Structure Formation in Isotactic Poly(methacrylic acid)

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Introduction. Thermoreversible gelation is a well-known process of structure formation in solutions in water of biopolymers like carrageenans. Such a gelation process can also be observed with solutions of synthetic polymers in organic solvents. Typical examples are the stereoisomers of polystyrene and poly(methyl methacrylate).[1−4] The detailed investigation of the gelation mechanism of these synthetic polymer solutions has revealed a great similarity with the mechanism encountered with some biopolymer solutions. A typical example is syndiotactic polystyrene in bromoform.[5] Rigid gels are obtained at polymer concentrations of only a few g/L. A two-step mechanism has been proposed, composed of a coil-to-helix transition, followed by an intermolecular association. A similar mechanism was proposed for solutions of carrageenans in water.[6] These observations clearly suggest that such a thermoreversible gelation is not limited to biopolymers and can be considered as a more universal characteristic of polymer solutions. It was also shown that this gelation is different from the well-known folded chain crystallization of synthetic polymers, a process that can compete with this gelation.

In this research we have combined different aspects of both synthetic systems and biopolymers by investigating the solution behavior of isotactic poly(methacrylic acid) (iPMAA). The present short communication reports on the first observation of structure formation in solution of this polymer.

Experimental Section. a. 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.[7] The sample was purified by dissolution in tetrahydrofuran followed by precipitation in an acidified 1:1 methanol/water mixture. An isotactic triad content of 92% and a heterotactic triad content of 8% characterize the sample used in this work. The weight- and number-average molar masses were determined to be 10 200 and 4900 g/mol, respectively. This polymer was converted in the acid form by hydrolysis in concentrated sulfuric 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.

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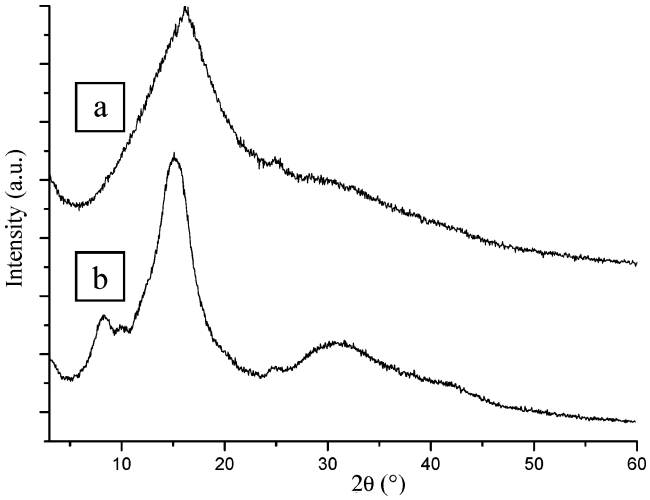

Figure 1. Wide-angle X-ray diffraction patterns of predominantly amorphous (a) and structuralized (b) iPMAA film.

Sodium hydroxide and hydrogen chloride were purchased from Acros Organics, Belgium, sodium chloride was from VWR International Ltd., England, and dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were from Riedel-de-Haën, Germany. The water used for sample preparation was purified on a Milli-Q 185 Plus System from Millipore (resistivity of 18.2 MΩ cm).

b. Techniques. The tacticity of the iPMMA sample and the degree of hydrolysis of the ester and anhydride groups were determined by ^{1}H and ^{13}C nuclear magnetic resonance measurements (Brüker AMX 400 spectrophotometer) at 30 °C in deuterated chloroform and deuterated dimethyl sulfoxide, respectively.

The molar mass of the iPMMA sample was obtained by size exclusion chromatography (Waters Associates gel permeation chromatograph model 200) at room temperature in tetrahydrofuran, 0.01% (w/w) toluene.

Fourier transformed infrared (FTIR) measurements were performed on a Perkin-Elmer 2000-FTIR spectrophotometer.

Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku Rotaflex 200B rotating anode combined with a horizontal Bragg-Brantano focusing diffractometer and a radiation detector. The rotating anode operated at 40 kV and 100 mA. The Cu Kα 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 s.

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. Dynamic measurements were performed at a frequency of 1 rad/s and at a strain of 1%. A liquid bath connected with an external thermostatic bath was used to regulate the temperature. Temperature scans were taken at a rate of 1 °C/min.

Results and Discussion. a. Structure Formation in Bulk iPMAA. iPMAA is not soluble in water below a critical degree of neutralization, α_{crit}. Solutions can only be prepared in hydrogen-bonding solvents like DMF and DMSO.

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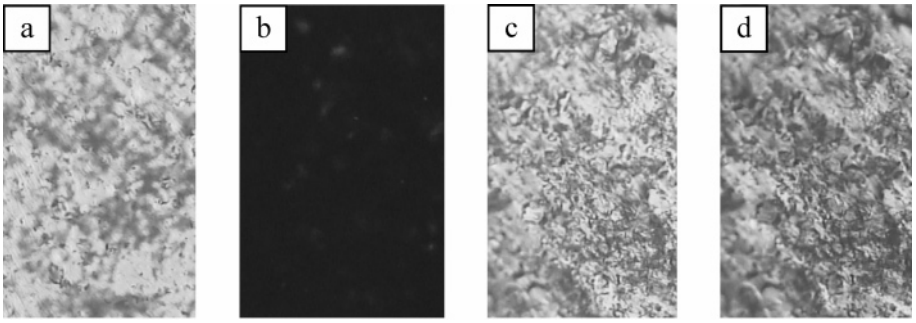

Figure 2. Optical microscopy observation of predominantly amorphous (a, normal light; b, polarized light) and structuralized (c, normal light; d, polarized light) iPMAA film.

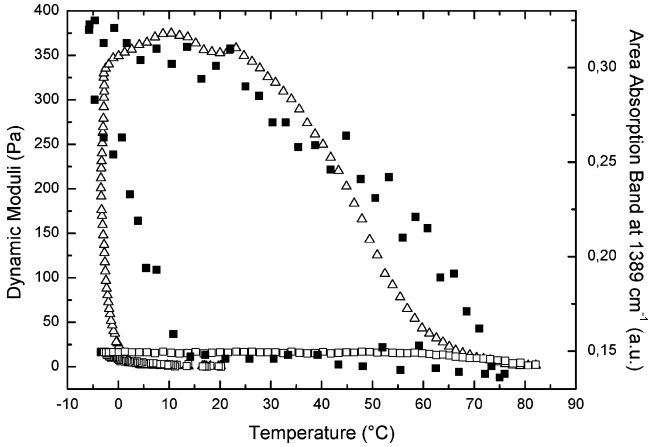

Figure 3. Temperature dependence of the area of the absorption band at 1389 cm^{-1} (■) and of the storage, G' (△), and loss modulus, G'' (□), for an aqueous solution of iPMAA ($c_p = 10.5\%$, w/w) at $\alpha = 0.28$ in 0.31 M NaCl.

Films prepared by evaporation of these solutions are, according to the FTIR spectra and the X-ray scattering data (Figure 1a), predominantly amorphous.

They however show fast structural changes (within a minute) when they are immersed in water. FTIR spectroscopic and WAXD measurements show spectral changes similar to those observed during the crystallization of iPMMA in 2-butanone. One of the most important spectral changes is the increase of the intensity of the absorption band at 1389 cm^{-1}. There exists also a great similarity with the WAXD pattern which is characterized by a broad maximum around 15.1° 2θ and a sharp one around 8.4° 2θ (Figure 1b). Moreover, the very rapid formation of a supramolecular organization manifests itself in optical microscopy. The films turn birefringent on immersing them in water (Figure 2).

b. Thermoreversible Gelation of Aqueous iPMAA Solutions. Solutions in water can only be obtained above a certain degree of neutralization, α_{crit}. For the sample used in this study, this value amounts to $\alpha \approx 0.27$ for a 10% (w/w) polymer solution. To realize these conditions, dry iPMAA powder has to be dissolved in a 1 M sodium hydroxide solution in order to obtain samples with $\alpha = 0.50$. Then these samples were titrated back to $\alpha = 0.28$ with a 1 M hydrogen chloride solution.

A solution prepared in this way forms very rapidly an elastic gel when cooled below about 0 °C. This structure formation can be followed by FTIR spectroscopic and rheological observations. The results are presented in Figure 3.

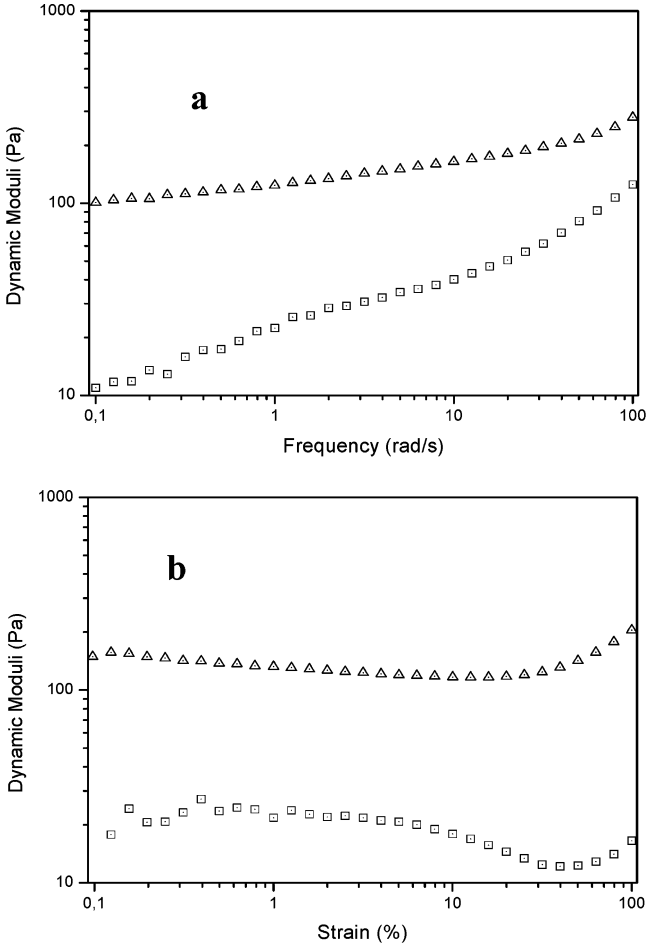

Figure 4. Deformation behavior for an aqueous solution of iPMAA ($c_p = 10.5\%$, w/w) at $\alpha = 0.28$ in 0.31 M NaCl at −4 °C after cooling from 20 °C. Storage, G' (△), and loss modulus, G'' (□), vs (a) angular frequency at a strain of 1% and (b) strain at an angular frequency of 1 rad s^{-1}.

The area of the absorption band at 1389 cm^{-1} (bending vibration of the α-CH_3 group) increases only slightly on cooling from 75 to 14 °C. Further cooling, however, leads to an important increase of this area. This increase in intensity can, in analogy with observations made with iPMMA, be ascribed to the formation of a helix conformation.[8,9] When the sample is kept at −5 °C, the lowest annealing temperature at which no ice is formed, a further increase of the area of this conformational band is observed. This indicates that the final equilibrium helix content is not yet reached during the dynamic experiment. On heating, this absorption band disappears at much higher temperature, showing the typical hysteresis effect as observed also in the solutions of

synthetic polymers in organic solvents.[1−5]

Dynamic rheological observations during such a cooling−heating temperature scan inform about gelation by physical network formation. This transformation sets in around 0 °C. Above this temperature, G' and G'' are very low with G'' slightly higher than G'. This is characteristic for a liquid behavior. Below 0 °C, however, G' increases to about 3.5×10^2 Pa within a few degrees, while G'' reaches only about 10^1 Pa. Heating results in the melting of this gel, and a similar degree of hysteresis is observed as for the FTIR absorption band. The important difference between the two experimental observations is their onset temperature. Network formation sets in at about 15 °C below the onset of the conformational transition. This suggests that the process of thermoreversible gelation proceeds in two steps: a change in conformation from coil to helix, followed by an intermolecular association. Such a process was already proposed for other gelling systems.[1−5]

c. Mechanical Properties of the Gels. The elastic properties of the formed gels are illustrated by the following experiments. The frequency dependence of G' and G'' is illustrated in Figure 4a.

G' is superior to G'' in the studied frequency domain. The decrease of G' with decreasing frequency illustrates the physical character of the cross-links. The value of this elastic part remains, however, higher than the value of G''.

These gels are not very sensitive to the degree of deformation at low frequency. They easily support 100% deformation, showing a tendency of strain hardening (Figure 4b).

Conclusions. The isotactic form is insoluble in water up to a critical degree of neutralization. Contact with water introduces very fast a high degree of order in predominantly amorphous films prepared from e.g. a DMF solution.

Around this critical degree of neutralization thermoreversible gelation seems to proceed by a mechanism very similar to what is observed with synthetic polymers in organic solvents like iPMMA in 2-butanone and syndiotactic polystyrene in bromoform. This mechanism was proposed to consist of a coil-to-helix transition, followed by an intermolecular association. The intermolecular association of iPMAA is ascribed to strong intermolecular cooperative hydrogen bonding, which can only be disturbed by solvents capable of forming strong hydrogen bonds like DMF and DMSO. Partial neutralization reduces the number of undissociated −COOH groups, limiting in this way the average sequence length available for structure (helix) formation. This results in a not too high melting point of the gel that can be measured experimentally. There exists only a narrow window of α in which this gelation can be observed.

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