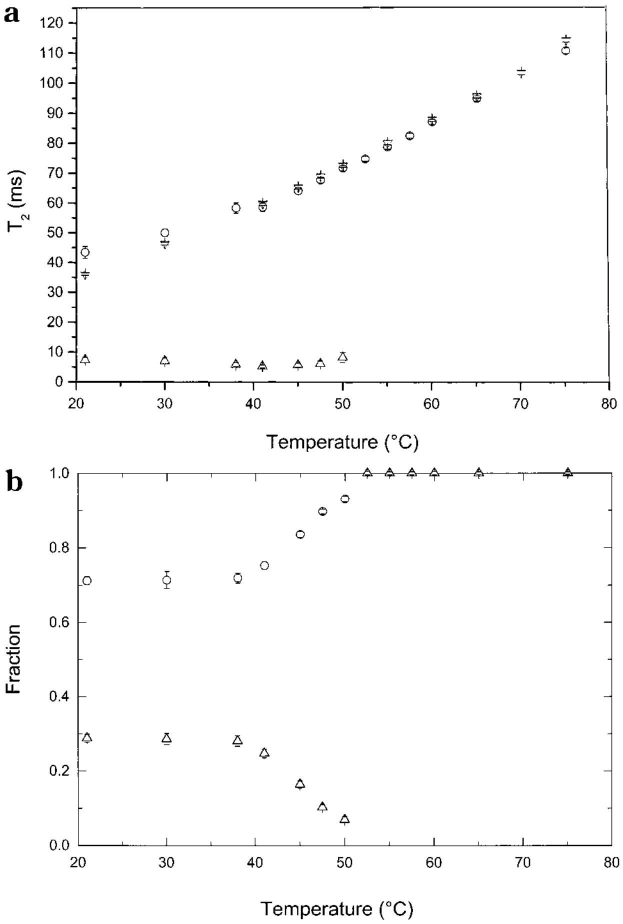

Figure 2. (a) Temperature dependence of T_2 for the (α−CH_3 group in toluene-d_8: (∇) aPMMA; (○) sPMMA, long T_2 or T_2^{l}; (△) sPMMA, short T_2 or T_2^{s}. (b) Temperature dependence of the fractions of groups with very low mobility, T_2^{s} (△), and with high mobility, T_2^{l} (○), for sPMMA in toluene-d_8.

III. Methoxy Group, Observations in Chloroform. To get a better understanding of the origin of T_2^{l} and T_2^{m}, the influence of the solvent and the possible structure formation in solution were investigated by performing the same measurements in $CDCl_3$ on sPMMA. It is well-known that no gelation takes place in this solvent. Even at low temperature, only two relaxation times can be observed, T_2^{l} and T_2^{m} (data not shown).

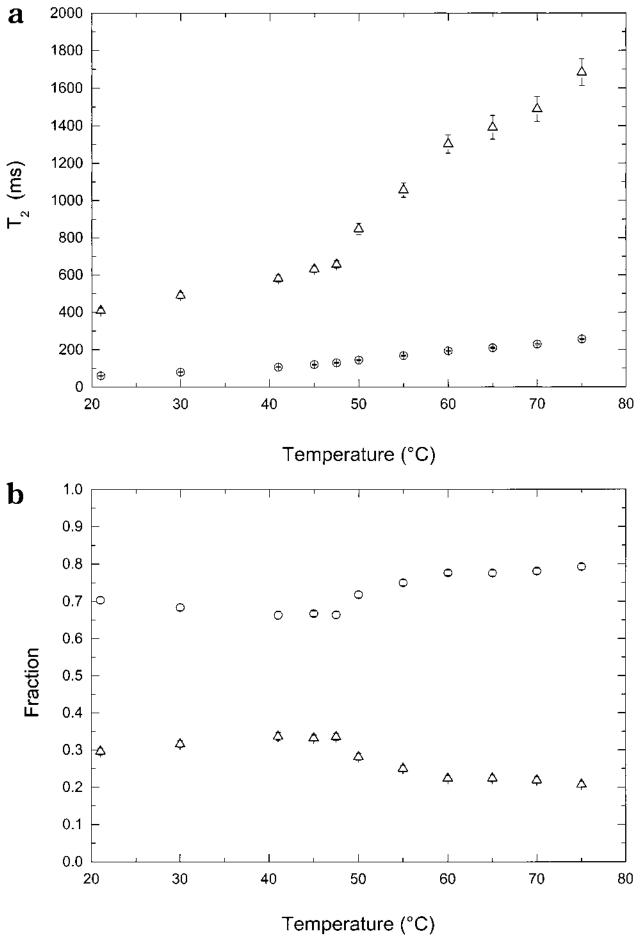

Figure 3. (a) Temperature dependence of T_2 for the OCH_3 group of aPMMA in toluene-d_8: long T_2 decay time (△) and medium T_2 decay time (○). (b) Temperature dependence of the fractions of groups with low mobility, T_2^{m} (○), and with high mobility, T_2^{l} (△), for sPMMA in toluene-d_8.

The fraction of methoxy groups with very low mobility is either absent or present at such a low concentration that no direct evidence could be found by NMR. This observation further confirms the origin of T_2^{s}. Namely, T_2^{s} must be considered as diagnostic of the presence of residues in highly cooperative sequences, which in turn are the prerequisite for gel formation. The fractional distribution of units with high and medium mobility that are responsible for the occurrence at 21 °C of T_2^{l} and T_2^{m} for aPMMA and sPMMA is $[T_2^{\mathrm{l}}]/[T_2^{\mathrm{m}}] = 0.32/0.68 = 0.47$. This value is in very good agreement with the values observed for both isomers in toluene, a solvent in which gelation of sPMMA takes place at low temperature. These observations also further confirm that this behavior is not tacticity dependent.

To obtain further insight into the simultaneous occurrence of T_2^{l} and T_2^{m}, the T_2 relaxation behavior of two model ester compounds, namely methyl propionate and methyl 2,2-dimethylpropionate, was investigated. Two relaxation times could in principle originate from the occurrence of cis−trans isomerism, due to hindered rotation around the O−CO bond, resulting in syn and anti orientations of the $-O-CH_3$ bond with respect to the C=O bond. However, the methoxy group of both compounds shows a monoexponential T_2 relaxation behavior.

IV. Concentration Dependence and Influence of Temperature. The concentration dependence of the ratio $[T_2^{\mathrm{l}}]/[T_2^{\mathrm{m}}]$ was investigated for solutions of aPMMA. With this isomer, the biexponential decay is observed, with no presence of T_2^{s}.

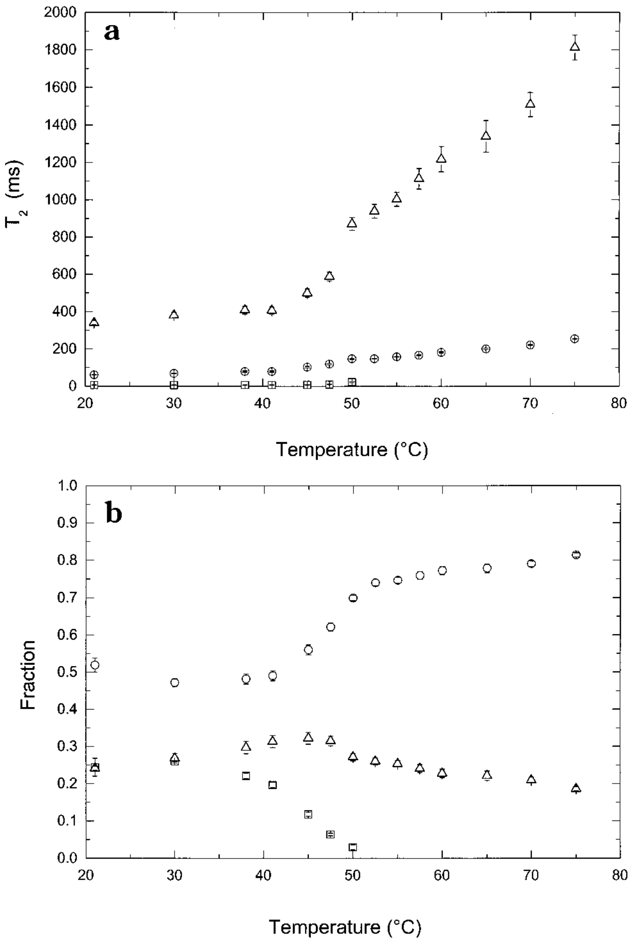

Figure 4. (a) Temperature dependence of T_2 for the OCH_3 group of sPMMA in toluene-d_8: long T_2 decay time (△), medium T_2 decay time (○), and short T_2 decay time (□). (b) Temperature dependence of the fractionof groups with very low mobility, T_2^{s} (□), with low mobility, T_2^{m} (○), and with high mobility, T_2^{l} (△), for sPMMA in toluene-d_8.

Solutions in Toluene. The T_2 relaxation behavior of the methoxy group was studied at two different temperatures in toluene-d_8 as a function of the polymer concentration in the range $0.20 > w_2 > 0.0001$.

At 21 °C (data not shown), the T_2 relaxation behavior is biexponential over the whole concentration range with $[T_2^{\mathrm{l}}]/[T_2^{\mathrm{m}}]$ (0.30/0.70) = 0.43. Both T_2 values increase upon lowering the polymer concentration due to the decrease of viscosity of the solutions. At 102 °C, the T_2 relaxation behavior however is quite different. For polymer concentrations $w_2 \geq 0.10$, $[T_2^{\mathrm{l}}]/[T_2^{\mathrm{m}}] \cong (0.20/0.80)$ over the whole concentration range while both T_2 values decrease slightly with increasing concentration (data not shown). In a lower range of polymer concentration, i.e., $0.10 \geq w_2 \geq 0.001$, the contribution of T_2^{l} (groups with the highest mobility) increases while both T_2 values decrease (Figure 5, parts a and b). At $w_2 = 0.0001$, the behavior becomes monoexponential.

Solutions in Chloroform. In $CDCl_3$ the fraction distribution remains unaffected and equal to 0.20/0.80 at 55 °C for polymer concentrations $w_2 \geq 0.01$. A decrease of the concentration to $w = 0.001$ brings about an increase of the relative contribution of T_2^{l}, which

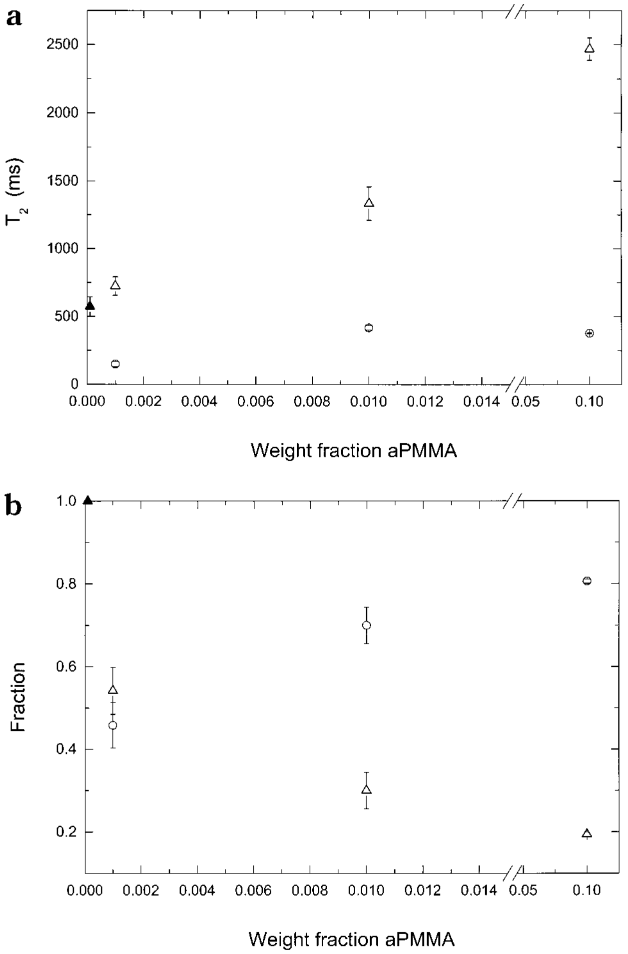

Figure 5. Concentration dependence of the methoxy group of a solution of aPMMA in toluene-d_8 at 102 °C. (a) T_2 as a function of concentration: (○) T_2^{m}; (△) T_2^{1}; (▲) monoexponential T_2 behavior. (b) Fraction distribution as a function of concentration: (○) T_2^{m}; (△) T_2^{1}; (▲): monoexponential T_2 behavior.

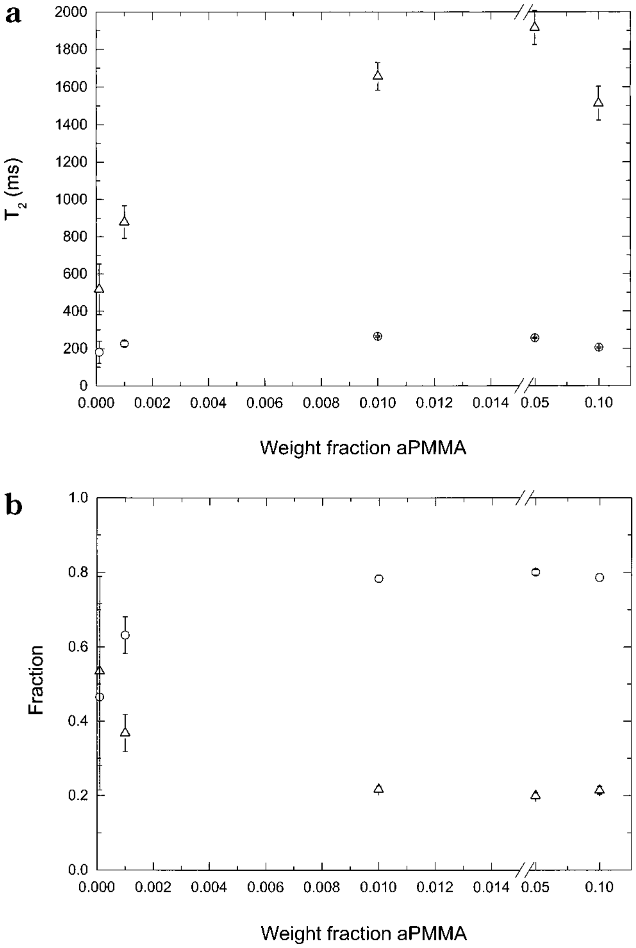

Figure 6. Concentration dependence of the methoxy group of a solution of aPMMA in $CDCl_3$ at 55 °C: (a) T_2 as a function of concentration: (○) T_2^{m}; (△) T_2^{1} (b) Fraction distribution as a function of concentration: (○) T_2^{m}; (△) T_2^{1}.

then becomes predominant at $w = 0.0001$. Meanwhile, both T_2 values decrease (Figure 6, parts a and b). At $w_2 = 0.001$ the T_2 behavior can still be analyzed biexponentially. The difference between the T_2 decay times has greatly decreased (the ratio of T_2 values has dropped from 7.5 at $w = 0.10$ to about 2.5 at $w = 0.0001$) while the error has seriously increased. This is a clear indication that a single T_2 decay time would be observed upon further dilution.

Discussion

The comparative analysis of the rheological results and of the spectroscopic ones straightforwardly indicate that the macroscopic gel formation is intimately related to polymer conformational changes. In a recent paper, a molecular mechanism for this gelation process was already proposed.[5] In turn, T_2 values monitor significant variations of the mobility of the different groups involved in those changes.

We can tentatively identify the following phenomena which interplay to produce this complex physical chemical behavior:

- *Conformational transition* of the chain backbone.
- *Conformational transition* of side groups.
- *Cooperativity* of the two latter processes, also in relation to chain tacticity.
- *Polymer–polymer* intersegmental interactions, either intramolecular (from distant parts of the chain) or intermolecular, in all cases strongly reducing the mobility.
- *Polymer–solvent* interactions, specifically related to the good-solvent character, invariably producing a high mobility of the interacting groups.

The temperature-induced conformational transition is the key process which underlies all the observed effects. Both the main chain and the side groups are involved in such a process. The change in the 860 cm^{-1} band proofs the involvement of the skeletal $-CH_2-$ units, whereas both IR (through the 1742 cm^{-1} band) and T_2 demonstrate the role of the methyl ester group in the transition. Finally, the effect produced on the α-methyl group is evidenced also by T_2 data.

The transitions of the three groups all take place in a very similar range of temperature. However, on the basis of the present data alone, it is not possible to assess whether they rigorously coincide or if they are slightly shifted with respect to each other on the temperature scale.

In the temperature range of existence of the gel, a dramatic decrease of the molecular chain dynamics is demonstrated by means of the appearance of T_2^{s} for both α-CH_3 and OCH_3. To a reasonable degree of accuracy, the fraction of either group involved in the helical regions which laterally associate to produce the junctions of the physical gel is numerically the same (i.e., 0.26 ± 0.02). Presumably, this value would also correspond to the fraction of the main chain units undergoing the same process, where it is possible to measure it from the 860 cm^{-1} band. The very short T_2 values and the T-lag in the cooling experiment (indicating a high activation energy) convergently suggest that several consecutive repeating units are involved in the conformational transition/association process. The stability of such cooperative units is very likely determined by intermolecular interactions in addition to the conformational features of the single (helical) chain per se.

Solute–solute interactions are hereby also proposed as the molecular origin of the separation of the OCH_3 groups into two groups, i.e., one characterized by a less restricted mobility (T_2^1), essentially unaffected by such interactions, and one by a more restricted mobility (T_2^m), heavily affected by them. The noteworthy observations that the two groups are both present also for sPMMA in chloroform as well as that they show an interesting concentration dependence will be addressed later on. The two groups are present both for aPMMA and for sPMMA in toluene, suggesting that they are to be correlated more with molecular properties of the given polymer/solvent system rather than with the tacticity of the chain. Under this hypothesis, the fractional distribution of the former isomer (Figure 3b) can be taken as the ideal reference type of behavior, devoid of long junction-forming stretches, for the latter polymer as well. A comparative analysis of the data of Figures 3b and 4b at 20 °C then reveals that the groups involved in the cooperative helical gel junctions of sPMMA originate mostly from the T_2^m group. More precisely, the fraction corresponding to this group passes from 0.70 in aPMMA to 0.52 in sPMMA. The difference (0.18) amounts to 75% of the fraction of groups of sPMMA with very low mobility, T_2^s (0.24). This brings further support to the proposed important role of intermolecular interactions in the buildup and stabilization of the cooperative helical junctions.

However, the conformational transition does not exclusively pertain to the latter units. In fact, the temperature profiles of the T_2^m and of the T_2^1 fractions, both for aPMMA and for sPMMA, are not as expected for a system of two species in equilibrium, differing only as to their mobility. On the contrary, they all show a nonmonotonic variation with T, with a significant departure in the T range of conformational change. In addition, the T dependence of T_2^1 is clearly bimodal with a break in the same range of temperature. It is not possible to properly quantify the fraction of either more mobile groups (T_2^1) or less mobile ones (T_2^m) which undergo a conformational change. Only a rough estimate can be made as follows. One can tentatively assume that the monotonic behavior of the fractions corresponding to T_2^1 and T_2^m for aPMMA and for sPMMA, in the range of temperature from 75 down to 60 °C is the "expected" trend, in the absence of conformational changes. From the deviation at lower temperatures from such an ideal "baseline", one can then approximately calculate that about 5% (and certainly not more than 10%) of residues which are not contained in highly cooperative stretches are nevertheless involved in a temperature-dependent conformational transition, with very little or no cooperativity at all. In the case of sPMMA such units anyway contribute to the overall buildup of chain rigidity and of junction formation. They could possibly be related to the "bump" of the G' curve in the heating mode (see Figure 1c). Such a "thermomechanical reshuffling" could explain a secondary role of theirs in gel structure formation, which can be manifested only in a system that possesses also the (much) longer conformationally regular tracts necessary for the primary events in gelation. As to the latter stereoisomer, from the temperature dependence of the T_2 relaxation times of the methoxy groups, one can conclude that some degree of conformational structure formation has taken place also in solutions of aPMMA in toluene. Although no gel formation has been observed, an already mentioned small but neat change in the temperature dependence of T_2^1 and T_2^m is observed around 48 °C. This corresponds to the temperature domain of gel melting in solutions of sPMMA. This allows one to conclude that even in solutions of the atactic isomer, a small fraction of chain repeating units is incorporated in helical segments, albeit of low cooperativity. Both because of their very low concentration and the low cooperativity, no direct evidence can be found from FTIR nor from any observation of T_2^s by NMR. All this also prevents the formation of a continuous "gel-network" but does indeed affect the solution behavior. Such a conformational transition was also observed by Katime et al.[11] by means of light scattering experiments on aPMMA in toluene. At any event, the fact that these structures "melt" in the temperature region where melting of the gel of sPMMA takes place suggests that the same basic conformational organization has to be responsible for this transition.

Still, the evolution of the conformational change is only a "modulation" of the quantitatively more relevant presence of two well-defined sets of OCH_3 groups also in aPMMA. The concentration dependence of their respective mole fractions suggests that the group with T_2^m is certainly not dominated by preferential interactions with the solvent, but rather by solute–solute ones. On the other side, whether such solute–solute interactions, which determine T_2^m, stem either from interpolymer intermolecular contacts or from intrachain contacts with units far apart on the same chain is not known. It is however soundly demonstrated that such interactions are correlated with the very macromolecular nature of the system, inasmuch as the presence of such two different types of T_2 groups is only found in polymer solutions and not in solutions of low molecular mass esters. The statement is further supported by the data obtained through the investigation of the concentration dependence of the relaxation behavior. This analysis was performed with solutions of aPMMA in which no gelation is taking place so that only T_2^1 and T_2^m are observed. At 102 °C and at high enough concentration, i.e., above the critical overlap concentration, the probability of interaction between ester groups is efficiently taking place and the equilibrium is shifted toward the low mobility side. On the contrary, at low concentration (eventually below the critical overlap concentration), interresidue contacts are strongly decreased and the "solvated" ester groups dominate. In toluene at $w_2 = 0.0001$, the relaxation becomes monoexponential: only the highly mobile, solvated groups remain. This is not yet fully observed at this concentration in chloroform, a better solvent than toluene. But it should be remembered that the measurements in chloroform were performed at 55 instead of 102 °C for practical reasons.

Conclusions

The following conclusions can be drawn from this investigation:

1. The combination of rheology, FTIR, and NMR relaxation measurements have led to the unambiguous correlation between a cooperative conformational transition and gelation of sPMMA in toluene. The average fraction of chain repeating units incorporated in the helical interchain junctions, calculated using the T_2 data, is 0.26 ± 0.02.

2. Solutions of aPMMA at room temperature show some degree of structure formation.

3. Two types of methoxy groups are present in chain units that are not incorporated in helix segments or in solutions where no structure formation did take place. Their difference in mobility arises from their different environment. Low mobility results from interresidue interactions while high mobility is ascribed to preferential interactions with the solvent.

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