Electrical conductivity of polydiacetylene P(4BCMU) gel: 2. A percolation model for elasticity and conductivity

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Tensile stress and electrical conductivity were studied on gels formed from toluene solutions of a polydiacetylene, poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxycarbonylmethyl urethane)], abbreviated to P(4BCMU). The gels exhibited stress–strain curves concave upwards, that is, opposite to the behaviour of ordinary flexible polymer networks. This behaviour indicates that the elasticity is not due to the conformational entropy due to deformation of the stiff ribbon-like P(4BCMU) molecules. The direct current conductivity σ_{dc}, the alternating current conductivity σ_{ac} and Young's modulus E increased with concentration C in proportion to $C^{0.88}$, $C^{0.89}$, and $C^{1.07}$, respectively. The similarity in the concentration dependences of σ_{dc}, σ_{ac} and E is explained with a percolation model. The σ_{ac} was almost independent of frequency in the range of 0.1–100 kHz.

(Keywords: electric conductivity; gel; polydiacetylene; poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxycarbonylmethyl urethane)]; stress–strain curve; Young's modulus; percolation)

INTRODUCTION

In the first paper in this series, we reported the sol–gel transition and the electrical conductivity of toluene (TOL) gels of a polydiacetylene, poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxycarbonylmethyl urethane)], abbreviated to P(4BCMU)[1]. From the conductivity enhanced with dopant iodine and from the photoconductivity of the gels, we concluded that the carrier species for the conduction is an electron and/or a hole.

To understand the electrical properties of P(4BCMU) gels, knowledge of their internal structure is essential. As pointed out in part 1, P(4BCMU) molecules may have a planar rod-like or ribbon-like structure below the sol–gel transition temperature[2–4]. We thus expect the carriers to migrate through the chains and occasionally jump from one molecule to the other at a junction point where the molecules are in contact with each other. Since the polymer concentration in the gels is of the order of 1 wt% and the chains are mostly surrounded by TOL molecules, the carriers hardly migrate from one chain to another without passing through junctions. However, the structure of the junctions has not yet been studied.

Two cases may be considered: one is that the junctions are just contacts of stiff chains; the other is that tight junctions are formed through the creation of microcrystallites or aggregates, as suggested by Wegner[5].

In both cases high connectivity of the gel network imparts paths for carriers to migrate and also stiffness to the gel. Thus we expected the stress–strain and electrical conductivity behaviour to be closely related and to provide information about the structure of the gel. The concentration and temperature dependences of the elastic modulus of P(4BCMU) gel have already been reported by Heeger *et al.*[4,6]. We attempted to examine the stress–strain relation of P(4BCMU)/TOL gels in more detail. Then we compared the conductivity and elastic modulus based on a percolation theory[7]. We expected some molecules not to be connected to the fully percolated molecules. Then the isolated molecules contribute to the alternating current (a.c.) but not to the direct current (d.c.) conductivity. We also analysed the a.c. conductivity to understand the relationship between the gel structure and conductivity.

EXPERIMENTAL

Samples

P(4BCMU) samples were prepared from 5,7-dodecadiyn-1,12-diol-bis(n-butoxycarbonylmethyl urethane) (4BCMU) by irradiation of ^{60}Co γ-rays *in vacuo* at room temperature. The synthesis and characterization of poly P(4BCMU) has already been reported by Se *et al.*[8] and also in part 1[1]. Two samples with weight-average molecular weight $\bar{M}_w = 28 \times 10^4$ and 180×10^4 were used and coded as P(4BCMU)-28 and P(4BCMU)-180, respectively.

Method

The apparatus used for the stress–strain measurement is schematically shown in *Figure 1*. To prevent evaporation of TOL, we carried out measurements on gel samples immersed in water. One end of the gel specimen was fixed, and the stress was applied to the other end with a high sensitivity balance. Elongation of the gel was measured with a travelling microscope. The sample cells

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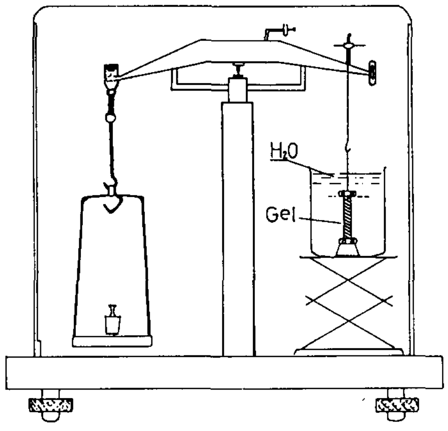

Figure 1 Apparatus for measurement of the stress–strain curve of P(4BCMU)/TOL gels

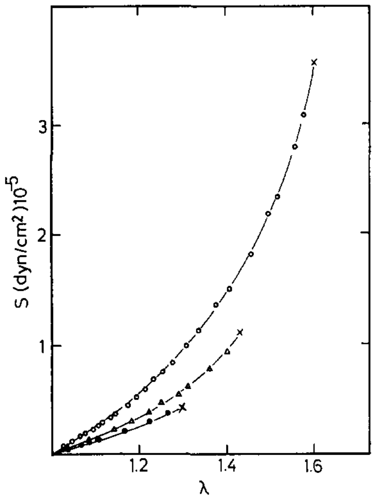

Figure 2 Tensile stress S *versus* elongation λ curves for P(4BCMU)-180/TOL gels at 298 K: (●) 0.59 wt%; (△) 1.05 wt%; (○) 1.88 wt%

for the conductivity measurement were described in part 1[1].

RESULTS AND DISCUSSION

Stress–strain curves

The stress–strain curves of P(4BCMU)-180/TOL gels at various concentrations are shown in *Figure 2*, where S denotes the engineering stress, that is the force divided by the area of the cross-section at the stress free state, and the abscissa λ denotes the elongation ratio. In each run measurement was carried out up to the maximum elongation ratio λ_r (marked with x), at which the gel specimen was ruptured. The stress S_r at rupture decreased with decreasing concentration. From the initial slope of the curve, the Young's modulus E was determined and is given in *Table 1*.

As is seen in *Figure 2*, all the curves show a concavity, that is $d^2S/d\lambda^2 > 0$. This behaviour is opposite to that of an ordinary flexible polymer network indicating that the molecular origin of the elasticity in the P(4BCMU) gel is quite different from such a polymer network. The elasticity of a flexible polymer network is mainly due to the conformational entropy. On the other hand, P(4BCMU) molecules in the gel state have a rod-like conformation as reported in part 1[1], and hence the change in the conformational entropy due to deformation is expected to be small. An important factor may be the deformation energy of the individual rod-like molecules.

Stress–strain relation in doped gels

In the first paper in this series, we reported that the electrical conductivity increased by doping with iodine[1]. We tested the stress–strain curve for the gel doped with iodine to detect possible differences in structure between doped and undoped gels. *Figure 3* shows the stress–strain curves of P(4BCMU)-180/TOL gels with concentrations of 1.7–1.9 wt% with various dopant concentrations Y. Here Y is defined as the molar ratio of $\frac{3}{2}I_2$ and the 4BCMU monomer. Comparing the stress–strain curves for the doped and undoped gels, we see that the stress level for the doped gels is only slightly higher than that for the undoped gel with concentration $C = 1.88$ wt%. Thus we conclude that the network structure of P(4BCMU) gels is independent of the dopant concentration. The increase in the conductivity by doping iodine reported in part 1 is thus attributable to the increase in the number of carriers. It is unlikely that the doping induces a structural change in the gel.

Concentration dependence of conductivity

Figure 4 shows double logarithmic plots of the a.c. conductivity σ_{ac}, the d.c. conductivity σ_{dc} and E against C for P(4BCMU)-180/TOL gels. The plots for σ_{dc}, σ_{ac} and E all conform to straight lines. The slopes (β) for the plots are given in *Table 2*. It is seen that the values of β for these quantities agree with one another and are close to unity within error.

We expect σ_{dc} and E to be proportional to the probability of the macroscopic connection of the molecules. Based on the percolation theory, de Gennes indicated that σ_{dc} and E should have the same C

Table 1 Young's moduli E of P(4BCMU)-180 gels at 298 K

C (wt%)	$10^{-4}E$ (Pa)
0.59	1.47
1.05	1.95
1.88	2.89
2.76	3.96
4.49	9.04

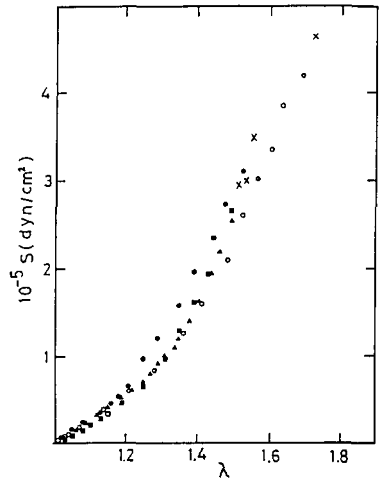

Figure 3 Tensile stress S *versus* elongation ratio λ curves for P(4BCMU)-180/TOL gels doped with iodine. The dopant concentration Y represents the molar ratio of $\frac{3}{2}I_2$ to 4BCMU monomer: (○) $Y = 0$; (■) $Y = 0.083$; (▲) $Y = 0.13$; (●) $Y = 0.27$

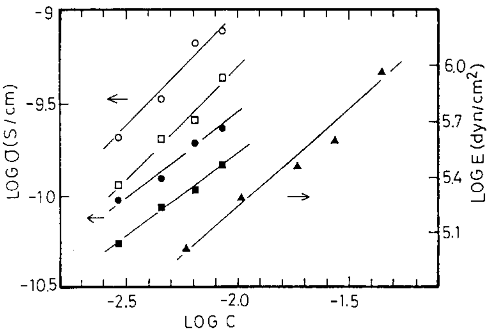

Figure 4 Double logarithmic plots of σ_{ac}, σ_{dc} and E *versus* C for P(4BCMU)-180/TOL gels: (○) σ_{ac} at 324 K; (●) σ_{ac} at 304 K; (□) σ_{dc} at 324 K; (■) σ_{dc} at 304 K; (▲) E at 298 K

Table 2 The exponent β of the percolation equation for σ_{ac}, σ_{dc} and E of P(4BCMU)-180/TOL gels

T (K)	σ_{dc}	σ_{ac}	E
298	–	–	1.07
304	0.88	0.89	–
324	1.20	1.20	–

dependence[7]. Present results agree approximately with this prediction.

However, the theoretical prediction of the slope is rather complicated. Obviously σ_{dc} is closely related to the number of paths connecting both electrodes. The problem is the same as that for gelation of a system, in which the molecules have a crosslink probability[7] p. When p is greater than a threshold value p_0, a gel is formed. According to the percolation theory[7], the gel fraction F_∞ is given by

$$F_\infty \propto (p - p_0)^\beta \qquad (1)$$

where β is a universal constant. The classical gelation theory proposed by Dobson and Gordon[9] predicts $\beta = 1.0$, but the scaling theory[7] predicts $\beta = 0.39$.

We expect p to be proportional to C if the contact occurs within any preferential interactions among the P(4BCMU) molecules. Then equation (1) may be rewritten as

$$F_\infty \propto (C - C_0)^\beta \qquad (2)$$

where C_0 is the critical concentration for formation of gel.

For P(4BCMU)-28 gels, we attempted to determine C_0 by visual observation. Formation of a homogeneous gel was confirmed in the range of $C > 0.04$ wt%. Below 0.04 wt%, the existence of gel and solvent phases was observed. Thus we conclude that $C_0 \simeq 0.04$ wt%. Sinclair *et al.*[4] reported $C_0 = 0.06$ wt% for P(4BCMU) with $\bar{M}_w = 1.2 \times 10^6$.

In the present study, we used gels with $C = 1$–10 wt%. Therefore, we may neglect the term C_0 in equation (2). Comparing this theoretical exponent with the observed values of β listed in *Table 2*, we see that the observed exponent agrees with the classical theory[9] rather than the scaling theory[7].

One of the origins for the disagreement between the observed values of β and the scaling theory may be considered as follows. As described above, we studied E and σ in the range of $C \gg C_0$. This indicates that almost all the molecules are in contact with each other and are incorporated in the gel. Therefore in the present gels, $F_\infty \simeq 1$. In such circumstances, equation (1) will not predict the C dependences of either σ_{dc} or σ_{ac}. We expect that when $F_\infty \simeq 1$, σ_{dc} and E may be proportional to C as seen in *Figure 4*.

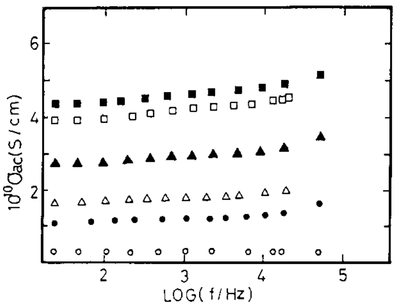

Figure 5 Frequency dependence of σ_{ac} for a P(4BCMU)-180/TOL gel with $C = 0.65$ wt%: (●) 298 K; (△) 303 K; (▲) 314 K; (□) 323 K; (■) 333 K; (○) 354 K

For P(4BCMU)/TOL gel, Sinclair *et al.*[4] reported that the dynamic shear modulus μ at 50 Hz is proportional to $(C - C_0)^{1.64}$, while Kapitulnik *et al.*[6] reported that $\mu \propto (C - C_0)^{2.9}$. These values for the exponent β are higher than the present result with static E.

In *Table 2*, it is seen that β for σ_{dc} and σ_{ac} increases with temperature. Comparing the behaviour of P(4BCMU)-180 and P(4BCMU)-28 around 303 K, we found that β for σ_{dc} does not depend strongly on molecular weight.

Frequency dependence of a.c. conductivity

In the case of a.c. conduction, we expect the local oscillations of the carriers due to the a.c. field to contribute to σ_{ac}.

Figure 5 shows the frequency dependence of the conductivity for the P(4BCMU)-180/TOL system. It is noted that the data at 354 K are for the sol state but the other data are for the gel. It is seen that σ_{ac} is almost independent of frequency. In *Figure 4* we see that σ_{ac} is approximately two times higher than σ_{dc}. This indicates that the dispersion of σ_{ac} occurs in a low frequency range below 100 Hz.

CONCLUSIONS

1. Stress–strain curves of P(4BCMU)/TOL gel were concave with a finite initial slope. This behaviour indicates that the P(4BCMU) molecules are rod-like in the gel state.
2. Doped gels exhibited similar stress–strain curves indicating that doping does not affect the gel structure strongly.
3. Both σ_{dc} and E vary in proportion to C. This is consistent with the percolation theory.

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