Gelation Dynamics and Mechanism(s) in Stereoregular Poly(Methyl Methacrylate)s

Alberto Saiani

School of Materials, The University of Manchester, Grosvenor Street, Manchester M1 7HS, United Kingdom
E-mail: a.saiani@manchester.ac.uk

Summary: Chain conformation and gel structure of syndiotactic PMMA thermoreversible gels have been investigated using small angle neutron scattering (SANS). A double helix model for the chain conformation is proposed alongside a gel network model where the fibrils are formed by the proposed double helix and the junctions by the aggregation of 3 double helices. Preliminary results, also obtained by SANS, for stereocomplex gels prepared in bromobenzene are presented.

Keywords: double helix; gelation; small angle neutron scattering; stereocomplex; stereoregular poly(methyl methacrylate)

Introduction

Polymer-solvent interactions have received considerable attention as these interactions, whether desirable or undesirable, are present in most of the applications involving the use of polymers. Of particular interest is the influence of the solvent on polymer conformation, which can strongly influence the resulting properties of the material. For instance, bromobenzene can induce, via polymer-solvent interaction, crystallisation of syndiotactic PMMA but, when the solvent is removed, the sample returns to the amorphous state[1]. It has been noticed that many synthetic (polystyrene, PMMA, poly(vinyl pyridine)) or biologic (agarose, gelatine) polymers exhibit temperature induced conformational transitions in dilute or semi-dilute solutions, which are solvent dependent[2].

A remarkable feature of stereoregular PMMAs is their ability to form helicoidal structures and especially double helix structures, which are often encountered in biological systems but more rarely in synthetic polymers[2]. These double stranded helices can be formed from the bulk, as in the case of isotactic PMMA, for which Kusanagi *et al.* have proposed a symmetric 10_1 double helix for the chain conformation in crystalline samples[3]. They can also be solvent-induced as in syndiotactic PMMA, for which Saiani and Guenet recently suggested the presence of an asymmetric double helix in syndiotactic PMMA gels[4]. A unique feature of stereoregular PMMAs is the existence of the so-called stereocomplex

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that is obtained by mixing isotactic and syndiotactic chains in a 1:2 ratio[5]. Shomaker and Challa have explained this ratio by the existence of an asymmetric double helix where the inner helix is made by an isotactic chain (9_1 helix) around which a syndiotactic chain wraps adopting a 18_1 conformation[6]. Interestingly, syndiotactic PMMA seems to be able to adopt several helicoidal conformations.

Another particularity of stereoregular PMMAs is their ability to form thermoreversible or "physical" gels in a large variety of solvents, yet not necessarily in the same solvent. For instance, while strong aggregation occurs in toluene for highly syndiotactic PMMA, this aggregation seems to be low for isotactic PMMA. The stereocomplex also has the ability to form gels in some solvents and particularly in bromobenzene, for which Fazel *et al.* have proposed the presence of a fibrillar network whose junctions consist of the aggregation of three double helices[7]. The same kind of network model was proposed for syndiotactic PMMA[8] and for κ-carrageenan gels[9]. Interestingly, this last biopolymer also forms double helical structures[1,5,10].

A unique advantage of synthetic polymers is the possibility of deuteration, which allows structural investigations via small angle neutron scattering (SANS). Using various labelling techniques it is possible to investigate the chain conformation in polymer gels as well as the gel structure itself[12]. In this article we will present recent results obtained by A. Saiani and co-workers on syndiotactic PMMA gels as well as preliminary results obtain on sterocomplex gels.

Experimental part

The deuterated and the hydrogenated polymers used were synthesized in our laboratory (for more detail see reference [4]). The tacticity of the hydrogenous polymer was determined in deuterated chloroform by means of proton NMR operating at 200 Hz. The following values were found for the triad arrangements:

syndiotactic PMMA:	iso = 2%	hetero = 9%	syndio = 89%
isotactic PMMA:	iso = 92%	hetero = 3%	syndio = 5%

Due to the low quantity of deuterated material obtained in the synthesis no NMR investigation was carried out. As the thermal behavior of a 5% gel prepared from the deuterated material exhibited no significant difference compared with that of a hydrogenous polymer it was accordingly considered that stereoregularity was little altered.

Gel samples were prepared directly in sealable quartz cells from HELLMA of optical path of 1 mm and 5 mm. After sealing from atmosphere appropriate mixtures of the different constituents, the system was heated up close to the solvent boiling point so as to make clear, homogeneous solutions. Gelation was achieved by a quench to 0 °C for a minimum of 24 hours.

The Small-Angle Neutron Scattering (SANS) experiments on syndiotactic PMMA were carried out on PAXE small-angle camera located at the Laboratoire Léon Brillouin (LLB) (CEN Saclay, France) and on LOQ facility located at ISIS (Rutherford-Appleton Laboratory, Didcot, UK). The experiment on the sterocomplexe gels where carried out on D22 small-angle camera located at the Institut Laue-Langevin (ILL) (Grenoble, France). For more detail on the data analysis see reference [4] and [8].

Results and discussion

Syndiotactic PMMA gels

Recently Saiani et al. have used small angle neutron scattering (SANS) to investigate the chain conformation and gel structure of syndiotactic PMMAs gels. By using different labelling techniques they were able to investigate the chain trajectory as a function of temperature as well as the structure of the gel[4,8].

In the first experiment, partially deuterated samples where used to investigate the conformation of the polymer chain in the middle of the gel. For this purpose gel samples containing 6% (v/v) of deuterated chain where prepared, the total concentration of the samples being 35% (v/v). In this case the coherent scattering observed is due to the deuterated chains. The measurements where performed at 3 different temperatures: room temperature, just above the gel melting temperature and close the solvent boiling temperature. In Figure 1 the scattering curves obtained at 25°C, 81°C and 145°C are presented, by mean of a Kratky representation ($q^2I_A(q)$ *vs* q^2), for a gel prepared in hydrogenated bromobenzene solvent.

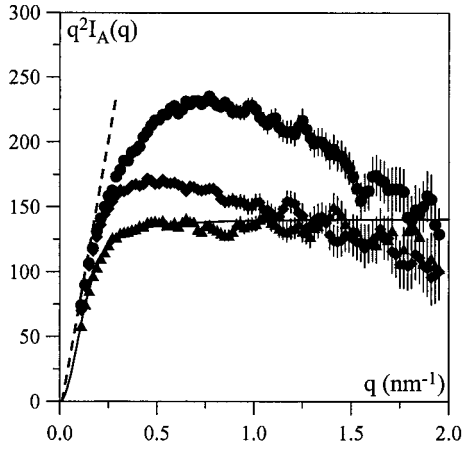

Figure 1. Kratky representation of the intensity scattered by a 35% (v/v) syndiotactic PMMA gel containing 6% (v/v) deuterated chains in bromobenzene: ●, room temperature; ◆, 81°C; ○, 145°C. Solid line stands for the best fit obtained by means of a Debye function, equation (1) (see text and reference [4] for more details).

As can be seen from figure 1 the scattering curves obtained are temperature dependent. At high temperature, close to the boiling point of the solvent, the scattering curve obtained could be fitted using a Debye function:

$$I_A(q) = C_D M_W \frac{2}{q^4 R_G^4}\left[exp(-q^2 R_G^2) + q^2 R_G^2 - 1\right] \quad (1)$$

where C_D is the deuterated polymer concentration, R_G the mean-square radius of gyration of the polymer and M_W the weight-average molecular weight. In the q range investigated the Debye function is a good approximation for a Gaussian conformation. The values obtained for $R_G \sim 10$ nm and for $M_W \sim 1 \times 10^5$ g mol^{-1} are in good agreement with the results obtained by size exclusion chromatography for the same polymer. This result suggests that at high temperatures bromobenzene is a good solvent for syndiotactic PMMA and the polymer chain adopts a Gaussian conformation.

At lower temperatures it can be seen that the scattering curves changes significantly. In particular at low q the scattering curves present a linear slope in the Kratky representation characteristic of the scattering of rod-like structures. In figure 2 the scattering curve obtained at room temperature is presented with the best fit obtained using a double helix model. It should be noted that single helix models were tested but no satisfactory fit could be obtained.

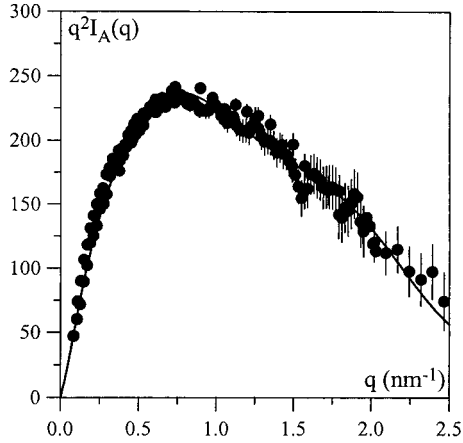

Figure 2. Kratky representation of the intensity scattered by a 35% (v/v) syndiotactic PMMA gel containing 6% (v/v) deuterated chains in bromobenzene at 25°C. The solid line corresponds to the best fit obtained by using adouble helix model, equation (2), and taking into account the presence of 30% Gaussian chains (see text and reference [4] for more details).

As can be seen a good fit of our experimental results is obtained using a double helix model. The scattering by helices has been the subject of a large amount of theoretical work[2]. In the q range used for these experiments helices can be approximated by cylinders. The fit presented in figure 2 has been obtained by considering a double helix model which is schematically depicted in figure 3. For this type of model the scattering can be written:

$$I_A(q) \propto \pi C_D \mu_L \left[\frac{f(qr)}{q} + o(q^{-2}) \right] \tag{2}$$

where μ_L is the linear mass of the double helix and $f(qr)$:

$$f(qr) = \left[2 \frac{r_1 J_1(q r_1) - \gamma_1 r_1 J_1(q \gamma_1 r_1) + r_2 J_1(q r_2) - \gamma_2 r_2 J_1(q \gamma_2 r_2)}{r_1^2(1-\gamma_1^2) + r_2^2(1-\gamma_2^2)} \right]^2 \tag{3}$$

where r_1 and r_2 are the outer radii of the inner and outer helix and $\gamma_1 r_1$ and $\gamma_2 r_2$ are the outer radii of the inner and outer helix respectively. The fit presented in Figure 2 was obtained, taking into account the presence of 30% of Gaussian chains, for the following values:

$r_1 \sim 1.1$ nm	$\gamma_1 r_1 \sim 0.6$ nm	$\mu_{L1} \sim 1760$ g mol^{-1} nm^{-1}
$r_2 \sim 2.3$ nm	$\gamma_2 r_2 \sim 1.8$ nm	$\mu_{L2} \sim 2870$ g mol^{-1} nm^{-1}

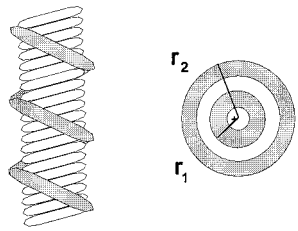

Figure 3. Schematic representation of the double helix model used to fit the experimental scattering results presented in figure 2.

The values obtained for the radius and the linear mass of the inner helix are in good agreement with the helical model proposed by Kusuyama et al. These authors suggested from X-ray scattering data a single 74_4 helix model for the chain conformation[1]. In our case it was necessary to consider a second outer helix in order to reproduce our results. It has to be noted that in our double helix model there is enough space in the centre of the helix and in between the two strands to accommodate solvent molecules. The existence of polymer-solvent complexes in syndiotactic PMMA gels has been shown using neutron diffraction and NMR. In addition neutron diffraction experiments have been shown to support the proposed double helix model[8].

Just above the melting temperature of the gel it can be seen that the scattering curve changes, suggesting the presence of a different chain conformation in the melt state. As alluded to earlier the linear slope at low q is characteristic of the scattering of rod-like structures, suggesting the presence of a new helical conformation. The probable presence of a significant amount of Gaussian chains makes the fitting of this scattering curve difficult and as yet no satisfactory fit has been obtained.

In order to investigate the structure of the gel itself, in a second series of experiments, syndiotactic PMMA gels were prepared in deuterated solvent in order to label all the chains. In this case the scattering observed is due to the gel network. In figure 4 the scattering curve obtained for a 10% (v/v) gel prepared in deuterated toluene is presented.

The scattering curve obtained could be explained using a network model were the single fibres are formed by the double helix proposed above and the junctions are formed by the aggregation of 3 of these double helices. The position of the scattering peak in figure 4 is very sensitive to the number of double helices in the junctions. Considering more than 3 helices in a junction results in a shift of the peak towards higher q values, while considering 2 double helices in a junction results in the peak being shifted towards lower q values.

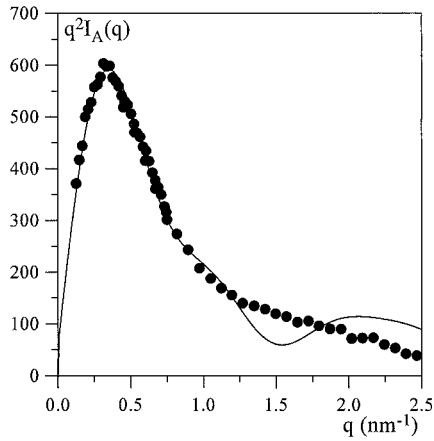

Figure 4. Intensity scattered by a 10% (v/v) syndiotactic PMMA gel prepared in deuterated toluene. The solid line corresponds to the best fit obtained by considering a network model schematically represented in figure 5 (see text and see reference [8] for more details).

Schematic representations of the network structure and the junctions proposed in our model are given in figure 5. It has to be noted that Fazel et al. used the same type of model for stereocomplex gels[7]. For this type of network model and in the explored q range the scattered intensity can be written as follow:

$$q^2 I_A(q) = \pi C_P \mu_L q \, f(q\,r)[\,1 + 2\,J_0(q\,D)(1 - B)\,] \qquad (4)$$

where C_p is the polymer concentration, μ_L the linear mass of the double helix, D the distance between the long axes of two adjacent double helices belonging to the same junction and B the weight fraction of junctions. $f(qr)$ is given by equation (3) and the value obtained above for the double helix model were used for r_1, r_2, γ_1 and γ_2.

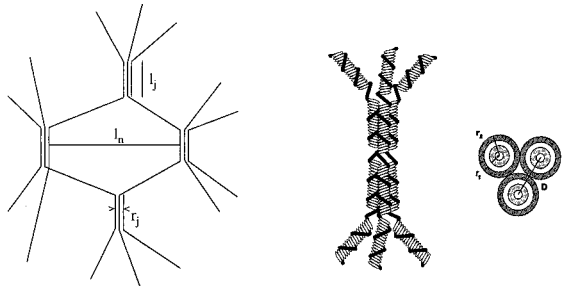

Figure 5. Schematic representation of the gel network model used to fit the experimental scattering results presented in figure 4.

The fit presented in figure 4 has been obtained for the following values of D, B and μ_L:

$$D \sim 4.6 \text{ nm} \qquad B \sim 50\ \% \qquad \mu_L \sim 3400 \text{ g mol}^{-1} \text{ nm}^{-1}$$

As can be seen from figure 5 the value obtained for D is in very good agreement with two double helices being closely packed in a junction. The external radius obtained from our previous experiments for the double helix was ~ 2.3 nm. The linear mass obtained for the double helix is also in very good agreement with the linear masses obtained for the inner and outer strands of the double helix. Finally a 50% weight fraction, which correspond to ~ 16% volume fraction of junctions is obtained which is a reasonable value for this type of gels.

One of the main limitation when investigating syndiotactic PMMA gels is that the two strands of the double helix can not be labelled independently. Indeed the two strand of the double helix being formed by syndiotactic chains when introducing in the sample deuterated chain they will form randomly inner or outer helices. The model used to fit our SANS results takes in consideration this problem.

Stereocomplex gels

In the case of the stereocomplex gels the double helix is formed by both isotactic and syndiotactic chains. In the model proposed by Shomaker and Challa the isotactic chain adopts a 9_1 single helix conformation and forms the inner strand of the double helix while the syndiotactic chain adopts a 18_1 helix conformation and raps around the isotactic chain to form the outer strand of the double helix[6]. This structure opens the possibility of labelling independently the inner and outer strands of the double helix. Indeed by deuterating the isotactic chain the inner helix will be labelled while by deuterating the syndiotactic chain the outer helix will be labelled.

Preliminary experiments where performed on stereocomplex gels prepared in bromobenzene with a total polymer concentration of 12% (v/v). In order to minimise the number of isolated chain the ratio between isotactic and syndiotactic chains used was 1:2 (4% isotactic chains + 8% syndiotactic chains) in accordance with Shomaker and Challa double helix model. The experiments were performed on D22 which is a high flux spectrometer allowing relatively short acquisition time, typically 5 min, compared to PAXE, typically 2 hours. This allowed us to do real-time experiments.

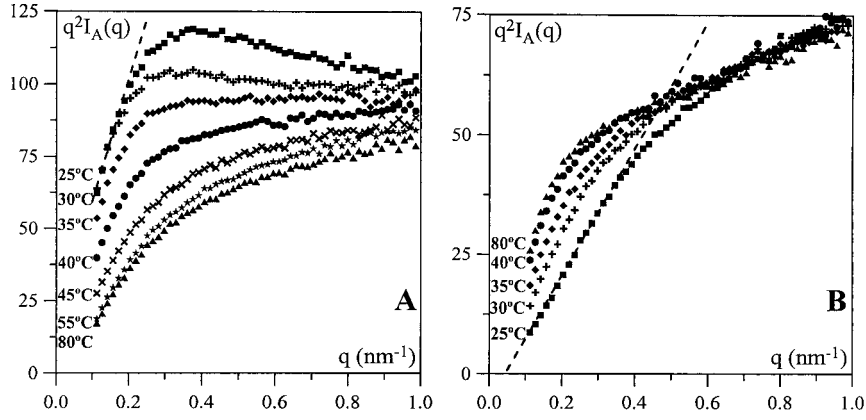

Figure 6. Intensity scattered by a 12% (v/v) stereocomplex gel prepared in bromobenzene. A: sample contains 4% (v/v) of deuterated syndiotactic chain; B: sample contains 4% of deuterated isotactic chains.

The first sample (sample A) was prepared by replacing 4% (v/v) of the protonated syndiotactic chains with their deuterated equivalent. The second sample (sample B) was prepared replacing all the protonated isotactic chains by their deuterated equivalent. In this way the concentration of deuterated polymer for both samples is identical, i.e.: 4% (v/v). The samples were subsequently melted at high temperature, 145°C and then cooled down stepwise (5°C steps) in order to follow the conformational changes of the syndiotactic and isotactic chains during the gelation process. The scattering curves were recorded for each sample at each temperature and are given in figure 6.

Different scattering patterns are obtained for the two samples suggesting, as expected, different chain conformations for syndiotactic and isotactic chains. This seems to be the case even at high temperatures. As the temperature is decreased in both cases the scattering curves change suggesting changes in the conformation of the polymer chains. In the case of the syndiotactic chain no significant changes are observed in the scattering curve from 145°C down to 45°C. In the case of the isotactic, however, no significant changes are observed in the scattering curves down to 35°C, thus suggesting that the syndiotactic chains go through a conformational change 10°C earlier than the isotactic chains. This result implies that the outer strand of the helix form first. Models are currently being developed to confirm this postulation.

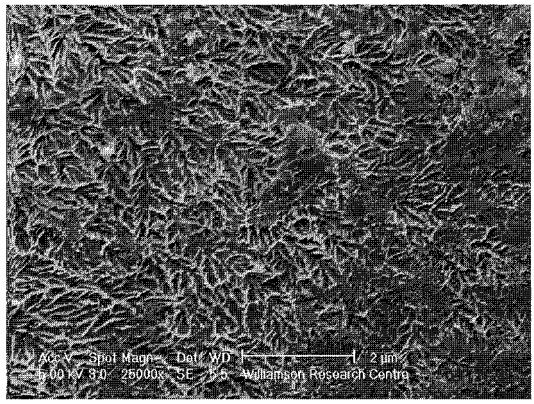

Figure 7. CryoSEM picture of a 12% (v/v) stereocomplex gel prepared in bromobenzene.

Further investigations are necessary in order to elucidate the exact conformation adopted by the two chains and the exact mechanism of the gelation process in relation to the conformational changes of the two polymer chains.

In order to observe the structure of the gel network cryo-electron microscopy experiments were performed. The same gel as used for the neutron scattering experiments were examined. A typical image of the gel structure is presented in figure 7. As can be seen a clear fibrillar structure is present. One characteristic feature of this network seems to be the relatively high number of branches observed. A large fraction of these branches seem to be pendant and not connected to the network.

Conclusion

It has been shown that SANS in combination with labelling techniques is a unique and powerful tool for the investigation of polymer gel structure. Based on our SANS results a double helix model is proposed for the chain conformation is syndiotactic PMMA gel. For the gel structure a fibrillar network model in which the fibrils are formed by the proposed double helix and the junctions by the aggregation of 3 double helices is proposed.

The development of high flux neutron facilities allows real-time investigation of these systems to be performed as has been shown for stereocomplex gels where the conformational changes of the polymer chains could be followed through the gelation process. The results presented here are preliminary results and additional work is in progress in order to elucidate the gelation mechanism of stereoregular PMMAs.

Acknowledgments

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