

Structure formation in solutions of isotactic poly(methacrylic acid) in dimethyl formamide

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Received: 8 July 2005 / Accepted: 11 January 2006
Published online: 8 February 2006 – © Springer-Verlag 2006

Summary

Structure formation in solutions of non-neutralised isotactic poly(methacrylic acid) in dimethyl formamide was studied. Fourier transformed infrared spectroscopic measurements, X-ray diffraction analysis and dynamic rheological observations revealed that two different processes of structure formation can take place. The first process can lead to the formation of very weak, thermoreversible gels. It is proposed to consist of an intramolecular coil-to-helix transition, followed by an intermolecular association. The second one shows the characteristics of a crystallisation into a supramolecular organisation different from what is obtained in the first process. These processes can compete with each other and this depends on the experimental conditions, the molar mass and the tacticity of the sample.

Introduction

Isotactic poly(methacrylic acid) (iPMAA) is, in contrast with the atactic isomer, not soluble in water below a certain critical degree of neutralisation, α_{crit} . The value of α_{crit} at which homogeneous solutions in water can be prepared depends strongly on the counterion. A typical example is a solution of 10% (w/w) of iPMAA (mass average molar mass: 10 kg/mol; 92% isotactic and 8% heterotactic triads) with sodium as the counterion for which $\alpha_{\text{crit}} = 0.28$. The only solvents in which iPMAA is soluble in its non-neutralised form are dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO), which are both strong hydrogen bonding solvents.

The insolubility of iPMAA in water below α_{crit} results from the very fast coil-to-helix intramolecular conformational change and an intermolecular association by the contact with water [1]. These conclusions are based on the similarity between the Fourier transformed infrared (FTIR) spectroscopic and wide angle X-ray diffraction (WAXD) data of these water-treated samples and crystalline isotactic poly(methyl methacrylate) (iPMMA). In the latter the polymer chains were found to adopt a double

helix conformation that can be stabilised by the solvent when this process takes place in solution [2-4].

This supramolecular organisation is thermostable in the presence of water. No melting is observed up to the boiling point of water. Heating in the dry state to 50°C does not destroy the structure. Isothermal annealing at higher temperature results in the formation of anhydride groups.

One can therefore conclude that iPMAA, obtained by hydrolysis of iPMAA, will show a high degree of order at the end of this preparation. This organisation will be (partly) destroyed by dissolving the samples in DMSO or DMF. WAXD patterns obtained with films prepared from these solutions confirm their predominantly amorphous state.

A solution in water at α_{crit} forms an opaque, elastic, thermoreversible gel on cooling below around 0°C [1]. The melting of the structures formed shows a very pronounced hysteresis. FTIR and X-ray scattering analysis reveal a structure similar to the one observed for the water-treated films prepared from solutions of the non-neutralised polymer in DMF and DMSO. From the combination of the data obtained from dynamic mechanical observations and FTIR spectroscopic measurements a two step gelation mechanism was proposed: a coil-to-helix conformational change followed by an intermolecular association.

In order to obtain a more general picture of the possibilities of structure formation in solutions of iPMAA, the behaviour in DMF was investigated.

Experimental

Materials

iPMAA was prepared by the hydrolysis of isotactic poly(methyl methacrylate) (iPMMA). This polymer was synthesized at room temperature in toluene, with phenylmagnesium bromide as the initiator [5]. The sample was purified by dissolution in tetrahydrofuran followed by precipitation in an acidified 1:1 methanol/water mixture. The characteristics of the different iPMMA samples used in this work are given in Table 1.

Table 1. Characteristics of the iPMMA samples from which the acid forms are used in this work.

Polymer	$\langle M \rangle_w$ (kg/mol)	$\langle M \rangle_n$ (kg/mol)	% isotactic triads	% syndiotactic triads	% heterotactic triads
iPMMA1	9	4	90	7-8	2-3
iPMMA2	6	3	> 97	-	< 3
iPMMA3	160	50	> 98	-	< 2

These polymer samples were converted in the acid form by hydrolysis in concentrated sulphuric acid under nitrogen flow. Anhydride groups introduced by this treatment were eliminated by refluxing the sample in water. The complete transformation into the acid form and the complete hydrolysis of the anhydride groups were verified by nuclear magnetic resonance and infrared measurements.

Dimethyl formamide (DMF) was purchased from Riedel-de-Haën, Germany.

Instruments

The tacticity of the iPMAA samples and the degree of hydrolysis of the esters and anhydride groups were determined by ^1H and ^{13}C nuclear magnetic resonance measurements (Brüker AMX 400 spectrophotometer) at 30°C in deuterated chloroform and deuterated dimethyl sulphoxide respectively.

The molar masses of the iPMAA samples were obtained by size exclusion chromatography (Waters Associates Gel Permeation Chromatograph Model 200) at room temperature in tetrahydrofuran, 0.01% (w/w) toluene.

For the Fourier transformed infrared (FTIR) measurements a PerkinElmer 2000-FTIR spectrophotometer was used.

Wide angle X-ray diffraction (WAXD) measurements were performed on a Rigaku Rotaflex 200B rotating anode combined with a horizontal Bragg-Brantano focussing diffractometer and a radiation detector. The rotating anode operated at 40 kV and 100 mA. The Cu-K α was Ni-filtered. Measurements were performed in transmission mode and diffraction was measured at 2θ changing from 3 to 60° in steps of 0.05° with a measuring time of 10 seconds.

Rheological data were obtained with a strain-controlled rheometer (Advanced Rheometrics Expansion System of Rheometrics Scientific), equipped with a 200FRTN1 transducer with parallel plate (25 mm diameter) geometry. A liquid bath connected with an external thermostatic bath was used to regulate the temperature.

Results and discussion

1. Phenomenology of structure formation

1.1. Static experiments: isothermal annealing

Solutions of iPMAA in DMF do not represent an equilibrium situation. This can be concluded from the following experimental observations: i. Annealing at -25°C for about ten minutes of a 10% (w/w) iPMAA3 solution in DMF in a test tube does not result in any observable structure formation; ii. Annealing for several weeks of solutions of iPMAA3 and iPMAA1 at -5°C and 22°C results in a precipitation of the polymer. Further annealing for about six months only results in an enhanced amount of polymer precipitate. Polymer precipitation seems to be enhanced by an increase in concentration and a decrease in annealing temperature.

1.2. Dynamic experiments

1.2.1. Stirring 10% (w/w) iPMAA solutions in a test tube with a magnetic stirrer bar

When the iPMAA3 solution in DMF is slowly stirred at room temperature by means of a magnetic stirrer bar, the solution becomes more viscous and less transparent after some weeks. Stirring at high rate, on the contrary, does not lead to this increase in viscosity and change in transparency. However, prolonged stirring of the sample at this high rate results in the formation of a polymer precipitate.

Slow stirring of solutions of iPMAA1 and iPMAA2 at room temperature by means of a magnetic stirrer bar results in precipitation after about two days. No apparent increase in viscosity can be detected. The fastest precipitation seems to take place with iPMAA1. From this it can be concluded that polymer precipitation is promoted by a lower isotacticity of the sample. The role of stirring is illustrated by the fact that,

under static conditions, a precipitate is only formed after one week in the solution of iPMAA1 (10%, w/w, in DMF).

From the observation of the solutions it also became clear that the amount of precipitate formed increases with stirring time.

1.2.2. Oscillatory deformation of 10% (w/w) iPMAA samples in a rheometer with parallel plate geometry

When a 10% (w/w) iPMAA3 solution in DMF is subjected at room temperature in the rheometer to a deformation with a frequency of 1 rad/s and a strain of 1% for up to 100 h, no structure formation is observed.

When such dynamic mechanical experiments are performed during the stepwise cooling of the solution from 25 to -2°C , network formation takes place. This is illustrated in figure 1.

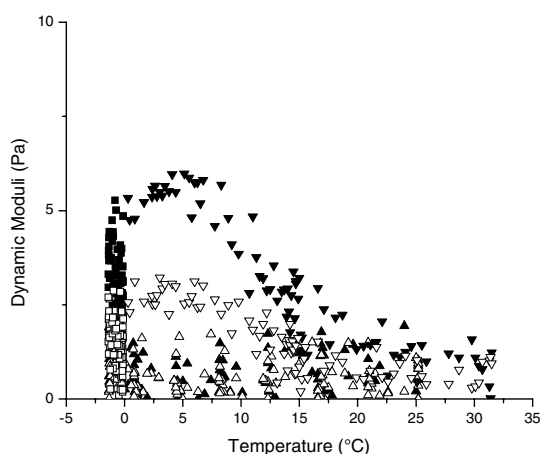


Figure 1. Dynamic moduli obtained on cooling a 10% (w/w) iPMAA3 solution in DMF (angular frequency of 1 rad/s and strain of 1%).

a) cooling in steps of 4°C with an annealing during 20 min/step;

b) annealing at -2°C for 30 min;

c) subsequent heating at a rate of $1^{\circ}\text{C}/\text{min}$.

(\blacktriangle) G' and (\triangle) G'' : cooling; (\blacksquare) G' and (\square) G'' : annealing at -2°C ; (\blacktriangledown) G' and (\triangledown) G'' : heating.

Both dynamic moduli, G' and G'' , start to increase around 0°C . G' becomes larger than G'' . Subsequent heating leads to a further increase until up to 7°C . Above this temperature the formed structure starts to melt and the original solution state is again reached at 24°C . The values of both G' and G'' stay very low, G' being equal to only 6 Pa at 7°C . The experimental conditions of frequency and strain are extremely important. An increase of this frequency to 10 rad/s and of the strain to 10% results in the behaviour shown in figure 2.

On cooling an almost linear increase of G' and G'' takes place up to -7°C . This increase becomes more pronounced at lower temperature. G'' is always larger in value than G' . Only a slight increase in the dynamic moduli is observed on annealing the sample at -21°C for 30 min when the sample is deformed during this annealing. When no deformation is applied on the sample during the annealing, a larger increase in the dynamic moduli is observed. Note that G' increases much more in value than G'' .

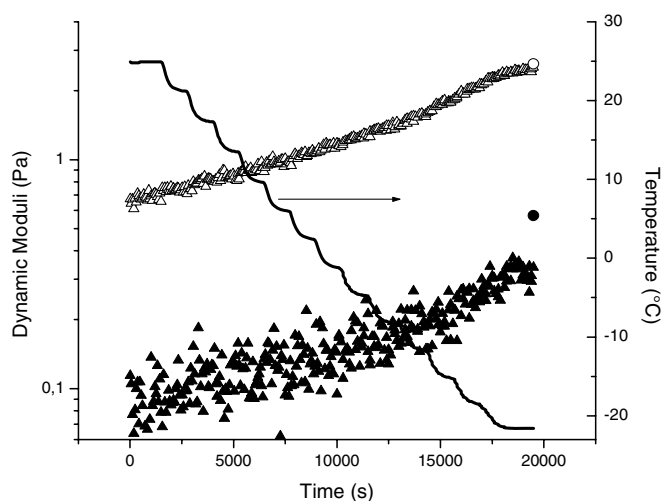


Figure 2. G' (\blacktriangle) and G'' (\triangle), obtained on cooling of a 10% (w/w) iPMAA3 solution in DMF in steps of 4°C with an annealing during 20 min/step and subsequent annealing at -21°C for 30 min. The sample was deformed during the whole experiment. G' (\bullet) and G'' (\circ) obtained on cooling the sample in steps of 4°C with an annealing during 20 min/step and on deforming the sample, and subsequent annealing at -21°C for 30 min without deforming the sample. (angular frequency of 10 rad/s and strain of 10%).

2. Analysis of the structures formed

The structures formed in the experiments reported in the previous part depend strongly on the experimental conditions. Two series of experiments were carried out. The samples are always investigated in the solvent free state.

2.1. FTIR analysis

2.1.1. Static preparation conditions versus slow stirring

The investigated samples were prepared using iPMAA1. With this polymer no apparent increase in the viscosity of the solution on stirring is observed. Only a precipitate can be formed. In figure 3 the FTIR spectra of three different samples are compared:

- i. a film prepared from a 10% (w/w) iPMAA1 solution in DMF before stirring (A);
- ii. sample A treated with water (B);
- iii. the precipitate formed in the 10% (w/w) iPMAA1 solution in DMF on slow stirring at room temperature and dried at 40°C for one night (C).

The non-water-treated film (A) is predominantly amorphous. Treating this film with water leads to a structure similar to the one obtained after gelation on cooling of a solution in water at $\alpha_{crit} = 0.28$ and for the precipitate formed in this solution.

The spectrum obtained for the polymer precipitate differs remarkably from the spectra obtained for the polymer film before and after treatment with water. Major changes (indicated by arrows) are observed around 500 cm^{-1} , 900 cm^{-1} , 1150 cm^{-1} and 1250 cm^{-1} .

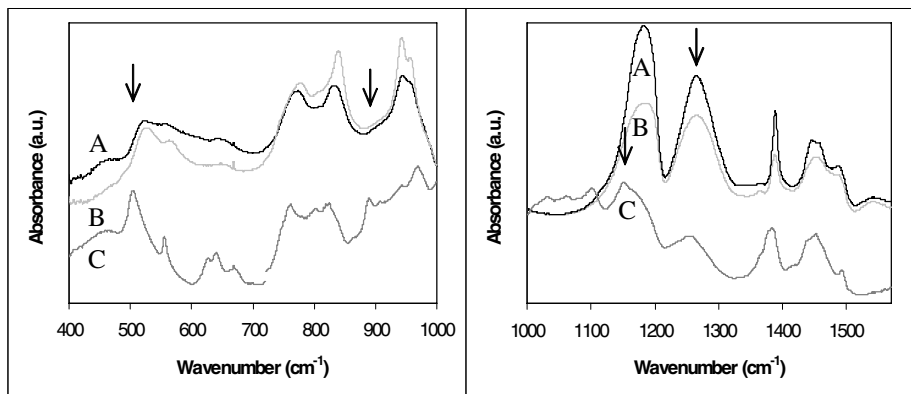


Figure 3. Infrared spectra of a film prepared from a 10% (w/w) solution of non-neutralised iPMAA1 in DMF before (A; black line) and after (B; light grey line) immersing the film in water. Infrared spectra of the dried precipitate formed in the 10% (w/w) non-neutralised iPMAA1 solution in DMF stirred for ten days (C; dark grey line).

In the precipitate the polymer chains clearly adopt a conformation different from the one found in the predominantly amorphous sample and also different from the one observed in the water-treated film and the structure formed in aqueous solution at $\alpha_{\text{crit}} = 0.28$.

2.1.2. Slow stirring of solutions of iPMAA3

The higher molar mass of this sample leads to a different behaviour under stirring.

On slow stirring of a 10% (w/w) iPMAA3 solution in DMF, the supramolecular organisation that is formed shows some similarities with what is found in the water-treated film and in an aqueous solution at $\alpha_{\text{crit}} = 0.28$.

In the infrared spectra of the films prepared from these slowly stirred solutions, a decrease in intensity of the absorption bands around 1181, 1267 and 1388 cm^{-1} is observed (Fig. 4). The remaining of the spectrum stays unchanged. No shift of these absorption bands is observed. The absorption bands at 1181 and 1265 cm^{-1} are both assigned to the stretching vibration of the C=O group coupled with the bending vibration of the O-H group. The absorption band at 1388 cm^{-1} is ascribed to the symmetric bending vibration (planar deformation) of the $\alpha\text{-CH}_3$ group, which is very sensitive for the steric conformation of the polymer chain [6].

The decrease in intensity of the absorption bands at 1181 and 1265 cm^{-1} can be due to the influence of hydrogen bonding on the extinction coefficients of these vibrations.

A decrease in intensity of these bands is also observed with the structure formation in the film of the non-neutralised polymer by the contact with water. But this contact with water induces also a shift of the absorption bands from 1176 to 1181 cm^{-1} and from 1261 to 1265 cm^{-1} .

This situation is different from what is observed when a gel is formed from an aqueous solution at α_{crit} . This gelation results in a shift of these absorption bands from 1186 to 1197 cm^{-1} and from 1255 to 1265 cm^{-1} , and this shift is accompanied by an increase in intensity of these bands.

The change in intensity of the absorption band at 1388 cm^{-1} is different from the increase in intensity of this band observed under the other circumstances.

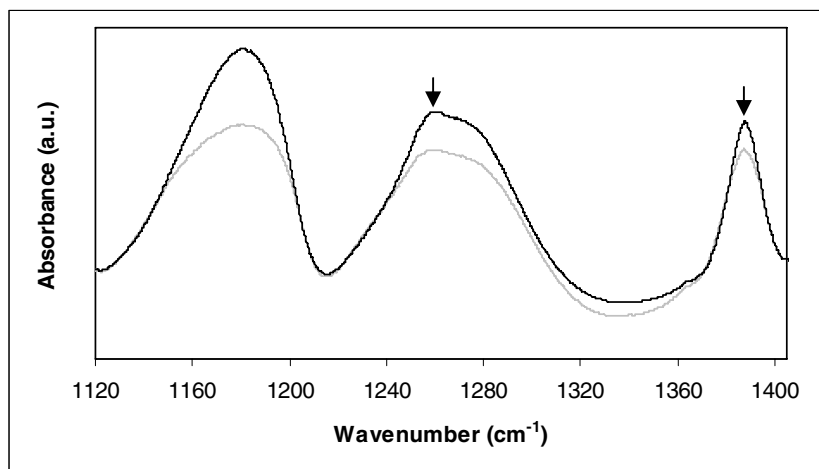


Figure 4. Infrared spectra of a 10% (w/w) iPMAA3 solution in DMF stirred for one week (black line) and stirred for 37 days (grey line). The absorption bands due to DMF rests in the film are marked by an arrow.

2.2. WAXD analysis

WAXD measurements (Fig. 5) confirm the differences in supramolecular organisation between the precipitate, the predominantly amorphous sample and the structure formed in the water-treated film and in aqueous solution at $\alpha_{\text{crit}} = 0.28$.

Treatment with water induces structure in the diffraction pattern. The maximum at $8.4^\circ 2\theta$ is also found with crystalline iPMAA and can correspond with the repeating distance in the double helix [2, 4, 7].

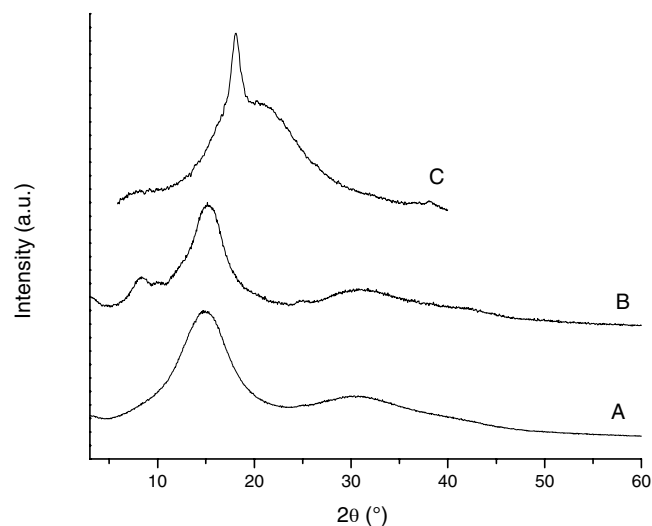


Figure 5. WAXD patterns obtained for a film prepared from a 10% (w/w) solution of non-neutralised iPMAA1 in DMF before (A) and after (B) immersing the film in water. WAXD pattern obtained for the dried precipitate formed in a 10% (w/w) non-neutralised iPMAA1 solution in DMF stirred for ten days (C).

A very sharp maximum at $18.1^{\circ}2\theta$ appears in the pattern obtained with the dried precipitate formed in a 10% (w/w) non-neutralised iPMAA1 solution in DMF stirred for ten days. The peak at $8.4^{\circ}2\theta$, on the contrary, is absent.

Conclusions

The solution behaviour of iPMAA is very complex and different types of supramolecular organisation can be found. This can be concluded from the differences in the FTIR spectra and the X-ray diffraction patterns. Important factors are the solvent, the temperature, the molar mass and the deformation of the solution.

a) Immersing an amorphous film in water leads to a structure similar to the one found in a thermoreversible gel obtained at a degree of neutralisation $\alpha_{\text{crit}} = 0.28$. Under these last conditions, a precipitate with the same supramolecular organisation can be obtained. A mechanism of coil-to-helix transition followed by an intermolecular association has been suggested. Such an organisation is also induced by a low degree of deformation of a solution of a high molar mass polymer in DMF. This can result, at low temperature, in the formation of a very weak gel.

b) A different structure is obtained in a solution of a low molar mass polymer in DMF. This can be concluded from the differences in the FTIR spectra and the X-ray scattering patterns. So far, no detailed information about this structure is available.

The experimental information obtained up to now allows us to draw the following preliminary conclusions:

- in water only one structure formation process takes place, which is responsible for the thermoreversible gelation at low temperature. This structure can also be found in the precipitate formed under different conditions of temperature and/or concentration. This we will call the “gel structure”;

- in DMF, on the other hand, two different structures can be formed: the “gel structure” and a (crystalline?) precipitate. This behaviour in an organic solvent is similar to the one observed with stereoregular vinyl polymers in such solvents. For these systems gelation and crystallisation are two competing processes. Their relative contribution to the structure formation depends on the nature of the solvent in combination with the polymer concentration.

Therefore we can expect the same competition to take place with iPMAA in DMF, but this needs further investigation.

Acknowledgements. This research was supported by FWO-Vlaanderen and the University of Leuven.

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