Thermoreversible gelation of syndiotactic poly(methyl methacrylate)

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The thermoreversible gelation of solutions of syndiotactic poly(methyl methacrylate) in *o*-xylene was studied. The temperature domain of the sol–gel transition is independent of the overall tacticity and polymer concentration. The extent of gelation increases with increasing tacticity. A minimum degree of tacticity, corresponding to a minimum average sequence length, is needed. The combination of infra-red and calorimetric data with rheological observations reveals a two-step mechanism. Gelation is induced by a fast conformational change, followed by an intermolecular association.

(Keywords: syndiotactic poly(methyl methacrylate); thermoreversible gelation; calorimetry; spectroscopy; rheology)

INTRODUCTION

Predominantly syndiotactic poly(methyl methacrylate) (s-PMMA) is an interesting polymer because of its ability to form ordered structures in many solvents. This phenomenon is thermoreversible, organization being introduced on cooling. It has been investigated by various techniques such as n.m.r. and i.r. spectroscopy, osmometry, viscometry and light scattering. The final structure of the solution depends strongly on the solvent. In *o*-xylene, transparent gels are obtained[1-6], but in butyl acetate flocculation and sedimentation are observed[7,8]. No influence of polymer concentration was established, while the thermal history of the solution was reported to have some influence[6]. The formation of ordered structures has been investigated also by high-resolution proton n.m.r. Integration of the polymer proton absorption bands made it possible to determine quantitatively the fraction of immobilized protons[4-6,9-11]. Infra-red observations clearly demonstrate the formation of sequences with regular conformation[12,15,16]. The appearance of a second peak at a higher frequency in the carbonyl stretching region is characteristic for intermolecular interactions. The transition from a predominantly TG to a TT conformation is revealed by an increase of the intensity of the $-CH_2-$ rocking vibration at 860 cm^{-1} at the expense of the intensity of the peak at 843 cm^{-1}. This intramolecular order is maintained after removal of the solvent[15,16]. Films obtained by this procedure are semicrystalline. The crystalline nature of highly concentrated solutions of s-PMMA was also proposed by Rehage[1-3]. Recently, an extended helical conformation was proposed for s-PMMA in oriented swollen films. The inclusion of solvent in the helix as well as its participation in the formation of intermolecular associations was suggested[13,14].

Although a large amount of information is already available, the exact mechanism of the thermoreversible gelation of solutions of s-PMMA is not yet fully understood. The purpose of this paper is to gain further information on this phenomenon by comparing calorimetric and spectroscopic data with rheological observations.

EXPERIMENTAL

Sample preparation

s-PMMA was prepared by polymerizing the monomer with a titanium (IV) chloride–triethylaluminium catalyst in toluene at −78°C (ref. 17). Under these conditions polymers with different tacticity were obtained. The molecular characteristics of the different samples used throughout this work are listed in *Table 1*. The different molecular weights were obtained from gel permeation chromatography. Tacticities were determined by ^{13}C n.m.r. measurements (Brucker 250)[18]. Solutions of these polymers in *o*-xylene were prepared at 85°C at concentrations of 5 and 10 wt%.

Study of the gelation phenomenon

Calorimetric observations were made with a Perkin–Elmer DSC-2C, equipped with a Thermal Analysis Data Station (TADS). Large-volume sample pans (75 μl) containing between 50 and 60 mg of solution were used. Infra-red investigations were made in sealed-liquid, variable-temperature cells.

Mechanical measurements were made with a Rheometrics RMS 705F rheometer with parallel plates test geometry. To avoid slippage between the sample and the plates, the latter were covered with porous glass layers. In this manner a mechanical anchoring was achieved, even when syneresis liberates solvent at the sample surface.

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Table 1 Molecular characteristics of s-PMMA

Sample	M_w	M_n	M_w/M_n	Triad content i	h	s
S.I	167000	63500	2.6	5.5	27.0	67.5
S.II	314000	72700	4.3	1.5	11.0	87.5
S.III	492500	220300	2.2	0.0	8.5	91.5
S.IV	233000	80900	2.9	0.0	10.0	90.0

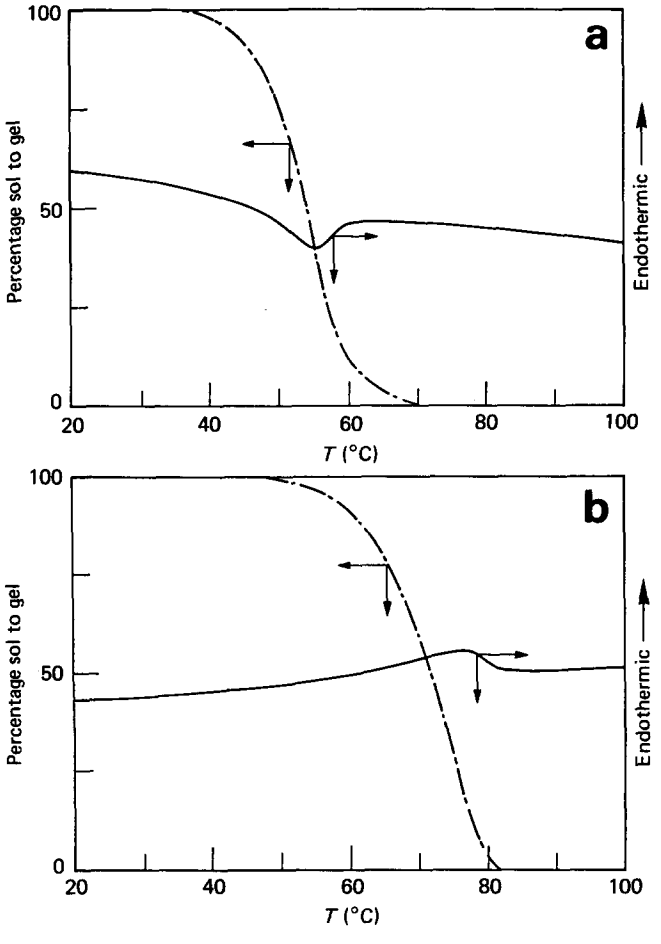

Figure 1 D.s.c. scans corresponding to the gelation (a) and the gel melting (b) of s-PMMA solution (———). The corresponding integral curve (%sol to gel transformation) is also given (–·–·–) S.III, 10% in *o*-xylene)

EXPERIMENTAL RESULTS

Optical observations

On cooling solutions of s-PMMA a transparent gel is immediately formed. On standing, no changes in its optical characteristics are observed. Heating results in a transition to a transparent solution. This phenomenon is fully reversible and does not depend on tacticity, provided the amount of syndiotactic triads exceeds the value of the atactic isomer. The gel formed on cooling is very brittle at any concentration; consequently, stretching, even in the presence of a coagulating agent such as methanol, is not possible.

Calorimetric observations

Dynamic experiments. The gelation of s-PMMA solutions can easily be followed by d.s.c. On cooling, an exothermic signal is observed. Heating results in an endothermic signal (*Figure 1*). At a scanning rate of $5°C\,min^{-1}$ an important hysteresis is observed, which is mainly due to thermal inertia. Extrapolation of the difference between the temperature at the maximum of the endotherm and at the minimum of the exotherm to scanning-rate zero results in a hysteresis of only a few degrees (*Figure 2*).

The appearance of the signals on the temperature scale is independent of tacticity and polymer concentration. Some fluctuations within a few degrees are observed but no direct relation with the overall tacticity can be found. These differences must be ascribed to differences in molecular weight distribution and/or to chain microstructure. The corresponding enthalpy change, however, increases with increasing tacticity. The data are reported in *Table 2*.

Isothermal gelation. To investigate the influence of the gelation time, annealing at constant gelation temperature was effected; sample S.IV was used for this purpose. Solutions were brought immediately to the gelation temperature and annealed for at least 48 h and before melting they were cooled to room temperature. After the first melting (1st run) a cooling at $-5°C\,min^{-1}$ was recorded and a second melting (2nd run) was performed. Two different domains can be distinguished. Annealing between room temperature and 53°C results in an increase of T_m by only 5°C; the melting domain is practically the same, only the maximum of the endotherm

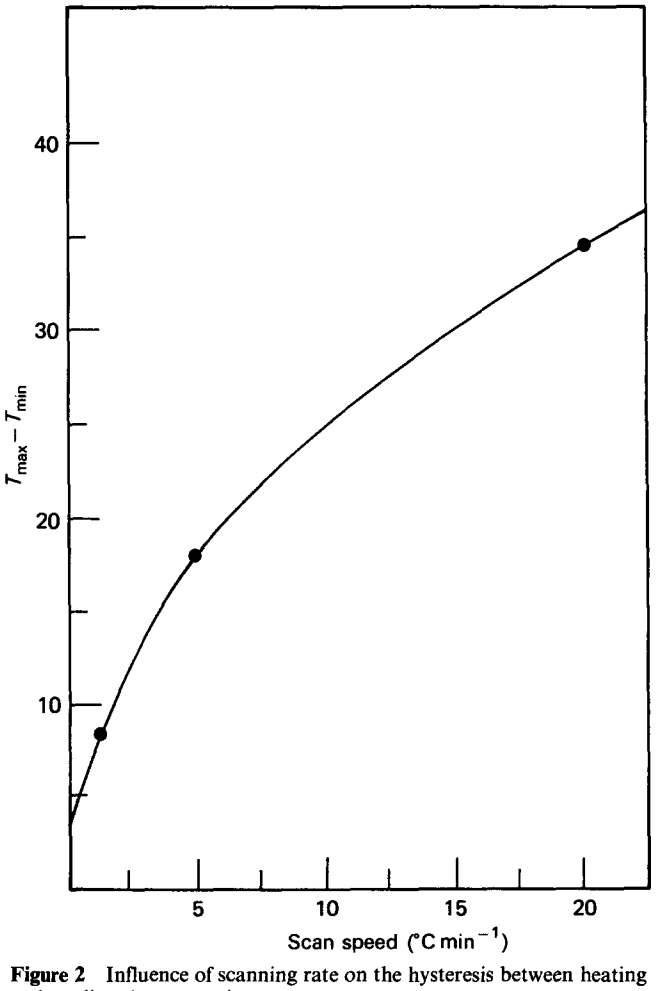

Figure 2 Influence of scanning rate on the hysteresis between heating and cooling d.s.c. experiments

Table 2 Change in enthaly (ΔH) during gel formation and gel melting

Polymer	S	ΔH_{exo}[a] (J g^{-1})	T_{gel}[b] (°C)	ΔH_{endo}[a] (J g^{-1})	T_m[c] (°C)
S.I	67.5	−6.4	49.7	6.4	75.6
S.II	87.5	−12.3	52.0	12.7	70.7
S.III	91.5	−17.8	54.5	17.7	74.9
S.IV	90.0	−17.1	47.0	17.0	72.5

[a] Reduced to the amount of polymer present in the solution; absolute ΔH values were determined by calibration with indium
[b] Gel formation
[c] Gel melting

Table 3 Isothermal annealing of s-PMMA (S.IV) gels

	1st run		2nd run	
T_{an} (°C)	T_m (°C)	ΔH (J g^{-1})	T_m (°C)	ΔH (J g^{-1})
23.0	72.1	20.7	70.9	17.6
48.4	75.2	23.6	71.0	17.8
50.7	74.6	22.2	71.9	20.2
51.6	75.3	22.0	70.3	16.4
53.2	75.0	18.9	70.3	15.0
54.4	77.0	20.4	72.2	16.8
56.8	79.4	23.8	71.3	14.0
59.1	80.2	24.8	71.8	17.0
66.0	70.5–87.4	19.2–3.8	73.4	13.2

is slightly displaced to higher temperatures. At higher annealing temperatures (T_{an}), the whole melting domain shifts to higher temperatures with increasing T_{an}.

The change in enthalpy on melting, ΔH, quickly reaches a constant value around 22 J g^{-1}. At the highest possible annealing temperatures, two melting domains are observed: one completely situated above T_{an}, while the onset of the other one is already found below T_{an}. The melting points and the ΔH values are always higher than those observed during the second run. The data are reported in *Table 3*.

In *Figure 3*, the melting endotherms recorded during the first run, the subsequent cooling and the second run for a low and a high T_{an} are reported. It is clear that at high T_{an}, an important sharpening of the melting endotherm during the first run is observed.

Infra-red observations

When solutions of s-PMMA transform into a gel, changes in the i.r. spectrum are observed. The most interesting frequencies are those at 843 and 860 cm^{-1}, which are ascribed to the $-CH_2-$ rocking vibration and correspond, respectively, to the *tt* and *tg* conformation. Consequently, an increase of the 860 cm^{-1} peak at the expense of the absorption at 843 cm^{-1} is characteristic for a transition from a random-coil into a regular all-*trans* conformation[12]. The ratio of these two peaks was followed as a function of temperature for the different s-PMMA samples. The reduced intensity ratio of a 10% solution in *o*-xylene of S.III is represented in *Figure 4*. This transition occurs in the same temperature domain as that observed in d.s.c. experiments. Its position on the temperature scale is also independent of tacticity and concentration. The same fluctuations on the temperature scale as those encountered in the d.s.c. experiments are observed. The hysteresis of a few degrees is comparable to that found in d.s.c. experiments on

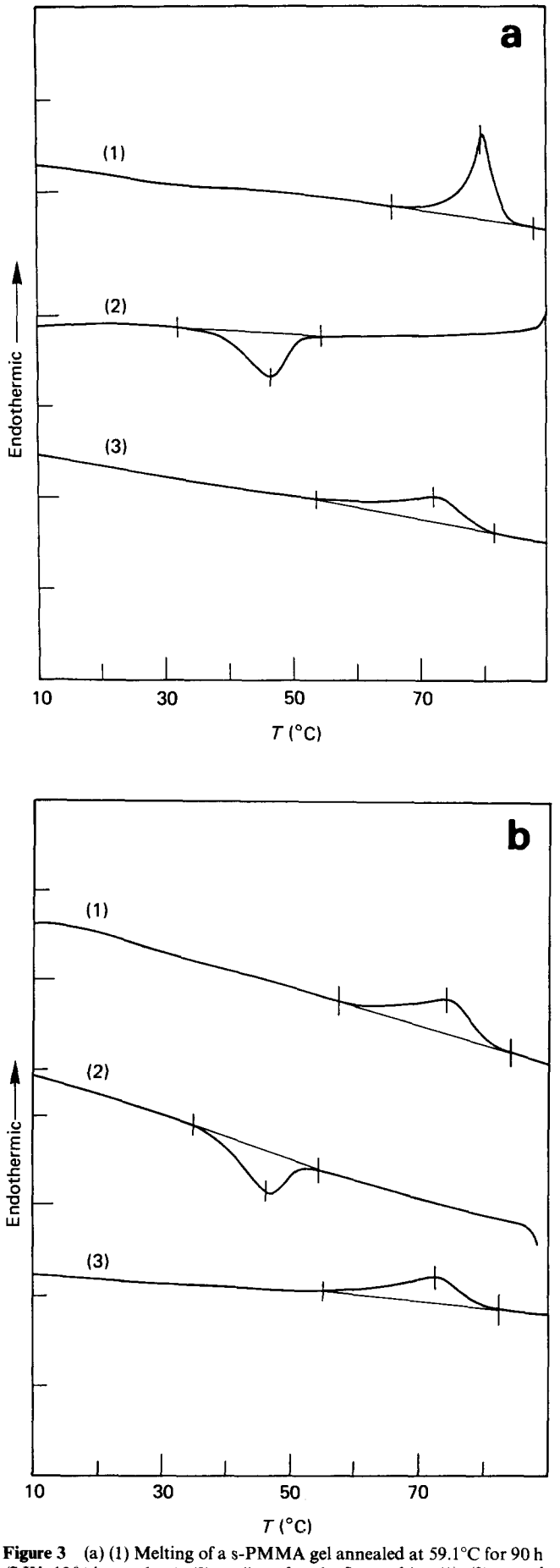

Figure 3 (a) (1) Melting of a s-PMMA gel annealed at 59.1°C for 90 h (S.IV, 10% in *o*-xylene); (2) cooling after the first melting (1); (3) second heating after (2). (b) (1) Melting of a s-PMMA gel annealed at 48.4°C for 16 h (S.IV, 10% in *o*-xylene); (2) cooling after the first melting (1); (3) second heating after (2)

extrapolation to zero scanning rate. The change in the i.r. spectrum is instantaneous and the intensity ratio remains constant as a function of time. Analogous data were obtained with the other s-PMMA samples.

Rheological observations

Mechanical measurements are especially suited to investigate network formation. Two types of measurement have been made.

In a first series of experiments, a gel is formed at constant temperature in a narrow U-shaped tube in an inclined position, then the tube is returned into the fully vertical position and heated. The temperature at which both liquid levels return to the same height is recorded as the onset of gel melting (T_{flow}). The data are reported for S.IV in *Figure 5*.

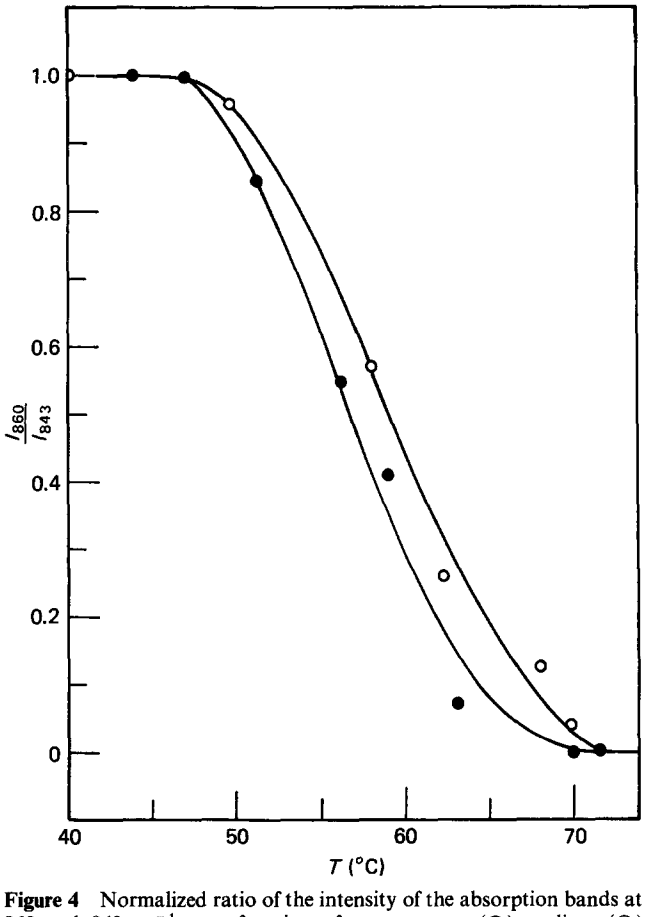

Figure 4 Normalized ratio of the intensity of the absorption bands at 860 and 843 cm^{-1} as a function of temperature: (●) cooling; (○) heating (S.III, 10% in *o*-xylene)

Instantaneous gel formation (points +) occurs only below 55°C. These points were obtained without cooling to room temperature and gel melting was studied by heating the gel from the gelation temperature. When a certain annealing time is applied, gels can be obtained at higher temperatures up to about 60°C. Most of the melting points were obtained after cooling to room temperature before melting. This cooling procedure, however, has no observable influence on T_{flow}.

At the highest temperature, no gel can be obtained on isothermal annealing. This annealing, however, has a pronounced effect when T_{flow} is determined after subsequent cooling the gel to room temperature before melting. An increase of the annealing time results in an increase of T_{flow}. Between room temperature and 45°C an increase of about 4.5 K is observed.

A second series of experiments was made with a rheometer (Rheometrics RMS 705F). Until now, only preliminary data concerning the modulus as a function of temperature have been available. Upon cooling to 63°C the moduli start to grow after a short induction period (*Figure 6*). The increase covers four decades during the first twenty minutes. The rate of change remains nearly constant for more than 1 h (*Figure 7*). Decreasing the temperature further to 58°C accelerates the gel formation and an equilibrium is now reached. This is also the case if the temperature is increased again to 63°C. A further change to 23°C and back to 63°C proves that there is no hysteresis effect in this temperature range. However, a

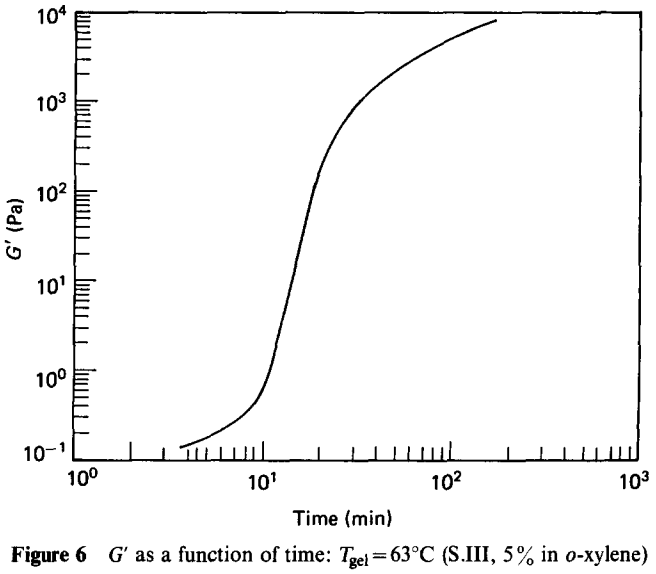

Figure 6 G' as a function of time: T_{gel} = 63°C (S.III, 5% in *o*-xylene)

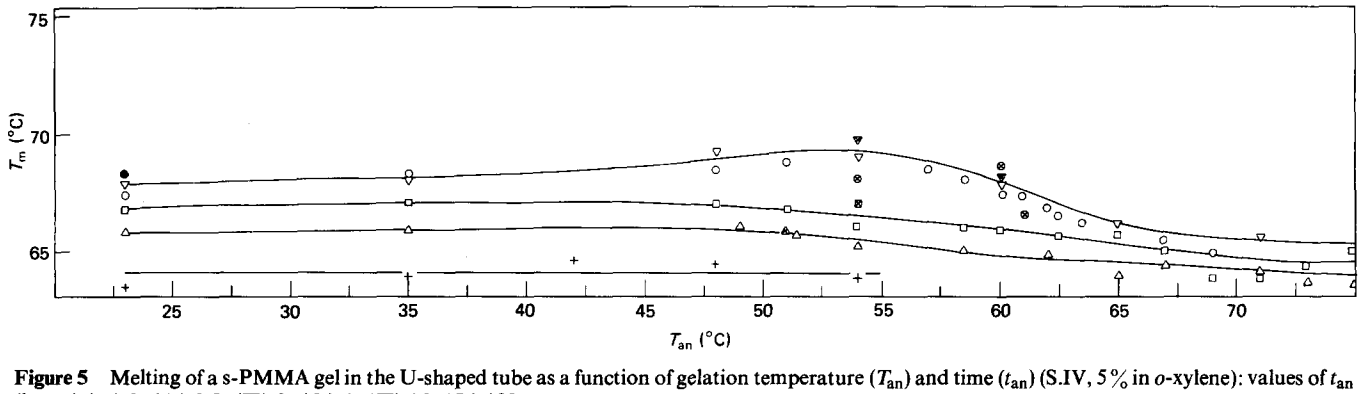

Figure 5 Melting of a s-PMMA gel in the U-shaped tube as a function of gelation temperature (T_{an}) and time (t_{an}) (S.IV, 5% in *o*-xylene): values of t_{an} (hours) (+) 0; (△) 0.5; (□) 2; (○) 4; (▽) 16; (●) 100

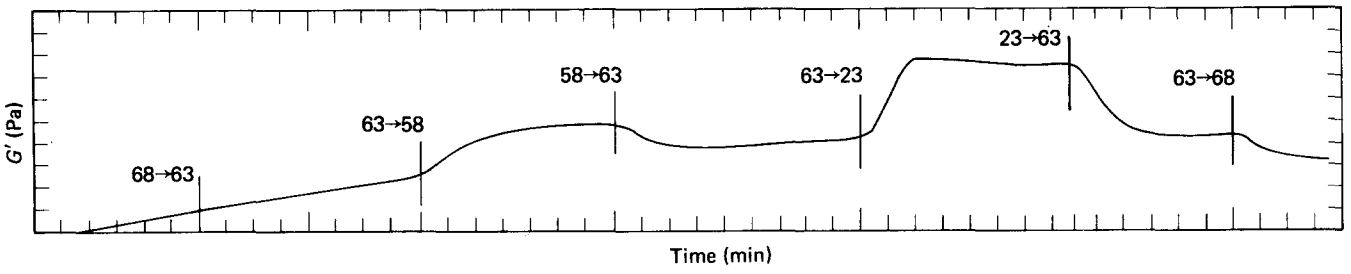

Figure 7 G' as a function of time (S.III, 5% in *o*-xylene). The distance between each scale tick represents 10 min

final increase to 68°C does not readily lead to melting. Such a hysteresis in this range would be in agreement with d.s.c. and i.r. measurements.

DISCUSSION

The main conclusion that can be drawn from the experimental data is that thermoreversible gelation of s-PMMA occurs in two steps by a mechanism quite different from the crystallization–gelation generally encountered. This last type of gelation is a nucleation-controlled phenomenon, occurring at a certain degree of undercooling[19]. A random coil diffuses from the surroundings (melt or solution) onto the growing crystal surface on which they are laid in a regular manner. Consequently, the polymer chains acquire their regular conformation only when entering the crystal lattice.

A different mechanism can be proposed for the gelation of s-PMMA. The two steps responsible for the thermoreversible gelation of s-PMMA are very fast intramolecular conformational changes, followed by an intermolecular association. The occurrence of an intramolecular conformational change is mainly deduced from i.r. observations and d.s.c. data. This transition is independent of polymer concentration and tacticity provided the number of syndiotactic triads is not below a certain limiting value and is at least larger than the amount of these triads in an atactic isomer. This last observation points to a certain degree of cooperativity.

Although i.r. data suggest a transition from a random coil to an all-*trans* conformation, no further comment on this question will be given here. The discussion will be limited to the fact that a 'conformational change' takes place. No quantitative data on the exact conformation are available, mainly because of the important difficulties encountered in stretching these gels.

The calorimetric observations reveal that the enthalpy change during gelation is strongly dependent on tacticity. The i.r. data also indicate that the amount of conformational change increases with decreasing gelation temperature and reaches an equilibrium value at every gelation temperature. Consequently, the amount of regular sequences available for network formation increases in a corresponding manner.

This network formation represents the second step in the gelation: it is responsible for the hysteresis observed in d.s.c. and i.r.; it occurs at a finite rate, which depends on the concentration of ordered sequences. Consequently, the rate of gelation will increase with decreasing temperature because of the increasing amount of regular sequences present. Instantaneous gelation occurs only when the temperature is reached where at least 50% of all the transformable sequences have a regular conformation (e.g. 54°C, *Figures 4* and *5*, S.IV). At higher temperatures, gels are formed at a measurable rate, as can be deduced from the rheological observations. A typical example is given in *Figure 7* where G' is plotted as a function of time. The temperature at which the change of the modulus was measured is situated at the beginning of the transition domain (*Figure 4*) where only a small fraction of regularly ordered sequences are present. In this domain of slow gelation, an increase of the melting point is observed. When annealing is achieved at lower temperatures (more than 50% transformed into regularly ordered sequences), this effect is not present. Annealing also has an important effect on the value of the enthalpy change on melting, which reflects a contribution of the intermolecular associations in this parameter.

From these data, the following scheme can be proposed:

$$m(n\mathrm{C}) \overset{K}{\rightleftharpoons} m(n\mathrm{R}) \rightarrow (n\mathrm{R})_m$$

where C and R represent a syndiotactic sequence, n monomer units long, respectively in a random coil and in a regular conformation. The number of sequences coming together in an intermolecular agglomerate is represented by m.

The first equilibrium apparently is dominated by an equilibrium constant with a position that changes with temperature. The second step, however, is not at equilibrium since a temperature hysteresis is observed as a consequence of intermolecular associations. Consequently, this second reaction has to shift the first equilibrium completely to the right side and the concentration of sequences with a regular conformation should increase with time, even at the highest temperatures. This is not observed and another explanation has to be found.

When the conformational change is a cooperative phenomenon, a minimum sequence length is needed to perform this transition. This minimum length will increase with temperature and at the highest temperatures only the longest sequences can participate. This is an important limitation of the first 'equilibrium' and no change in the position of this 'equilibrium' is observed, even when the concentration of sequences with a regular conformation decreases as a consequence of intermolecular association. Consequently, a fractionation on sequence lengths occurs as a function of gelation temperature.

CONCLUSIONS

The thermoreversible gelation of s-PMMA in *o*-xylene proceeds by a two-step mechanism, different from the

usual crystallization–gelation. A fast conformational change is followed by a slower intermolecular association.

A minimum degree of stereoregularity, corresponding to a minumum average sequence length, is needed. This is characteristic for a certain degree of cooperativity in the conformational change. The relation between this minimum length and the gelation temperature is responsible for the temperature dependence of the gelation phenomenon.

The average degree of syndiotacticity influences only the total amount of ordering in the solution.

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