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To cite this version:
Zarmina Fazel, Nazir Fazel, Jean-Michel Guenet. Swelling and rheological properties of poly methyl methacrylate thermoreversible gels. Journal de Physique II, EDP Sciences, 1992, 2 (9), pp.1745-1754. <10.1051/jp2:1992231>. <jpa-00247763>

HAL Id: jpa-00247763
https://hal.archives-ouvertes.fr/jpa-00247763
Submitted on 1 Jan 1992

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Swelling and rheological properties of poly methyl methacrylate thermoreversible gels

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(Received 17 March 1992, accepted in final form 9 June 1992)

Abstract. — The stress relaxation as well as the variation of the isochrone compression modulus as a function of concentration have been studied with PMMA thermoreversible gels. Two solvents have been used: bromobenzene and ortho-xylene. The swelling behaviour has also been examined. Only gels in bromobenzene swell significantly. The swelling ratio vs. polymer concentration has been interpreted by means of a theory derived for two-phase systems. In both solvents considerable stress relaxation is observed. In the early stage this relaxation obeys a power law \( \sigma \approx t^{-m} \) with \( m \approx 0.08 \) to 0.13 in bromobenzene and 0.23 in ortho-xylene. For this reason isochronal moduli at 120 s have been considered. Modulus-concentration relations are as follows: \( E \approx C_p^{1.86} \) for non-swollen gels in bromobenzene, \( E \approx C_p^{1.99} \) for gels swollen to equilibrium in bromobenzene, \( E \approx C_p^{2.66} \) in ortho-xylene. These results are discussed by means of theories developed for rigid gels in the light of the molecular structure determined by small-angle neutron scattering (preceding paper published in the issue of August).

Introduction.

The aggregation phenomenon of stereoregular PMMAs in dilute solutions has received growing attention the past twenty years [1]. Curiously enough, the gel state has been little studied. Correspondingly, the rheological properties of these gels have been but barely investigated. So far experimental results have been essentially obtained on the modulus behaviour as a function of either temperature [2] or ageing time [3]. Although numerous studies of the variation of the modulus with polymer concentration have been performed with chemically-cross-linked gels [4] and, also, with many thermoreversible gels [5-7], no such investigation has been reported so far for PMMA thermoreversible gels. These investigations

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should be of importance as there exist theories that relate this variation with the molecular structure [8].

To our knowledge, so far no investigations into the swelling properties have been carried out either. Information gained from the swelling behaviour may prove relevant to the understanding of the rheological properties and also give an insight into the gel structure [8]. It is the aim of this paper to report on results obtained on the swelling behaviour as well as on the rheological properties such as the variation of the modulus as a function of polymer concentration. The results will be examined in the light of the molecular structures as deduced from small-angle neutron scattering which have been presented and discussed in the preceding paper [9].

**Experimental.**

**MATERIALS.** — The mechanical properties have been studied with sPMMA1 (see preceding paper for the sample characteristics [9]). The gel samples have been prepared from hydrogenated bromobenzene and ortho-xylene purchased from Prolabo and Aldrich, respectively. These solvents were employed without further purification.

**SAMPLE PREPARATION.** — To determine the compression modulus with sufficient accuracy, the samples must be cylindrically-shaped with a height being approximately the same as the diameter. Moreover, the faces of the cylinder must be as parallel as possible to avoid artifactual problems. To achieve highly parallel faces in the first place is also a necessity dictated by the need to maintain parallelism after gel swelling, the latter amplifying all sorts of defects. The principle of the preparation technique relies upon injection-moulding in a cylindrical mould. A homogeneous solution is obtained first in a hermetically closed syringe, by heating at a given temperature a mixture of solvent and polymer under sporadic stirring (155 °C in bromobenzene and 149 °C in ortho-xylene). The gel is obtained after injection into the mould followed by a quench to 0 °C for the appropriate time while an adequate pressure is maintained manually on the syringe to compensate for volume shrinkage that unavoidably takes place during cooling. Examination between crossed-polarizers indicates that this preparation technique does not induce much orientation as the sample is only slightly birefringent near the injection hole.

All the gels have been prepared by a quench at 0 °C and aged for a minimum of 1 h at this temperature.

This procedure allows the determination of the modulus to within ±5 % and does not depend in a systematic way upon the experimentalist all things being equal. In particular, it is not sensitive to the pressure applied by the experimentalist while cooling the system.

**GEL SWELLING.** — Samples used for the swelling experiments are also prepared by the method described above. The gel samples are immersed in an excess of preparation solvent to achieve equilibrium swelling. The swelling kinetics are followed by measuring the sample weight until equilibrium is reached. The swelling ratio, \( G_w \), is defined as the ratio of the final weight, \( P_\infty \), to the initial weight, \( P_0 \) of the sample. In this study the concentrations are expressed in w/w.

**MECHANICAL TESTING.** — Compression modulus measurements as well as compression stress relaxation experiments were carried out with a home-built apparatus, the principle of which is described elsewhere [10]. This apparatus is operated through a micro-computer which monitors the vertical displacements of a micro-motor and collects the data. Thanks to this set-up, displacements needed to achieve a given deformation can be performed automatically within less than one second.
Measurements were carried out at 20 ± 0.5 °C. As usual the compression modulus (static or isochrone) was calculated after the relation:

\[ E = -\frac{F}{A_0(\lambda - 1/\lambda^2)} \]  

(1)

where \( F \) is the force resulting from the application of a strain \( \lambda \) (\( \lambda = \ell/\ell_0 \), \( \ell_0 \) is the sample’s initial height and \( \ell \) the displacement) on a sample of initial area \( A_0 \). The compression modulus \( E \) is then one third of Young’s modulus. Here, the concentrations are expressed in g/cm².

As neither bromobenzene nor ortho-xylene are miscible with water, the latter was used as a thermostatic bath to prevent solvent evaporation which takes place at long relaxation times.

Results and discussion.

Swelling behaviour. — Whereas PMMA/bromobenzene gels swell when immersed into an excess of preparation solvent, gels in ortho-xylene do not. This suggests two comments:

i) Ortho-xylene is probably a bad solvent to PMMA. Such a result is reminiscent of the swelling behaviour of block-copolymer gels that lie far below the critical temperature of the equivalent solution [11]. This may also be the case for PMMA gels prepared from this solvent. If this statement is true, then gelation of PMMA in ortho-xylene interferes with a liquid-liquid phase separation [12].

ii) Bromobenzene is probably a good solvent to PMMA. Here, it seems quite likely that no liquid-liquid phase separation was involved whatsoever. However, this statement does not imply that the gel is a one-phase system as are chemically-cross-linked gels. On the contrary, SANS do show that the gels under study are micro- phases separated which certainly originate in a liquid-solid phase separation. The occurrence of gel swelling implies that the rod-like segments, or at least part of them, are freely hinged as their conformation cannot be further stretched. This in turn may suggest that, to allow for flexibility, there exists a significant proportion of amorphous physical junctions such as those already described for polysaccharides gels [13] (flail-like model see Fig. 1).

In the case of PMMA/bromobenzene gels the evolution of the degree of swelling as a function of polymer concentration has been further investigated (see Fig. 2). As can be seen, the slight yet noticeable discrepancies observed at the level of the molecular structure between as-received and « treated » PMMAs are also evidenced here, particularly at high concentrations. The degree of swelling is significantly more important in the as-received sPMMA_I sample than in the « treated » sPMMA_I. As opposed to what has been observed with isotactic polystyrene gels, for which the existence of polymer-solvent compound is now well-documented, no plateau is reached [14]. This does not necessarily imply that no compound is formed in these gels. As said above this behaviour is consistent with the presence of amorphous material (or, more precisely expressed, of non-organized material).

This swelling behaviour is reminiscent of what can be theoretically obtained from the relation derived by He et al. [11]:

\[ G_{woo} = 1 + (C_\alpha/C_\gamma - 1) \times X_\alpha \]

(2)

where \( C_\alpha \) and \( C_\gamma \) are the concentrations in the gel phase before and after swelling, respectively, and \( X_\alpha \) the proportion of gel phase in the sample prior to swelling. As \( C_\alpha \) is supposed to be a constant at a given temperature, so must be \( C_\gamma \). \( X_\alpha \) is proportional to
Fig. 1. — Schematic representation of an amorphous junction (flail-like model). The cylinder-like connecting objects are purposefully darkened so as to make no assumption as to the type of helicity (single or double helices).

Fig. 2. — Equilibrium swelling ratio, $G_\infty$, vs. the preparation concentration, $C_{\text{prep}}$ for PMMA bromobenzene gels: $\bigcirc$ = gels prepared from as-received PMMA, $\bullet$ = gels prepared from «treated» PMMA.

$C_{\text{prep}}$ and as such is the only variable in equation (2). If one assumes that the polymer concentration of the polymer-poor phase (chains non-incorporated in the network) is negligible with respect to $C_{\text{prep}}$ then $X_\alpha$ can be approximated to $X_\alpha = C_{\text{prep}}/C_\omega$. Relation (2) becomes:

$$G_{\infty} = 1 + \left( \frac{1}{C_\gamma} - \frac{1}{C_\omega} \right) \times C_{\text{prep}} = 1 + \Delta_s \times C_{\text{prep}}.$$  \hspace{1cm} (3)

As a result, a plot of $G_\infty$ vs. $C_{\text{prep}}$ should yield a linear variation. There is a good agreement with relation 3 for gels prepared from the «treated» PMMA sample, yet not so good with gels obtained from the as-received sample.
The following slopes $\Delta_s$ for relation 3 are derived:

- as-received PMMA: $\Delta_s = 8.6$
- «treated» sPMMA: $\Delta_s = 7.25$

Although $C_\alpha$ is not known we can nevertheless estimate $C_\gamma$ from $\Delta_s$. By varying $C_\alpha$ from 0.4 to 1, one finds that $C_\gamma$ lies in the vicinity of 0.1 g/g (which is about 0.15 g/cm$^3$). This suggests a rather high solvent content for the so-called polymer-rich phase. This may be an indication of the existence of solvent organized together with the polymer as has been reported for solvated crystals [15].

It is worth adding that these results cannot be interpreted in the light of the $C^*$ theorem derived by de Gennes [16]. This theorem states that the gel will tend to swell to a concentration corresponding to the overlap concentration, $C^*$, of the objects joining the junctions. This entails that the swelling ratio $(v/v$ this time) simply reads:

$$G_{v\infty} \approx C/C^*$$

Provided the $C^*$ theorem applies in the present case, since the mesh size, $\xi$, varies like $\xi \approx C^{-1/2}$ for rods and $C^*$ varies like $\xi^{-2}$ [17], $G_{v\infty}$ should be a constant and $G_{v\infty}$ too.

STRESS RELAXATION. — Strictly speaking, a gel is a solid-like material which ought to possess a measurable storage modulus, $G'$, at zero frequency. In terms of stress relaxation, this implies that the rate of relaxation should reach zero, that is, the stress should reach a plateau after some length of time. PMMA gels investigated here do not obey this rule. At an early stage, the relation between the stress $\sigma$ and the time $t$ is to within experimental uncertainties linear in a double logarithmic plot. As can be seen in figures 3 and 4, the stress relaxation rate

![Fig. 3](image)
![Fig. 4](image)

Fig. 3. — Stress-relaxation for PMMA/bromobenzene gels at a deformation of $\lambda = 0.85$. Upper curves = as-received PMMA gels, middle curves = «treated» PMMA gels and lower curves = «treated» PMMA gels swollen to equilibrium.

Fig. 4. — Stress-relaxation for PMMA/ortho-xylene gels at a deformation of $\lambda = 0.85$. Upper curves = as-received PMMA gels and lower curves = «treated» PMMA gels.
\( m = d \log \sigma / d \log t \) is quite noticeable. At short relaxation times \( (t < 1000 \, \text{s}) \) the following values are measured:

- In \textit{bromobenzene} \( m = 0.13 \pm 0.01 \) with sPMMA
- \( m = 0.1 \pm 0.01 \) with \textit{« treated »} sPMMA1
- \( m = 0.08 \pm 0.005 \) with \textit{« treated »} sPMMA1 in swollen gels
- In \textit{ortho-xylene} \( m = 0.23 \pm 0.02 \) for all samples.

As can be seen the relaxation rate is sensitive to the kind of sample for \textit{bromobenzene} gels. In particular it decreases quite noticeably with swollen gels. Conversely, there is little PMMA sample effect in the case of \textit{ortho-xylene} gels.

Over longer periods of time the relaxation rate remains approximately unchanged in PMMA/bromobenzene gels. Conversely, it is seen to increase quite significantly in PMMA/\textit{ortho-xylene} gels (see Fig. 5). After \( t = 5000 \, \text{s} \) increases up to \( m = 0.46 \pm 0.01 \).

These high relaxation rates constitute a possible indication of how the physical junctions are labile (the higher the value of \( m \), the more labile the junctions). Such high values were also observed with isotactic polystyrene gels and attributed to the absence of crystalline order in the physical junctions [6], a possibility also contemplated here. Cases where the junctions are crystalline, and presumably non-labile, yield \( m = 0.01 \) to 0.03 [11, 17], values quite similar to those reported for chemical gels with permanent cross-links [18].

![Graph showing stress relaxation](image)

**Fig. 5.** — 24 h-stress relaxation observed at constant deformation for \textit{ortho-xylene} gels (upper curve with solid line giving a slope of \( m = 0.46 \)) and for \textit{bromobenzene} gels (lower curve with solid line giving a slope of \( m = 0.13 \)). For the sake of clarity, the PMMA/bromobenzene curve has been shifted downwards by subtraction of a constant.

**Modulus versus Concentration.**

\textit{Theoretical.} — Before presenting and discussing the results it seems appropriate to elaborate on recent theories that may prove relevant to the present study in the light of the molecular structure determined by neutron scattering [9].

Jones and Marques have derived theoretical power law relations between the gel modulus and its polymer concentration based on the fractal dimension of the objects connecting the junctions [8]. Two types of elasticity are envisaged: \textit{enthalpic} and \textit{entropic}.

\textit{Enthalpic elasticity} relies on the deformation of rigid objects, such as rod bending, whose...
conformation is frozen and, therefore, cannot be altered. Conversely, entropic elasticity originates in the change of conformation that can undergo flexible objects. In the case of gels, if both the junctions and the object connecting these junctions are rigid, then enthalpic elasticity only will result. On the other hand, if the junctions are flexible, whatever the rigidity or flexibility of the connecting object, one will be dealing with entropic elasticity. Flexibility of the junctions means that there is no constraint on the angles \( \alpha \) between two objects meeting at a same junction (see Fig. 1 for example). The latter system is usually referred to as a network of freely-hinged structures. In other words, the angle fluctuations, \( \langle \delta \alpha^2 \rangle \), take some finite value whereas it is zero in the previous situation.

Concerning enthalpic elasticity (modulus \( G_e \)) Jones and Marques [8] arrive at the following relation for the modulus under the implicit condition that \( L \gg r \):

\[
G_t \approx \frac{e r^4 n}{N^{3 \nu + 1} a^4}
\]  

(5)

where \( N \) is the number of elements of length \( a \) in the connecting object (proportional to its contour length, \( L \)), \( \nu^{-1} \) its fractal dimension, \( r \) its cross-section radius and \( e \) the intrinsic material Young’s modulus. \( n \) is simply the number of objects merging at the same junction (functionality).

The network concentration is expressed as follows:

\[
\varphi = n N ar^2 R^3 = n N^{1 - 3 \nu} r^2 a^2.
\]  

(6)

If the network concentration is identical to the polymer concentration, then \( G_t \) eventually reads at constant functionality \( n \):

\[
G_t \approx \frac{e r^4}{a^4} \left( \frac{\varphi a^2}{nr^2} \right)^{(3 \nu + 1)(3 \nu - 1)}
\]  

(7)

For rods (\( \nu^{-1} = 1 \)) relation (7) becomes:

\[
G_t \approx e \varphi^2 / n.
\]  

(8)

In this case only (\( \nu^{-1} = 1 \)) is \( G_t \) independent of the object cross-section.

It is worth dwelling upon the fact that the polymer concentration, \( C_p \), and the network concentration, \( \varphi \), may significantly differ. Neither pendant chains nor non-incorporated chains contribute to the elasticity of the network which entails that, in most cases, \( C_p \gg \varphi \). This has obviously an impact on the actual, experimental exponent.

Concerning entropic elasticity (modulus \( G_e \)) a simple approach [16] consists of considering the modulus to be proportional to the reciprocal of the cube of the mesh size, \( \xi (G_e = \frac{1}{\xi^3}) \). Scaling arguments yield [19]:

\[
\xi \approx \varphi^{-\nu/3 \nu - 1}
\]  

(9)

which eventually gives for \( G_e \):

\[
G_e \approx \varphi^{-3 \nu/3 \nu - 1}
\]  

(10)

For rods one obtains:

\[
G_e \approx \varphi^{3/2}
\]  

(11)

Now, one must bear in mind that a system can contain both types of elasticity in which case the resulting modulus is expressed through [8]:

\[
G^{-1} = G_t^{-1} + G_e^{-1}
\]  

(12)
Under these conditions the variation as a function of concentration will not obey a power law although power laws may be observed experimentally due to the experimental uncertainties. If such is the case, the exponent will be intermediate between 1.5 and 2 for rods.

**Experimental.** — As has been discussed above gels either in bromobenzene or ortho-xylene display considerable relaxation. Consequently, the modulus cannot be determined by simply varying the strain. We have then recourse to the determination of the isochrone modulus measured at constant deformation during a relaxation experiment. Here, we have considered the modulus at 120 s. We have found that the value of the modulus is little dependent upon the deformation so that the gels can be regarded as neo-hookean in the range investigated. We have also checked that only the front factor of the relation modulus-concentration is affected when considering values of moduli at different relaxation times (60 s and 180 s). We have also examined the modulus variation with ageing time since it is known that these gels display noticeable kinetics of formation [1-3]. We have found out that the equilibrium modulus is reached within 1 h at a quenching temperature of 0 °C. Consequently, this ageing time has been used throughout this study.

**Gels from bromobenzene.** — Results gained from gels prepared in bromobenzene are reported in figure 6 by means of a double logarithmic scale. As can be seen, linear variations are found for non-swollen gels and for swollen gels, both prepared from «treated» PMMA. Conversely, gels prepared from the as-received sample show a significant departure from linearity. In addition, the magnitude of the moduli at a constant concentration is larger in swollen gels than in non-swollen gels and also higher with «treated» PMMA than with as-received PMMA.

Linear regressions provide one with the following relations:

- gels from as-received PMMA: \( E = 1.6 \times 10^2 C_p^{1.86 \pm 0.1} \) (kPa) \((13)\)
- gels from «treated» PMMA (non-swollen): \( E = 2.08 \times 10^2 C_p^{1.86 \pm 0.05} \) (kPa) \((14)\)
- gels from «treated» PMMA (swollen): \( E = 1.94 \times 10^3 C_p^{1.99 \pm 0.05} \) (kPa). \((15)\)

Relations (13) and (14) give an exponent, 1.86, which, for rods, turns out to be intermediate between \(3/2\) (entropic elasticity) and 2 (enthalpic elasticity). This exponent most probably points to the co-occurrence of entropic + enthalpic elasticity, as discussed above.

Fig. 6. — Compression modulus (in kPa) determined at 120 s from relaxation experiments vs. concentration (in g/cm³) for PMMA/bromobenzene gels. (+) as-received PMMA; (O) «treated» PMMA; (●) gels prepared from «treated» PMMA and then swollen to equilibrium.
This is in agreement with the swelling experiments that do hint at the existence of flexible junctions. The value of this exponent may also arise in part from the effect of non-incorporated chains that are suspected to exist in the non-swollen gels. An exponent of about 2 is found with the swollen gels which is consistent with the behaviour of a network of rigid rods that chiefly displays enthalpic elasticity and consistent with the conclusions drawn from neutron scattering data (array of connected rigid rods).

These experiments reveal that swelling diminishes the angle fluctuations $\langle \delta \alpha^2 \rangle$, considerably, an effect which, it is worth remembering, occurs together with the occurrence of a lower relaxation rate.

Gels prepared from ortho-xylene. — As above the results yield a linear variation when plotted by means of a double logarithmic scale (Fig. 7). The following relation has been obtained:

$$E = 3.6 \times 10^3 C_{\rho}^{2.66 \pm 0.05} \text{ (kPa)}.$$  \hspace{1cm} (16)

![Graph](image)

Fig. 7. — Compression modulus (in kPa) determined at 120 s from relaxation experiments vs. concentration (in g/cm$^3$) for PMMA/ortho-xylene gels. (O) as-received PMMA; (+) « treated » PMMA.

Unlike gels in bromobenzene, no significant discrepancies have been observed whether as-received or « treated » PMMA were used.

At first sight, these results seem unaccountable with the above theoretical relations as they lead to conclusions apparently inconsistent with the neutron scattering data. As a matter of course, whether enthalpic or entropic elasticity is considered one derives the following fractal dimensions from the exponent 2.66:

- **enthalpic** $\nu^{-1} = 1.36 \pm 0.05$
- **entropic** $\nu^{-1} = 1.87 \pm 0.05$.  

Neither fractal dimension appears to be in agreement with the neutron scattering results for which the intensity varies like $q^{-n}$ with $n > 2$. Yet, this inconsistency might not necessarily express that the above theoretical approach does not apply to these gels. In this solvent, it is said that the gel consists of fibrils with cross-sections significantly larger than in bromobenzene. This is what reflects the scattered intensity in the $q$-range investigated. To determine the fractal dimension of these fibrils will most probably require to investigate the gel sample prepared from ortho-xylene at lower $q$-values. Only then will it be possible to decide whether the theoretical treatment derived by Jones and Marques is relevant to this system or not.
Now, if the theory does break down, then the reason may be found in the presence of rod-like objects with very large cross-sections. In this case, the implicit condition of a mesh size larger than the object cross-section is no longer obeyed.

Concluding remarks.

In this paper we have shown that rheological and swelling properties of PMMA gels are strongly dependent upon the solvent type. In particular the relations between modulus and concentration display power law variations with differing exponents. In the case of bromobenzene all the results are well accounted for with theories developed for rigid gels and in agreement with the molecular structure as deduced from small-angle neutron scattering.

However, if one considers gel systems that display an elastic modulus at zero frequency, then these networks are not strictly gels as they show considerable relaxation.

Furthermore, these gels are much reminiscent of isotactic polystyrene gels for which similar relaxation rates have been reported [6]. They are also reminiscent of some poly saccharides, such as carragenaans [7] or agarose [20, 21] for which similar exponents are found although their moduli turn out to be several times larger.

References

[12] In the case of physical gels the liquid-liquid phase separation is frozen in at its early stage so that the system is only microphase-separated. The polymer-rich phase after a liquid-solid transformation produces the network. See for instance Tohyama K. and Miller W. G., Nature 289 (1981) 813.
[15] Solvent organized together with polymer means that helices constituting the rods are probably stabilized by solvent molecules which is much reminiscent of crystallosolvates. For further reading see Guenet J. M., Thermoreversible gelation of polymers and biopolymers (Academic Press, London, 1992).