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Thermoreversible gelation of solutions of isotactic poly(methyl methacrylate) in 2-butanone

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Abstract

The mechanism of thermoreversible gelation in solutions of isotactic poly(methyl methacrylate) (iPMMA) was investigated through the study of the temperature-concentration relations, the melting behavior of the solvent and the gel, the change in molecular conformation by FTIR spectroscopy and structural analysis by wide angle X-ray scattering. Such a gelation proceeds very fast below −20°C while crystallisation from solution necessitates an induction period of several weeks, even at high degrees of undercooling. The molecular conformation is different from the one in crystalline samples. The mechanism consists of different steps: a coil to (double) helix transition followed by an intermolecular association that finally leads to a macroscopic crystal lattice. The data clearly illustrate that such a crystalline state is reached by a mechanism that is different from the well-known folded chain crystallisation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Isotactic poly(methyl methacrylate); Gelation; Crystallisation

1. Introduction

Isotactic poly(methyl methacrylate) (iPMMA) is a very slow crystallising polymer [1]. Nucleation from the melt or from solutions takes several days or even weeks [1–3]. An orthorombic unit cell ($a = 41.96$, $b = 24.34$ and $c = 10.5$ Å) with the polymer chain in a double-stranded helix has been proposed [3,4]. This unit cell contains eight double helices with left and right handed ones in a hexagonal-like closest packing mode. The proposed space group is Fddd-D_{2h}. This slow process of structure formation will be further called “crystallisation”.

iPMMA is also able to form gels in several organic solvents. The mechanism of gelation depends on the kind of solvent. In aliphatic alcohols, solidification of the solutions proceeds through the interference of liquid–liquid demixing and vitrification [5]. This liquid–liquid demixing can also interfere with crystallisation of the polymer [5]. Hazy gels are formed in 2-butanone [5] and butylacetate [6]. The melting point of the gel in 2-butanone is concentration independent. This process of structure formation will be further called “gelation”.

The purpose of this article is to investigate in more detail the gelation process in 2-butanone. This behaviour will be compared with the process of crystallisation.

2. Experimental

2.1. Materials

iPMMA was synthesized at room temperature in toluene, with phenylmagnesiumbromide as the initiatior [7]. The polymerisation was performed under high vacuum.

The molecular mass was determined by GPC at room temperature, using tetrahydrofuran as the solvent. The samples have a bimodal molecular mass distribution [8]. The two fractions could easily be separated because of their large difference in average molecular mass. The high molecular mass fraction was precipitated from a 2% solution in toluene by adding the nonsolvent petroleum ether. The second fraction was then isolated from the remaining solution by precipitation in petroleum ether. From the different polymerisation’s that were carried out, three polymers were selected for this study. Their characteristics are summarized in Table 1.

The tacticity was determined by ^{13}C NMR. No signal of hetero or syndiotactic triads could be detected with iPMMA2 and 3. iPMMA1 has a heterotactic triad content of 2%.

2-butanone (Aldrich, p.a.) and 4-heptanone (Aldrich, p.a.) were used without further purification.

2.2. Experimental methods

The calorimetric measurements were performed with a

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Table 1
Characteristics of the iPMMA samples

Name	$\bar{M}_n$ ($\times 10^3$)	$\bar{M}_w$ ($\times 10^3$)	$\bar{M}_w/\bar{M}_n$
iPMMA1	20	41	2
iPMMA2	40	56	1.4
iPMMA3	832	1300	1.6

Perkin–Elmer DSC-7, connected to a Thermal Analysis Data Station. The polymer solutions were made in large volume pans. All the experiments were carried out at a scanning rate of 5°C/min.

The WAXS measurements were performed with a Rigaku Rotaflex 200B.

The infrared spectra were measured with a Perkin–Elmer 2000-FTIR spectrometer. Thin films were casted from solution on NaBr-pellets. Solutions were measured using an ATR-MIR-cel (attenuated total reflection-multiple internal reflection). The temperature in the cell was controlled through an external thermostat. The heating and cooling rate was 0.7°C/min.

The concentration of the solutions is expressed in mass fraction of polymer, w_2.

3. Results

3.1. Crystallisation, gelation and glass transition

The synthetic procedure followed in this work results in an amorphous polymer that dissolves easily at room temperature in 2-butanone to form a homogeneous solution. Three different thermal transitions can be observed in these solutions: crystallisation, gelation and glass transition.

When a solution for e.g. $w_2 = 0.2$ is left for several weeks at room temperature, no crystallisation takes place. At −20°C, the formation of a white crystalline precipitate requires an induction period of 16 days. This crystalline phase dissolves on heating at around 50°C at this specific concentration. WAXS analysis reveals the presence of the same crystalline structure as the one obtained by crystallisation from the melt (Fig. 1(a) and (b)).

Below −20°C a hazy gel is formed within minutes and this gel melts on heating around 5°C ($w_2 = 0.10$). Crystallisation with the formation of this crystalline precipitate does not take place anymore below this temperature limit.

A glass transition, T_g, can be observed in solutions with a high polymer concentration ($0.60 < w_2 < 1.00$). In a concentration range of $0.7 \leq w_2 \leq 1.00$ vitrification of the solution takes place in the DSC experiment at a scanning rate of −5°C/min. At lower polymer content ($0.50 < w_2 < 0.70$) quenching of the solution will also lead to an amorphous, vitrified system. Such vitrification does not take place at lower polymer content and the result of quenching is always a structured solution. The T_g–w_2 relationship is represented in Fig. 2.

3.2. Phase relations in solution

3.2.1. Crystal melting points

The concentration dependence of the melting point

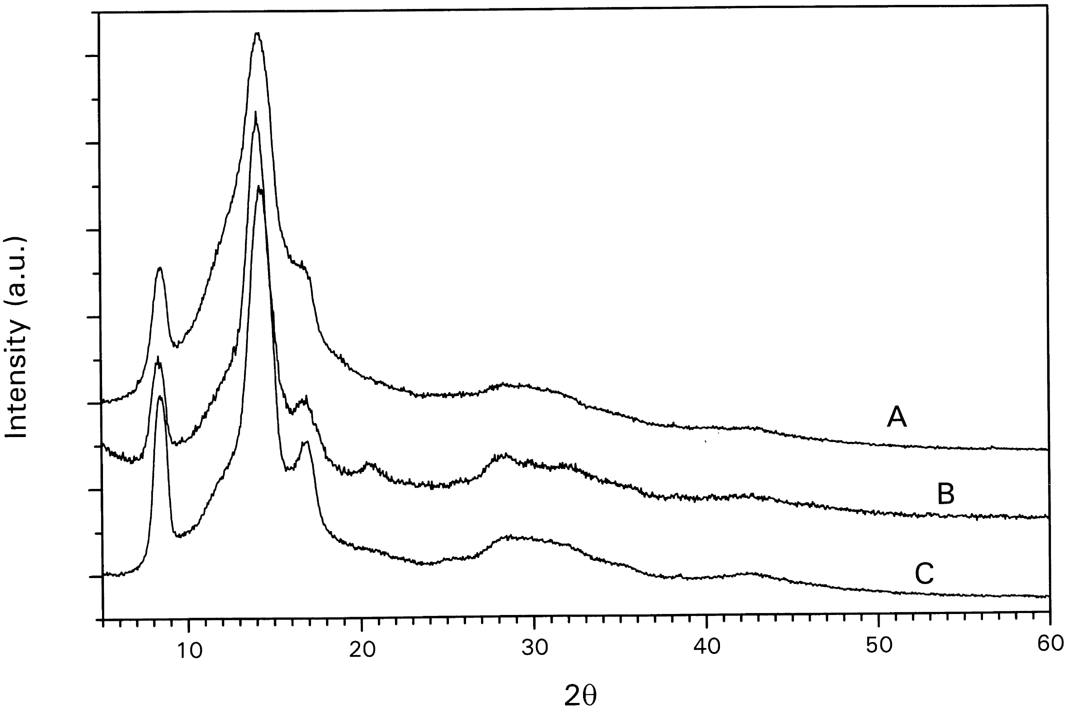

Fig. 1. WAXS spectra of semicrystalline iPMMA: (A): crystallised from 2-butanone solution at −20°C; (B): crystallised from the melt at 120°C; (C): crystallised from 4-heptanone solution at 20°C.

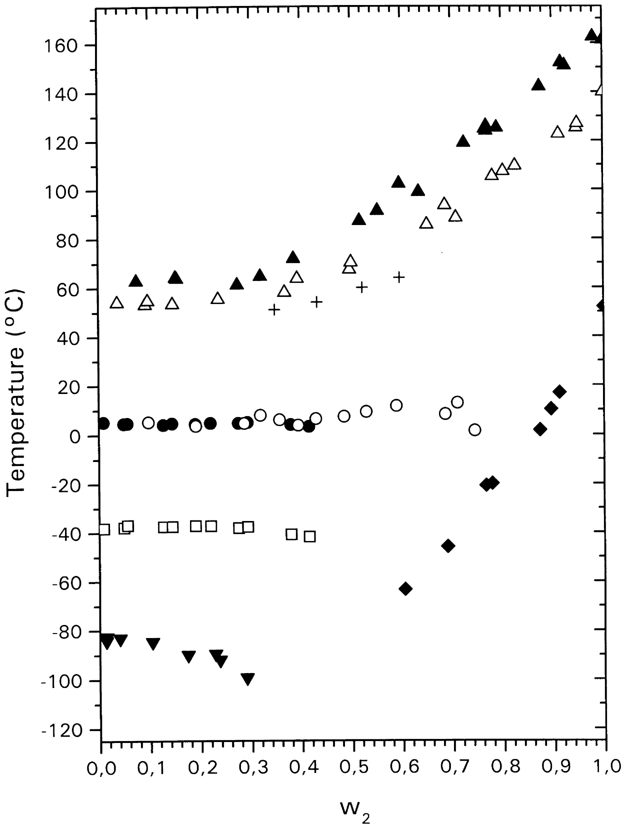

Fig. 2. Temperature-concentration diagram of the system iPMMA/2-butanone; melting after crystallisation in 2-butanone solution (+); melting of a suspension of crystals obtained from a 4-heptanone solution, △—iPMMA2, ▲—iPMMA3; melting of the gel, T_m^g, ●—formed on cooling at −5°C/min, ○—formed through annealing at −30°C for 7 days; (□) temperature of formation of the gel, T_f^g, at −5°C/min; (◆) glass transition temperature, T_g; and, (▼) melting point of the solvent.

(T_m–w_2 relation) of the system iPMMA/2-butanone was investigated by the DSC. The temperature at the end of the melting endotherm was taken as the melting point of these two component systems. The data were obtained in two different ways. Most of them result from the heating of suspensions of crystals of iPMMA, prepared in a separate experiment by isothermal crystallisation from a dilute solution ($w_2 = 0.02$) in 4-heptanone at 20°C. The crystalline precipitate obtained in this crystallisation process has the same crystal morphology as melt-crystallized samples and samples crystallised from 2-butanone. They are separated from the solvent and suspended in 2-butanone. Suspensions with different polymer content were heated in the DSC. This method was preferred prior to the direct crystallisation from 2-butanone because of the very low rate of crystallisation in this last solvent. Both methods lead to the same shape of the T_m–w_2 relation but with a small difference in the values of the melting points. An increase of the molecular mass leads to shifts in the T_m–w_2 relation to higher temperatures (Fig. 2).

Table 2
Degree of crystallinity of iPMMA crystallised in different ways

Crystallisation method	Melting enthalpy (J/g)	Crystallinity (%)[a]
Melt, 120°C	26.25	52
2-butanone, −20°C	12.65	25
4-heptanone, 20°C	29.40	58

[a] Crystallinity calculated with the melting enthalpy of the perfect crystal proposed by Kusy [11].

The crystallinity of the samples depends on the method of crystallisation. The highest crystallinity is obtained by crystallisation in 4-heptanone solution. Crystallisation in 2-butanone leads to the lowest degree of crystallinity. This can be deduced from the WAXS patterns (Fig. 1) and the DSC observations (Table 2). An explanation for this influence of the solvent can be found in the difference of solvent quality of 2-butanone and 4-heptanone. The last one is a Θ-solvent for iPMMA and it is well known that crystallisation from a poor solvent proceeds much faster than from good solvents and results in a much higher degree of crystallinity. This pronounced influence of solvent quality on crystallisation can be ascribed to the interference with a liquid–liquid demixing (L–L demixing) [9,10]. The temperature at the maximum in the demixing curve with samples in the molecular mass range used in this work is situated around 30°C.

3.2.2. Gel formation and melting

Cooling a solution in the DSC at −5°C/min results in an exothermic transition that leads to gelation of the solution. The temperature at the onset of this signal is situated around −40°C. This temperature will be further called the gelation temperature, T_f^g. Heating at 5°C/min results in an endothermic melting with a final melting temperature, T_m^g, around 5°C. This last transition temperature is concentration and molecular mass independent and is not influenced by the time or temperature of annealing. These two transition temperatures are plotted in the temperature-concentration diagram in Fig. 2.

Under these dynamic conditions no transition is observed on cooling in solutions with $w_2 > 0.5$. This is mainly due to the proximity to the glass transition temperature in this concentration range, which prevents structure formation.

Isothermal treatment at temperatures above T_f^g on the contrary allows the usage of samples with higher polymer content. The upper limit of this structure formation is situated at a few degrees below −20°C. Above this limit, crystallisation takes place with the formation of the crystal structure similar to the one obtained in melt crystallisation. The T_f^g–w_2 relation in the high concentration range in Fig. 2 was obtained by annealing solutions at −30°C. Concentrations as high as $w_2 = 0.75$ could be used.

3.2.3. Melting of the solvent

In previous studies on polymer-solvent systems with such a complex behaviour, it has been shown that the solvent can play an important role in the supramolecular organisation. A polymer-solvent compound is in many cases involved in the

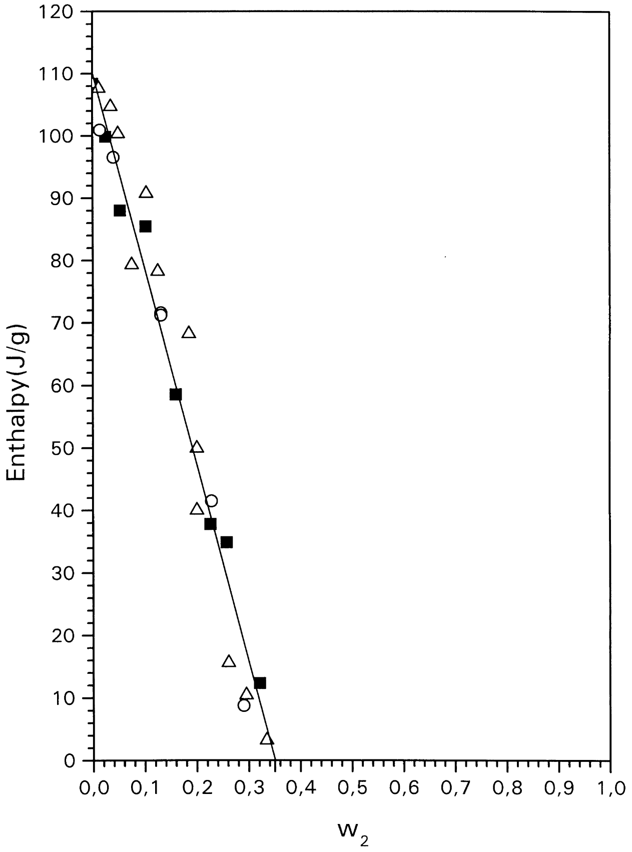

Fig. 3. Concentration dependence of the melting enthalpy of the solvent after different cooling procedures: (△) quenched in liquid nitrogen; (○) cooling at 5°C/min; and (■) isothermal annealing at −30°C.

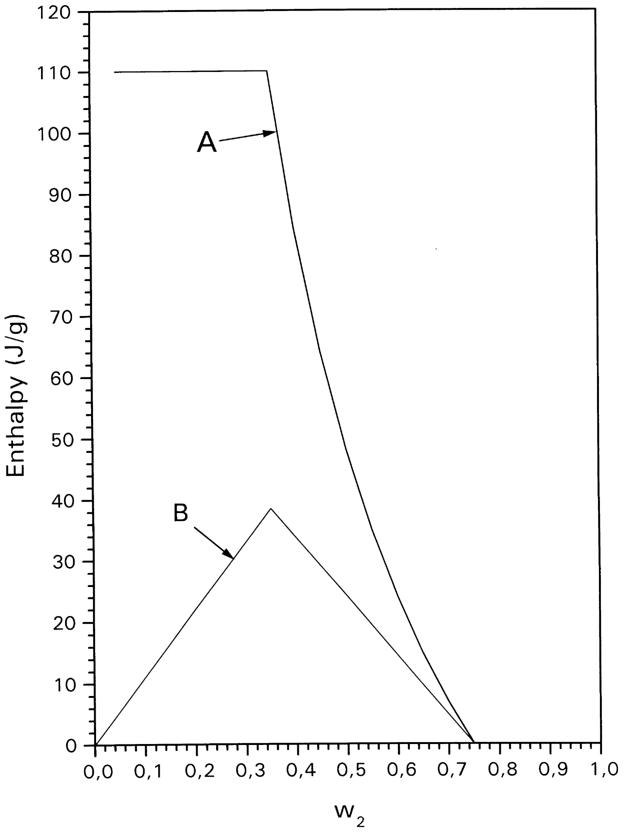

Fig. 4. Schematic representation of the ideal concentration dependence of the melting enthalpy of a compound per gram of polymer (A) and per gram of solution (B).

gelation process [12–19]. Indirect evidence for the formation of such a compound can be found in the concentration dependence of the melting behaviour of the solvent [17]. Crystallisation of the solvent was performed in three different ways. The samples were cooled from room temperature in the following ways:

1. cooling in the DSC at 5°C/min to −120°C;
2. cooling to −30°C with isothermal annealing for 30 min at this temperature, followed by quenching in liquid nitrogen;
3. quenching in liquid nitrogen.

The samples were heated in the DSC and the melting point of the solvent and the corresponding melting enthalpy were recorded.

The concentration dependence of the melting point of the solvent (T_m^s), reported in Fig. 2, was obtained from calorimetric observations. The highest polymer concentration at which crystallisation of the solvent can be observed is $w_2 = 0.35$.

The melting enthalpy decreases linearly with increasing polymer content, w_2, and this decrease is independent of the cooling procedure (Fig. 3). The melting enthalpy always becomes zero at $w_2 = 0.35$.

It was observed that structure formation on cooling could not be avoided whatever the cooling procedure was. Moderately concentrated solutions are always in the gel state when heated above the melting point of the solvent.

These observations point into the direction of the formation of a polymer-solvent compound with a composition $w_2 = 0.35$. This corresponds with 2.5 molecules solvent per repeating unit.

3.2.4. Melting enthalpy of the gel phase

The melting enthalpy of the gel phase was measured as a function of the solution composition. This structure formation is suppressed in the high concentration region because of the interference with the glass transition of the solution. The upper concentration limit depends on the experimental procedure. In a dynamic experiment at 5°C/min, the limit is $w_2 = 0.60$. In an isothermal experiment at −30°C, this limit shifts to $w_2 = 0.75$.

Between $w_2 = 0$ and this upper limit, a maximum has to be found at the composition of the compound ($w_2 = 0.35$) when this enthalpy is expressed in Joules per gram solution [17]. When this enthalpy is expressed in gram of polymer present in the solution, a constant value has to be observed between $w_2 = 0$ and the composition of the compound, followed in the higher concentration range by a gradual decrease to zero at the upper limit reported earlier. Such a

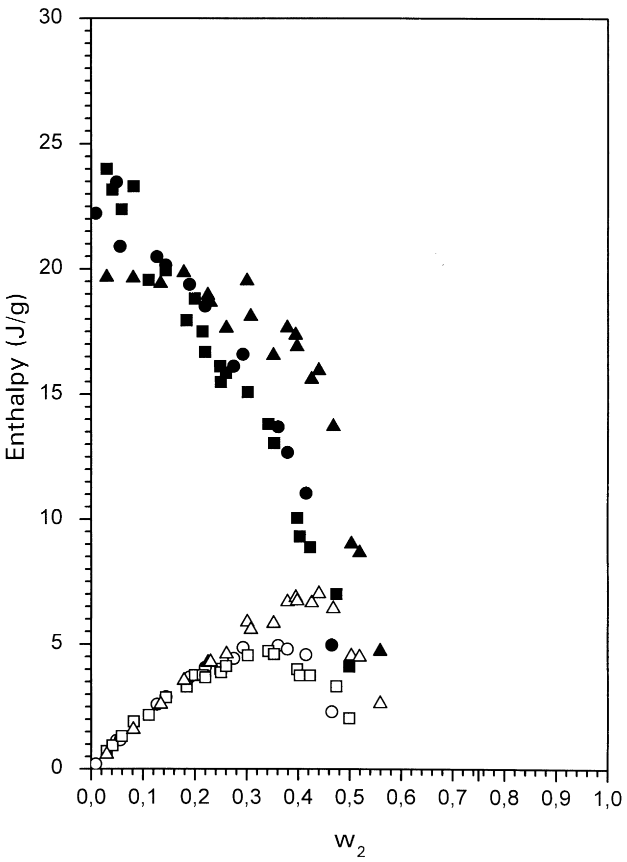

Fig. 5. Melting enthalpy of the gel after dynamic gelation (−5°C/min): iPMMA1: △ J/g gel; ▲ J/g polymer; iPMMA2: ○ J/g gel; ● J/g polymer; iPMMA3: □ J/g gel; ■ J/g polymer.

behaviour is schematically represented in Fig. 4. The calculations that led to this figure are based on the coexistence of a very dilute solution and the compound in the concentration range $0 < w_2 < 0.35$ and the compound and glassy phase with $w_2 = 0.75$. This corresponds to a situation where gelation is performed at −30°C. The nonlinear decrease at the high concentration side results from the coexistence of a compound with fixed composition and the glassy state with $w_2 = 0.75$.

The experimental data obtained in a dynamic experiment at −5°C/min and after annealing for seven days at −30°C are represented in Figs. 5 and 6, respectively. In the dynamic experiment, the melting enthalpy per gram solution goes through a maximum at $w_2 = 0.35$ for the two samples with the highest molecular mass, but is situated at $w_2 = 0.45$ for the low molecular mass sample. Isothermal annealing results in a shift of this maximum to higher concentrations (Fig. 6).

The difference between the deviation of the position of this maximum and the composition of the compound deduced from the melting data of the solvent, is the direct consequence of the limited “degree of crystallinity” of the structured solutions. The ideal concentration dependence of the melting enthalpy per gram polymer, represented in Fig. 4, is not followed by any of the samples. A continuous decrease is found in the concentration range $0 < w_2 < 0.35$. In order to get an idea about the limitation in “degree of crystallinity”, the theoretically expected behavior represented in Fig. 4 was fitted with the experimental data obtained after annealing at −30°C of the sample with the lowest molecular mass (Fig. 7). This will not result in a correct picture of the situation, but will illustrate the problem and will allow to estimate the difference between the experimentally realisable situation and 100% transformation.

The curve was fitted starting from $w_2 = 0.75$ through the experimental points obtained at high concentration. This implicitly includes that we accept full transformation in the high concentration range. A value of 110 J/g is obtained for complete transformation into the compound. If this complete transformation is not realised in the high concentration range, then this value will be even higher.

Using this value for the low molecular mass sample, a “degree of crystallinity” of 0.45 is obtained in the very dilute solutions and 0.25 at $w_2 = 0.50$. Samples with a higher molecular mass have an even lower degree of crystallinity.

This problem of limited degree of crystallinity and the influence of time is illustrated by the data reported in Fig. 8. A sample ($w_2 = 0.10$) was annealed at −30°C for different time durations and the melting enthalpy was measured after each annealing period. A linear increase of the transition enthalpy with the log of time is observed up to about 400 min. Then the relation levels-off but even after 10^4 min this crystallinity is still increasing and the value obtained after 10^4 min or seven days, corresponds to the value reported in Fig. 7 for this specific concentration. This value is still far below the final value of the melting enthalpy (110 J/g, $0 < w_2 \leq 0.35$) that should be reached when 100% transformation is obtained.

4. Conformational changes during gelation

4.1. Characteristics of the helix conformation in the gel

Changes in molecular conformation during gelation were followed by FTIR spectroscopy. A solution with $w_2 = 0.10$ was investigated. The region between 1500 and 1000 cm^{-1} is the most sensitive to conformational changes [19–21]. The spectra obtained in this frequency range with three different samples are represented in Fig. 9. The gel spectrum contains three absorption bands that are not observed with the crystalline or amorphous sample. They were also not predicted by normal mode calculations based on the helix conformation proposed for the melt crystallised samples [21]. These observations indicate the formation of a helix conformation different to the one obtained in melt crystallised samples. It is clear that this hypothesis has to be further verified through other techniques like WAXS.

The typical bands for each conformation are summarised in Table 3.

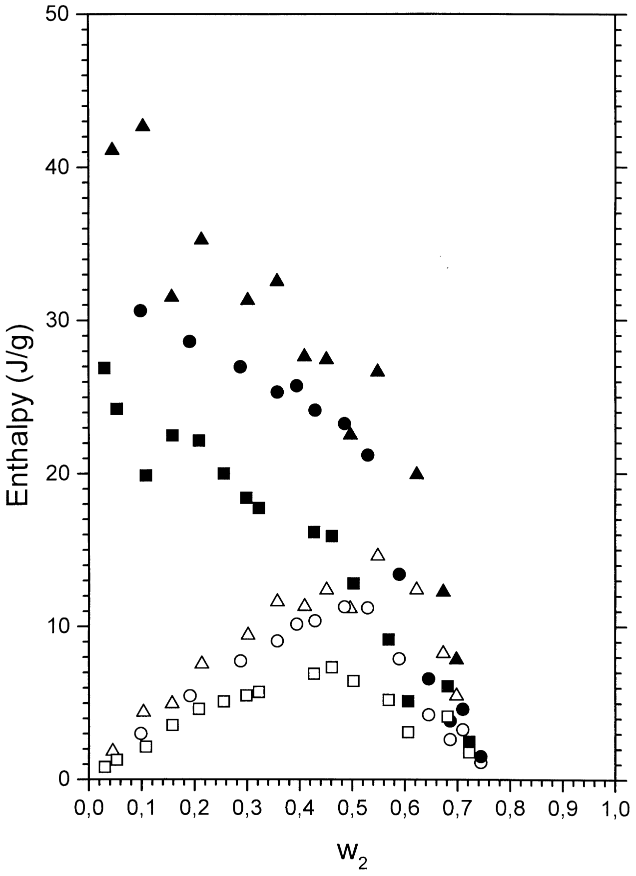

Fig. 6. Melting enthalpy after isothermal annealing at −30°C: iPMMA1: △ J/g gel; ▲ J/g polymer; iPMMA2: ○ J/g gel; ● J/g polymer; iPMMA3: □ J/g gel; ■ J/g polymer.

An important difference with the spectra of the amorphous and the melt crystallised sample is the increased resolution in this frequency region. A typical example is the splitting of the peak at 1150 cm^{-1}, a characteristic band of a carboxylic ester. This separation in two absorption bands was only obtained up to now with a melt crystallised, strongly oriented, sample. The absorption band at 1144 cm^{-1} shows an high intensity when polarised light is used with the polarisation direction perpendicular to the stretching direction. The band at 1160 cm^{-1} is clearly defined when the polarisation direction is parallel to the stretching direction. The absorption band at 1250 cm^{-1} (asymmetric stretching of the C–C–O coupled with symmetric stretching of C–O [19]) on the contrary decreases in intensity.

The absorption band at 1295 cm^{-1} originates from backbone and methylene vibrations and can be seen for both the semicrystalline and the gel samples. However, a better resolution is observed in the gel.

4.2. Temperature dependence of intensity of the absorption band

For practical reasons (mainly the ease of integration) the intensity absorption band at 1295 cm^{-1} was followed as a function of the temperature at a cooling rate of 0.7°C/min. The data are reported in Fig. 10.

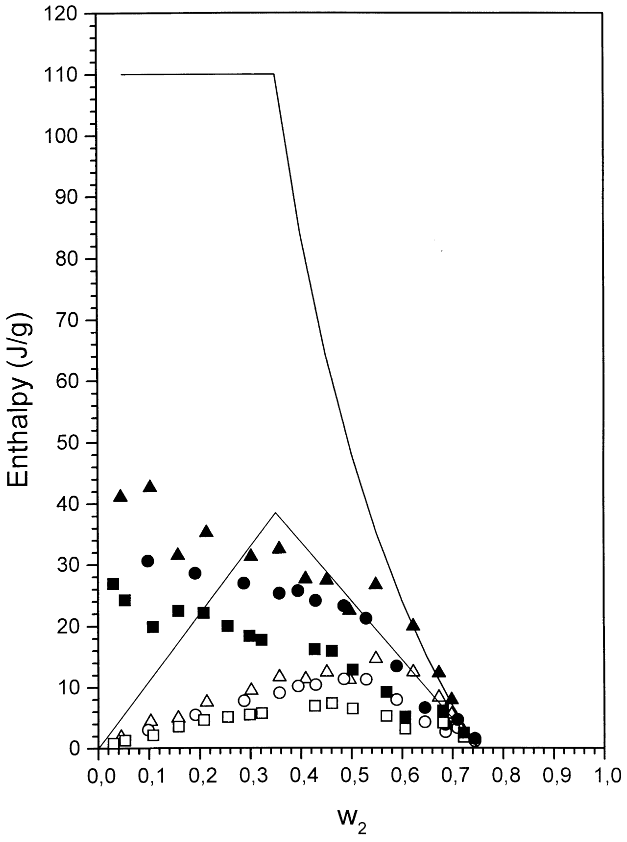

Fig. 7. Fitting of the schematic representation of Fig. 4 onto the data of Fig. 6.

The intensity remains constant up to −28°C, and an important increase takes place within 10°C. Heating results in a large hysteresis and the regular conformation disappears completely at around 0°C. The final melting point observed in the DSC experiments is situated around 5°C. One can conclude that both techniques follow the same structure formation and melting. The difference in the final melting point is the consequence of the difference in scanning rate: 0.7°C/min in IR vs. 5°C/min in the DSC. Lower scanning rates could not be used in the DSC because of the low enthalpy values involved.

4.3. Time dependence of the intensity of the absorption band

Isothermal annealing at −30°C results in an increase in the intensity as a function of time till a plateau value is reached after about 35 min (Fig. 8). This intensity increase proceeds linearly with the log of time. Extrapolation of this linear relationship leads to an induction period of only 2.5 min. We can therefore conclude that the change in the conformation from coil to helix sets in without any delay when the annealing temperature is reached.

The plateau value is situated exactly on the heating curve

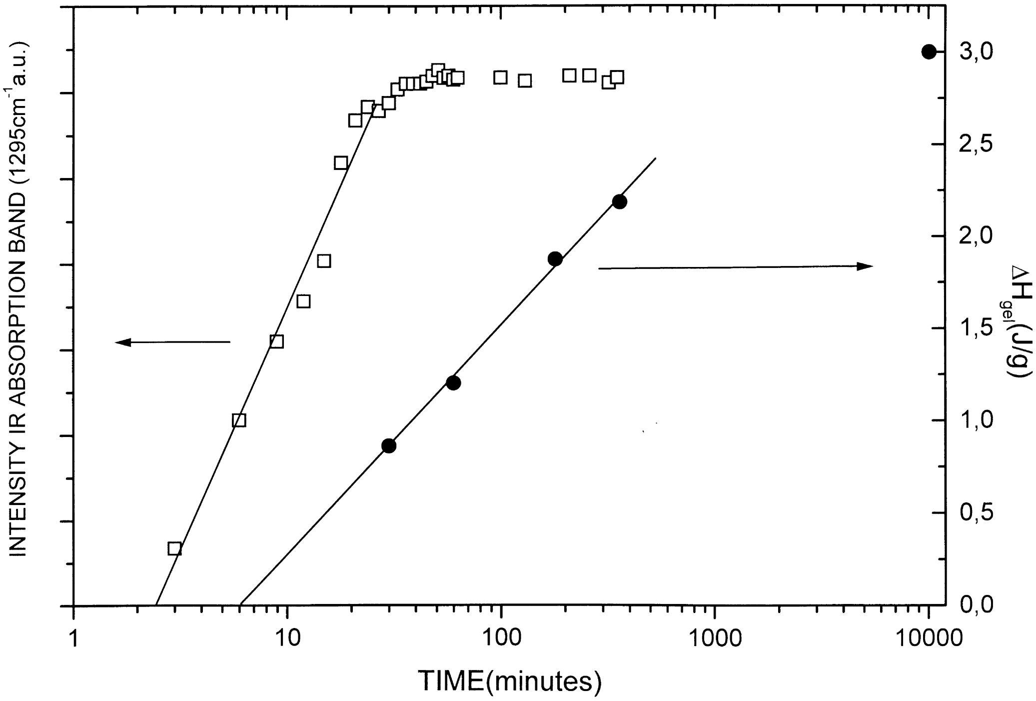

Fig. 8. Time dependence melting enthalpy of the gel per gram gel (●) and of the intensity of the IR absorption band at 1296cm^{-1} (☐) (isothermal annealing at −30°C, $w_2 = 0.10$).

in Fig. 10. This observation is similar to what was observed with the syndiotactic isomer in toluene [22]. In this last case, such a behaviour observed at different annealing temperatures, led to the conclusion that the change in the intensity on heating represented an equilibrium value. This change with temperature represents the temperature dependence of the equilibrium constant of the equilibrium between coil and helix. The similarity between Fig. 10 and the data reported in Ref. [22] suggests that one is dealing with the same equilibrium phenomenon of coil–helix and that the heating curve in Fig. 10 represents the change with the temperature of the equilibrium value of the degree of helicity.

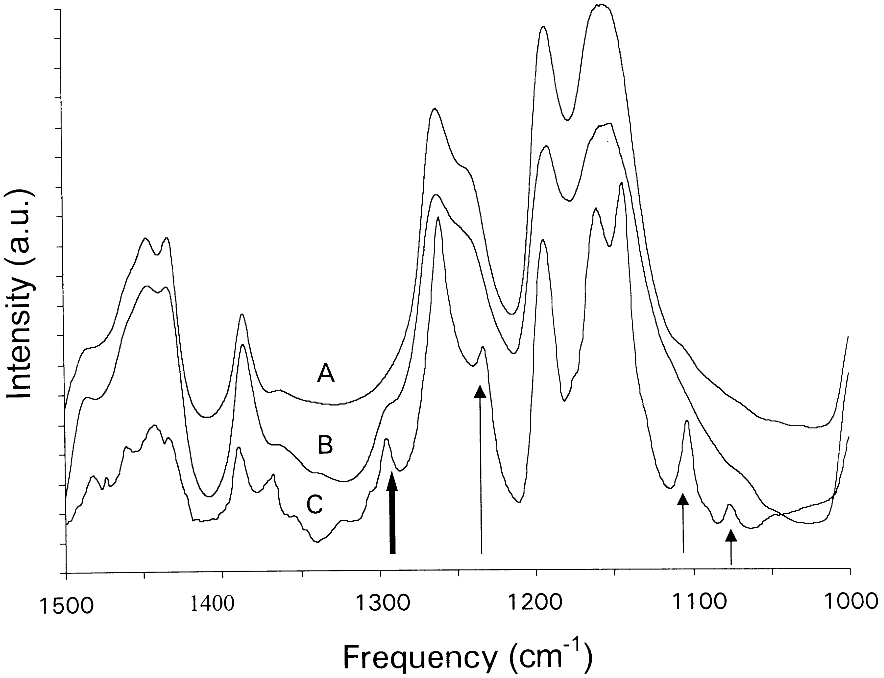

Fig. 9. Representative FTIR spectra of iPMMA: (A): amorphous; (B): melt crystallised; and (C): gel in 2-butanone.

Table 3
Characteristic IR absorption bands of iPMMA

Characteristics bands of the amorphous phase (cm^{-1}) [19]	Characteristics bands of the crystalline phase (cm^{-1}) [19]	Characteristics bands of the gel phase (cm^{-1}) (experimental)
938	882	1232
1047	1295	1104
	1339	1077

From Fig. 8 it is also clear that the change in the molecular conformation proceeds much faster than the increase of the melting enthalpy of the structures formed. Absence of flow on the contrary is already observed after 5 min.

5. Discussion

Gelation of solutions of iPMMA differs in several aspects from melt or solution crystallisation.

- The molecular helix conformation in the gel phase is different from the one observed in the crystalline phase. These differences are clearly seen in the FTIR spectra. The formation of these helices at −30°C proceeds quickly and the final degree of conformational transformation is reached within 35 min. In this process the solvent plays an important role: the melting enthalpy of the solvent becomes zero at $w_2 = 0.35$ in a solution that is given the time to reach complete coil-to-helix transition. But even quenching in liquid nitrogen leads to the same result and even this very fast cooling procedure cannot prevent the formation of the polymer-solvent helix compound. The concentration $w_2 = 0.35$ corresponds with the formation of a molecular compound with 2.5 solvent molecules per chain repeating unit.
- Parallel with this conformation change, a physical network is formed: only 5 min are needed to observe the absence of flow.
- The initially transparent gels become very opaque with time. This reflects the formation in the early stages of very small supramolecular organisations that will grow with time. The time scale of such a growth is very long and can continue for months. At the end a crystalline lattice will be obtained that will give rise to a WAXS pattern. A large part of the thermal effect of this structure formation process is due to this association step.

One can therefore conclude that gelation is a crystallisation process that differs from the well known process that takes place in the melt or under certain conditions of solution concentration, temperature and kind of solvent. There is

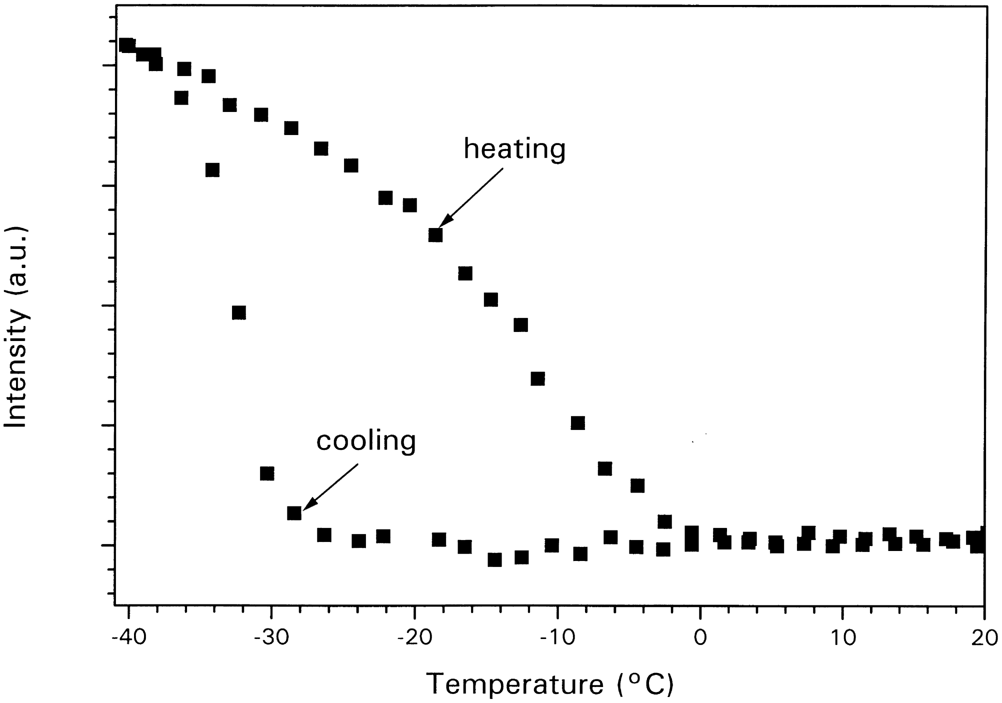

Fig. 10. Temperature dependence of the intensity of the peak at $1296 cm^{-1}$ in a cooling and heating experiment (iPMMA1 in 2-butanone, $w_2 = 0.1$).

a clear distinction between the change in molecular conformation (FTIR) and the intermolecular association (DSC).

The first step leads to a stable helix in solution with the participation of the solvent. The simultaneous formation of a physical gel leaves two possibilities open.

1. The structure formation proceeds through the formation of single helices which associate in a second step into a dimer.
2. A double helix similar to the one proposed for the melt crystallised samples is formed in one step.

With the available results no preference can be expressed for a particular mechanism.

In a second step these dimers or double helices will agglomerate to form a supramolecular organisation similar to a crystal lattice. This proceeds much more slowly than the formation of the helix conformation.

These data are very similar to those observed with syndiotactic poly(methyl methacrylate) in toluene [22]. This suggests that one is dealing here with a more general "crystallisation" process that is completely different from the well known nucleation controlled growth of crystalline lamellae. In this last process the helix conformation is only stable once the molecular segment is incorporated in the crystal lattice. In this "gelation crystallisation", the (double) helix conformation can be stable by itself and incorporation in the lattice will only increase the degree of stability.

However, the final melting point of these structures is almost not influenced by the time of annealing and corresponds with the temperature at which the intensity of the conformational band of the helix structures becomes zero.

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