A conducting polymer gel prepared by gamma -ray irradiation and its characteristics

LETTER TO THE EDITOR

A conducting polymer gel prepared by γ-ray irradiation and its characteristics

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Abstract. Soluble and fusible poly(3-alkylthiophene) can be transformed into a conducting polymer gel by γ-ray irradiation. This polymer gel can be processed because it is still fusible. Reversibility of the volume change of this polymer gel has been demonstrated by changing the solvent composition and the temperature and also by doping. The anisotropic shape change of a drawn polymer gel prepared by γ-ray irradiation has been also demonstrated.

Conducting polymers and their unique characteristics have attracted much attention because various new physical concepts such as solitons, polarons and bipolarons have been introduced to explain them (Su *et al* 1979, Chen *et al* 1980, Scott *et al* 1983, Bredas *et al* 1983) and also various new functional applications utilising them have been proposed (Yoshino *et al* 1983, 1985a, b). Among the various conducting polymers, poly(3-alkylthiophene) is the most interesting because it is the first soluble (Sato *et al* 1986, Elsenbaumer *et al* 1986) and even fusible conducting polymer (Yoshino *et al* 1987a, b) and also because it demonstrates a drastic colour change upon change in temperature (Yoshino *et al* 1988a, b).

The study of polymer gels has greatly progressed since the finding and unique interpretation of the remarkable volume instability of gels caused by changing the solvent and temperature (Tanaka 1978, Tanaka *et al* 1980, 1987, Ohmine and Tanaka 1982, Irie 1986). However, the polymer gels studied so far have been limited only to insulating polymers such as polyacrylamide gel (Tanaka 1978, Tanaka *et al* 1980).

Recently, we have demonstrated that some non-soluble parts of poly(3-alkyl-thiophene) which were obtained during polymerisation behave just like polymer gels (Yoshino *et al* 1989a, b). We have explained these unique characteristics in terms of an apparent cross-linking formation due to a strong inter-chain coupling.

In this letter, we report that the soluble parts of poly(3-alkylthiophene) can be converted into a polymer gel by γ-ray irradiation and also that they demonstrate unique characteristics.

Poly(3-alkylthiophene)s of various alkyl chain lengths n ($-C_nH_{2n+1}$) were prepared by the chemical method previously reported by the author. That is, a 3-alkylthiophene monomer was polymerised utilising $FeCl_3$ as the catalyst in chloroform for about 10 h at room temperature. The reaction product was poured into methanol and the residual

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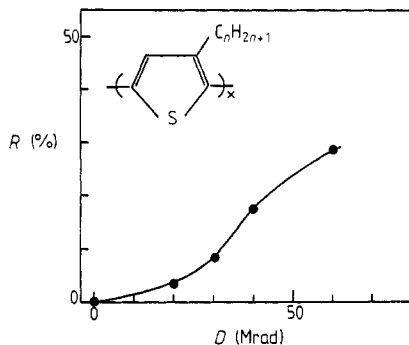
Figure 1. The dependence of the gel formation ratio (R) of γ-ray irradiated poly(3-hexylthiophene) on irradiation dose (D). Inset: molecular structures of poly(3-alkylthiophene) gel, $n = 6$: poly(3-hexylthiophene), $n = 8$: poly(3-octylthiophene), $n = 10$: poly(3-decylthiophene), $n = 12$: poly(3-dodecylthiophene).
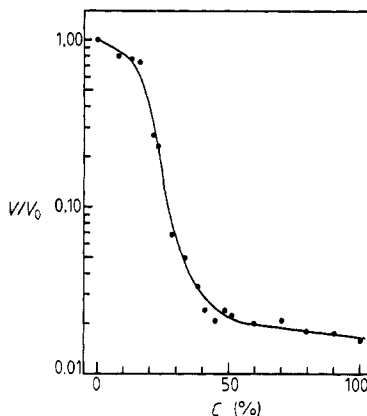

Figure 2. The dependence of the shrinkage ratios of volume in poly(3-hexylthiophene) gel formed by an irradiation dose of 60 Mrad on the ethanol concentration in chloroform (C).

poly(3-alkylthiophene) was purified by repeated washing with methanol. Details of the preparation method and procedure have already been reported in our previous paper (Yoshino *et al* 1984b). The soluble part of the poly(3-alkylthiophene) obtained was used as a starting material.

By casting the solution of poly(3-alkylthiophene) in chloroform onto a glass substrate, thin films about 100 μm thick were obtained and then peeled off the substrate as free standing films. The films obtained were sealed in glass tubes under vacuum. Then the sample in the glass tube was irradiated with γ-rays from a ^{60}Co radiation source.

The electrical conductivity was measured by two- and four-probe methods. Absorption spectra were measured utilising a Hitachi 330 spectrophotometer.

Soluble poly(3-alkylthiophene) films were drawn uniaxially at a rate of 2×10^{-3} cm s^{-1}, utilising a specially designed piece of equipment, at 30 °C under a dried Ar gas atmosphere. The drawing ratio (l/l_0) is the ratio of the drawn length (l) to the undrawn length (l_0).

The shrinkage ratio of volume (V/V_0) was defined as the ratio of the volume of gel (V) to the maximum expanded state volume (V_0) in this study. The expansion ratio of length ($l_\perp/l_{0\perp}$, $l_\parallel/l_{0\parallel}$) was defined as the ratio of the length of gel ($l_\perp$, $l_\parallel$) to the maximum shrunken state length ($l_{0\perp}$, $l_{0\parallel}$). Here, $l_\perp$ and $l_\parallel$ are the lengths measured perpendicular and parallel to the drawn direction, respectively.

By putting the irradiated film in chloroform for 24 h at room temperature, the soluble part was removed and the remaining non-soluble part was used as the sample.

Figure 1 indicates the dependence of the gel formation ratio, defined as the ratio of the gel part to the soluble part in poly(3-hexylthiophene), on irradiation dose. Among various poly(3-alkylthiophene)s, mainly poly(3-hexylthiophene) and poly(3-decylthiophene) etc whose molecular structure is shown in the inset of figure 1 were used as samples in this study. As evident from this figure, the non-soluble part increases with increasing radiation dose above 20 Mrad, tending to saturate above about 60 Mrad.
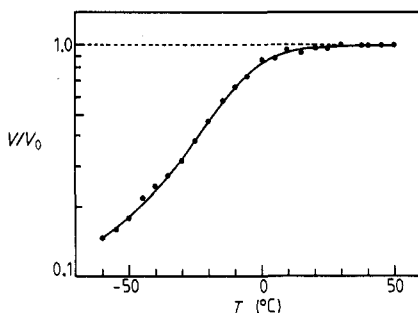
Figure 3. The temperature dependence of the shrinkage ratios of volume in poly(3-hexylthiophene) gel formed by an irradiation dose of 60 Mrad in chloroform.
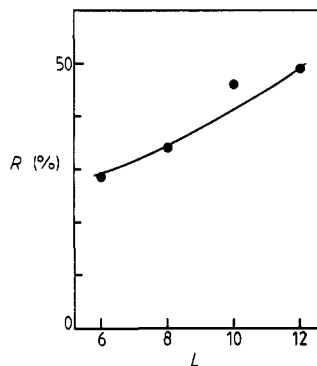
Figure 4. The dependence of the gel formation ratio (R) in poly(3-alkylthiophene) gel formed by an irradiation dose of 60 Mrad on the alkyl chain length (L).

Similar dependences on the γ-ray irradiation dose were also observed in other poly(3-alkylthiophene)s with different alkyl chain length.

This non-soluble part of the γ-ray irradiated poly(3-alkylthiophene) has been confirmed to exhibit the typical characteristics of a gel. That is, for example, the volume of the non-soluble part of the γ-ray irradiated poly(3-alkylthiophene) decreased remarkably on changing the solvent composition and temperature.

Figure 2 indicates the dependence of the shrinkage ratio of the volume of γ-ray irradiated poly(3-hexylthiophene) on the ethanol concentration in chloroform. The volume of the sample put in chloroform increased drastically but the introduction of an amount of ethanol into the chloroform produced a marked decrease in volume.

Figure 3 indicates the dependence of the shrinkage ratio of the volume of γ-ray irradiated poly(3-hexylthiophene) on temperature. It should also be noted that the volume of the sample changed drastically on decreasing the temperature as shown in this figure.

These are characteristics that are similar to those of insulating polymer gels and also to chemically and electrochemically prepared poly(3-alkylthiophene) gels. That is, poly(3-alkylthiophene) turns into a typical polymer gel on γ-ray irradiation.

The origin of gel formation has not yet been fully understood. However, we are speculating at this stage as follows. Two gel formation processes are considered possible. The first possibility is the formation of cross-linking, at hydrocarbon side chains, of neighbouring polymer chains. We have already reported that the conjugated electron system is quite resistive to γ-ray irradiation (Yoshino *et al* 1984a) but the saturated alkyl chain polymers, such as polyethylene, are made cross-linked relatively easily by irradiating with these ranges of irradiation dose (Yoshino *et al* 1978). Therefore gel characteristics might originate in the cross-linking formation at alkyl side chains of neighbouring polymer main chains.

The second possibility is the radiation induced, apparently physical, cross-linking formation. That is, when two neighbouring conjugated chains with co-planar structures face each other within a short distance, the inter-chain interaction should be strong, resulting in the apparent cross-linking formation and non-fusibility. If some torsion of bonds exists between thiophene rings on a polymer main chain, the inter-chain inter-
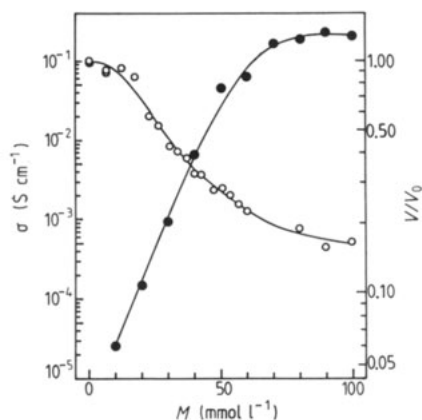
Figure 5. The dependence of electrical conductivity (σ) and the shrinkage ratios of volume in poly(3-dodecylthiophene) gel formed by an irradiation dose of 60 Mrad on the iodine concentration in a chloroform solution (M).
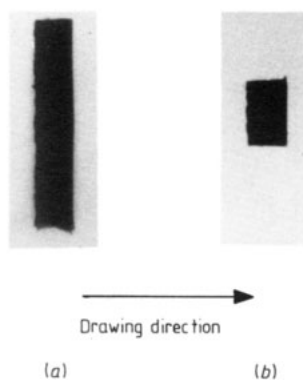

Figure 6. Photographs of the volume change of drawn poly(3-decylthiophene) gel formed by an irradiation dose of 60 Mrad upon a drawn soluble poly(3-decylthiophene) (a) in the expanded state in a chloroform solution and (b) in the shrunken state in an ethanol solution.

action should not be strong. However, polarons, with a quinoid-like structure, which is co-planar, will be formed upon γ-ray irradiation. In such a case, the possibility of the formation of strong inter-chain interaction seems to be enhanced, resulting in the formation of apparent physical cross-linkings.

Figure 4 shows the gel formation ratio of a γ-ray irradiated polymer gel versus the alkyl chain length. The γ-ray irradiation dose is 60 Mrad. In this case, the formation of the γ-ray irradiated polymer gel increases with increasing alkyl chain length. The fact that the whole volume of the gel part is higher in poly(3-alkythiophene) with longer alkyl chains under constant γ-ray irradiation dose suggests that the former process described above seems to be the more probable explanation of gel formation. However, at this stage, the latter process cannot be completely discounted.

It should also be mentioned that the colour of the γ-ray irradiated polymer gel changed drastically upon changing the solvent composition and temperature just as in the chemically prepared poly(3-alkylthiophene) gels. In the expanded state in chloroform and at higher temperature the sample is yellow in colour, and in the shrunken state in a chloroform–ethanol mixture and at lower temperature, it is red. That is, the colour change of the sample is related to the volume change. This means that the conjugation length becomes effectively shorter in the expanded state. In the expanded state, the alkyl chains seem to be bulky due to a *gauche*-conformation which results in the twisting of bonds between thiophene rings, contrary to the shrunken state in which alkyl chains are expected to have a *trans*-conformation and a smaller steric hindrance effect is expected.

The volume of the γ-ray irradiated polymer gel was also changed drastically by doping. For example, as is evident in figure 5, γ-ray irradiated poly(3-dodecylthiophene) in the expanded state shrank anomalously with iodine doping. In this case, the dopant should interact with two polymer chains and form apparent cross-linkings, resulting in the shrinkage of the gels.
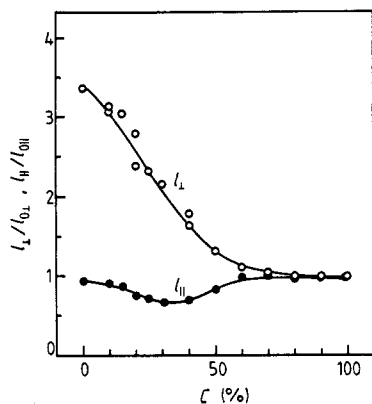
Figure 7. The dependence of the anisotropic expansion ratio of lengths in drawn poly(3-decylthiophene) gel formed by an irradiation dose of 60 Mrad upon a drawn soluble poly(3-decylthiophene) on the ethanol concentration in chloroform (*C*).
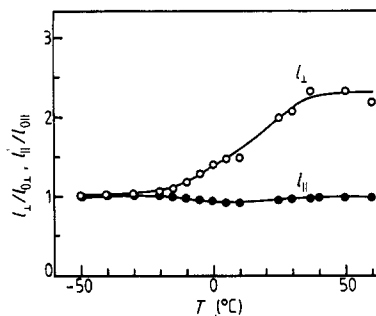
Figure 8. The temperature dependence of the anisotropic expansion ratio of lengths in drawn poly(3-decylthiophene) gel formed by irradiation with a dose of 60 Mrad of a drawn soluble poly(3-decylthiophene).

By the introduction of iodine, the electrical conductivity of the polymer gel in chloroform was also enhanced remarkably and the colour changed from yellow to black. As shown in figure 5, the electrical conductivity of the poly(3-decylthiophene) gel formed by γ-ray irradiation became higher as the iodine concentration in the chloroform solution increased. A quantitative discussion of this cannot be made at this stage. However, at least we can conclude that a γ-ray irradiated polymer gel can be well doped thereby inducing an insulator–metal transition.

The speed of change of volume and electrical conductivity upon doping was very fast in these cases, because the doping speed in gels is extraordinarily fast.

A highly drawn poly(3-alkylthiophene) gel formed by γ-ray irradiation upon a drawn soluble poly(3-alkylthiophene) film exhibited anisotropic gel characteristics. This drawn polymer gel expanded in chloroform only in the direction perpendicular to the drawn direction but not in the direction parallel to the drawn direction. The shrinkage of the drawn polymer gel ($l/l_0 = 4$) in chloroform upon introduction of ethanol was very marked in the direction perpendicular to the drawn direction as shown in figure 6.

The anisotropic shrinkage of the drawn polymer gel ($l/l_0 = 4$) as a function of the solvent composition is more clearly indicated in figure 7.

The change in volume with temperature of this drawn polymer gel was also anisotropic and the length of the sample perpendicular to the drawn direction decreased below some critical temperature as is evident in figure 8.

As shown in figures 7 and 8, the minimum point of increase in the ratio of lengths is also observed in the direction parallel to the drawn direction. However, the reason for this is not clear at this stage.

These results can be explained as follows. In drawn polymer gels, the polymer main chains are aligned in the drawing direction. The change of conformation of the alkyl side chains with solvent and temperature should induce the changes of inter-polymer–main-chain interactions and therefore inter-chain distance, resulting in the expansion only in the direction perpendicular to the aligned direction.

These polymer gels prepared by γ-ray irradiation and especially anisotropic gels are also important from a practical point of view.

The present experimental results from poly(3-alkylthiophene) gels formed by γ-ray irradiation can be summarised as follows.

(i) Poly(3-alkylthiophene) turns into a typical polymer gel on γ-ray irradiation.

(ii) The gel formation ratio increases as the γ-ray irradiation dose is increased.

(iii) The gel formation ratio due to γ-ray irradiation increases as alkyl side chains become longer.

(iv) The volume of the γ-ray irradiated polymer gel shrinks remarkably on changing the solvent composition and temperature.

(v) In the expanded state in chloroform and at higher temperature the γ-ray irradiated polymer gel is yellow in colour and in the shrunken state in a chloroform–ethanol mixture and at lower temperature it is red.

(vi) A drawn poly(3-alkylthiophene) gel formed by γ-ray irradiation exhibited anisotropic gel characteristics. That is, this drawn polymer gel expanded in chloroform and at higher temperatures only in the direction perpendicular to the drawn direction but not in the direction parallel to the drawn direction.

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