Electrical conductivity of polydiacetylene, poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxy carbonylmethyl urethane)] gel: 1. Sol–gel transition and conduction mechanism

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Electrical conductivity, colour change and sol–gel transition behaviour were studied for a polydiacetylene, poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxy carbonylmethyl urethane)] abbreviated as P(4BCMU), in toluene gels. For P(4BCMU)-28 with weight average molecular weight of 280000, the sol–gel transition temperature was determined to be around 348 K varying slightly depending on the methods employed for the determination. The alternating current (a.c.) and direct current (d.c.) conductivities of P(4BCMU)-28 gels exhibited a broad maximum at ~336 K. Upon heating the gels, the colour changed from red to yellow at ~348 K, while upon cooling a sharp colour change was observed at ~340 K indicating the supercooling of the sol phase. These characteristic temperatures increased with increasing molecular weight. The a.c. and d.c. conductivities were enhanced approximately 20 times by adding a dopant iodine to the gels. We also observed a weak photoconductivity similar to the bulk P(4BCMU). These results suggest that the conduction mechanism of the gels is due predominantly to electronic origins through the gel networks rather than ionic ones in the toluene medium.

(**Keywords: electrical conductivity; polydiacetylene; gel; poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxycarbonylmethyl urethane)]; sol–gel transition; colour change; photoconductivity**)

INTRODUCTION

A class of polydiacetylenes (PDA) with alkoxy carbonyl methylurethane substituent groups, has attracted great interest from polymer scientists because these PDAs show substantial solubility in some organic solvents in contrast to other polymers with long conjugated backbones[1,2]. Thus these PDAs can be characterized by applying dilute polymer solution techniques such as gel permeation chromatography (g.p.c.)[3]. Among various PDAs, electrical properties of poly[4,6-decadiyn-1,10-diol-bis(n-butoxy carbonylmethyl urethane)], abbreviated as P(3BCMU), and poly[5,7-dodecadiyn-1,12-diol-bis-(n-butoxy carbonylmethyl urethane)], abbreviated as P(4BCMU), have already been studied extensively in the states of solvent cast films and single crystals[4–9].

Recently Sinclair *et al.*[10,11] reported that toluene (TOL) solutions of P(4BCMU) exhibited reversible sol–gel transition at 344 K accompanied by a sharp change in electrical conductivity from the order of 10^{-10} S cm^{-1} for the gel phase to the order of 10^{-12} S cm^{-1} for the sol. They also reported that the P(4BCMU)/TOL system exhibited a sharp colour change from red in the gel phase to yellow in the sol phase[12]. This change was ascribed to the change in the conjugation length in the P(4BCMU) backbone around this temperature region[13–16]. However, the mechanism of conduction in the gel state is not fully understood.

In this study we first examined correlation among the characteristic temperatures of the sol–gel transition in P(4BCMU)/TOL systems by observing temperature dependences of alternating current (a.c.) and direct current (d.c.) conductivities, absorbance for ultraviolet-visible light (u.v.–vis), elasticity, and of differential scanning calorimetry (d.s.c.) thermograms. We especially measured the change in absorbance at 530 nm wavelength light around the sol–gel transition temperature in order to examine possible effects on the conductivity of the changes in the chain conformation as well as in the gel structure.

If the carriers in the gel are electrons and/or holes, we expect that the gel exhibits an enhanced conductivity upon doping and also photoconductivity similar to solid P(4BCMU) films. On the other hand, if the conduction is due to impurity ions, the dopant effect and the photoconductivity should not be observed. Based on this view we also examined the effects of dopant iodine on the conductivity and photoconductivity of P(4BCMU)/TOL gels.

EXPERIMENTAL

Samples

P(4BCMU) was prepared as previously by Se *et al.*[3–5] from 5,7-dodeca-diyne-1,12-diol-bis(n-butoxy carbonyl methylurethane) (4BCMU) having the structure R–C≡C–C≡C–R, with

$$R = -(CH_2)_4CONHCH_2COOC_4H_9,$$

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by irradiation of ^{60}Co γ-rays in vacuum at room temperature. The total dose was 5×10^4–4×10^5 Gy. Unreacted monomer was removed by dissolving the reaction products in acetone. The polymer samples thus prepared were purified by repeated precipitation with a good solvent (chloroform) and a non-solvent (hexane), and then dried for 24 h under vacuum of 5×10^{-2} Pa at room temperature.

The weight-average-molecular weight M_w was determined on a gel permeation chromatograph equipped with a low-angle light scattering detector (Tosoh LS-8000). Five samples with M_w values of 7.8×10^4, 28×10^4, 44×10^4, 180×10^4 and 201×10^4 were obtained, and coded as P(4BCMU)-8, P(4BCMU)-28, P(4BCMU)-44, P(4BCMU)-180 and P(4BCMU)-201, respectively. These polymers were dissolved in toluene at 360 K in the concentration range from 0.04 to 5 wt%.

Method

Two types of sample cells, I and II, were used. Cross-sectional views of the electrodes are shown in *Figure 1*. Cell-I was a condenser cell described previously[17]. The electrodes of cell-I were gold-plated and were separated by ~0.2 mm. The electrodes of cell-II were made of thin copper plates with an area of ~2 cm^2 and separated by ~0.5 mm. The electrodes were suspended with platinum wire in a glass container as shown in *Figure 1*. Sample solutions were loaded at ~350 K in the cell and on cooling the gel was formed between the electrodes. In both cases the cell was filled with argon to prevent moisture. The d.c. conductivity σ_{dc} was measured with an electrometer (Keithley-640) under a voltage of ~1 V. The a.c. conductivity σ_{ac} and dielectric constant were measured with an automatic capacitance bridge (Yokogawa-Hewlett-Packard 4270A) at 5 V in the frequency range from 1 to 100 kHz. The conductivity measurement was made by raising the cell temperature with a heating rate of ~0.3 K min^{-1}.

The d.c. conductivity σ_{dc} was measured as follows. When a constant d.c. voltage was applied, the current decreased rapidly during the initial 100 s to a level of about half the value just after the application of the d.c. voltage, and then it reached an equilibrium value within 15 min. We defined σ_{dc} as the conductivity calculated from the equilibrium current.

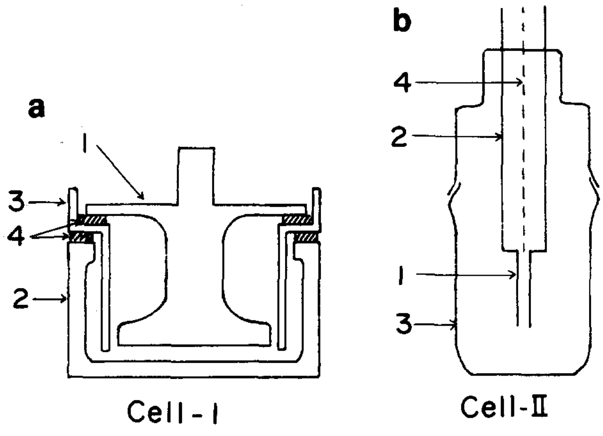

Figure 1 (a) Cross-sectional view of cell-I: 1, guarded electrode; 2, unguarded electrode; 3, guard; 4, glass spacer. (b) Cross-sectional view of cell-II: 1, parallel plates type electrode; 2, lead wire; 3, glass container; 4, guard

In the conductivity measurements, we encountered a serious problem in the data reproducibility. This is due to a phenomenon known as syneresis: the gel shrinks with time and a very small amount of pure toluene comes out on the surface[18]. When cell-I was used, syneresis caused formation of a thin toluene layer between the sample gel and the electrodes, leading to a serious increase in contact resistance because the distance between the electrodes is fixed by a glass spacer as shown in *Figure 1*. In cell-II, however, a toluene layer was formed between the glass container wall and the gel but not between the electrodes and the gel. More reliable data were thus obtained with cell-II.

We employed a falling ball method to determine the mechanical sol–gel transition temperature. A sample gel was sealed in a glass ampoule together with a steel ball of 0.25–0.90 mm diameter, which was initially suspended at an appropriate position in the gel. The height of the steel ball was monitored with a cathetometer, while temperature was increased in steps of 2 K at a rate of ~0.5 K min^{-1}, and then annealed for ~1.5 min to allow the sample to equilibrate. The temperature of the gel was measured with a thermocouple attached to the outside of the ampoule after equilibration.

U.v.-vis. absorption spectra were determined on a spectrometer (Shimadzu model UV-200). The change in the absorbance with temperature was observed around the sol–gel transition temperature using monochromatized (530 nm) light from a high power xenon lamp (Nihon Bunko Co., model LH-X500). The transmitted light through the sample sealed in the ampoule was measured with a photodiode.

Thermal behaviour was observed by d.s.c. with a differential scanning calorimeter (Seiko Denshi Kogyo SSC/580). The heating rate was 5 K min^{-1}.

RESULTS AND DISCUSSION

Sol–gel transition temperature

First we compare the characteristic temperatures related to the sol–gel transition which were determined from electrical conductivity, mechanical strength, d.s.c. thermograms and u.v.-vis. absorbance. As will be described later, these temperatures depended slightly on molecular weight. We thus compared them on a sample with a fixed molecular weight. Taking the reference molecular weight as 2.8×10^5, we reduced the characteristic temperatures observed for the gels of P(4BCMU)-8, P(4BCMU)-44, and P(4BCMU)-201 to those of P(4BCMU)-28 gel as described below.

Conductivity. Figure 2 shows the temperature dependence of a.c. conductivity σ_{ac} at 1 kHz for P(4BCMU)-28 gels with concentration C ranging from 0.3 to 1 wt%. Each σ_{ac} curve exhibits a peak around 336 K and the peak temperature is denoted as $T_{ac}(\mathrm{I})$. In the sol state above ~350 K, σ_{ac} was of the order of 10^{-12} S cm^{-1} and much smaller than that below ~350 K. In the range from $T_{ac}(\mathrm{I})$ to 350 K, σ_{ac} decreases sharply as seen in *Figure 2*. The most sharply decreasing portion of each σ_{ac} curve was approximated with a straight line. Then the crossover temperature, at which the straight line crossed the level of σ_{ac} for the sol state, was defined as $T_{ac}(\mathrm{II})$. Since the slope of the σ_{ac} curve was high, the ambiguity in the determination of $T_{ac}(\mathrm{II})$ was less than ± 0.5 K.

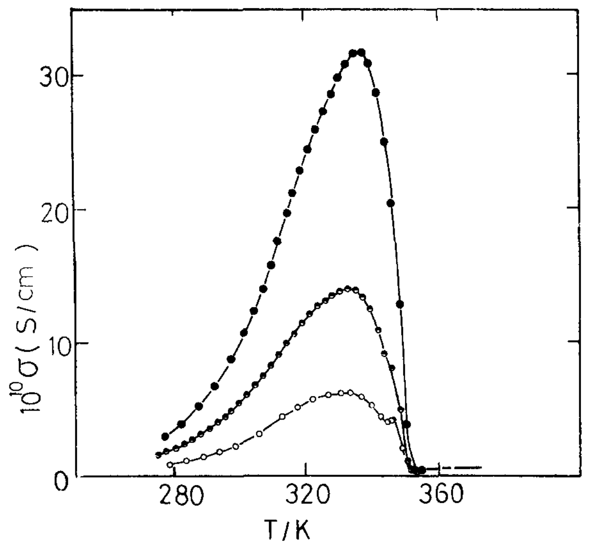

Figure 2 Temperature dependence of a.c. conductivity σ_{ac} at 1 kHz for P(4BCMU)-28/TOL gels: ○, 0.34 wt%; ◓, 0.50 wt%; ●, 1.04 wt%

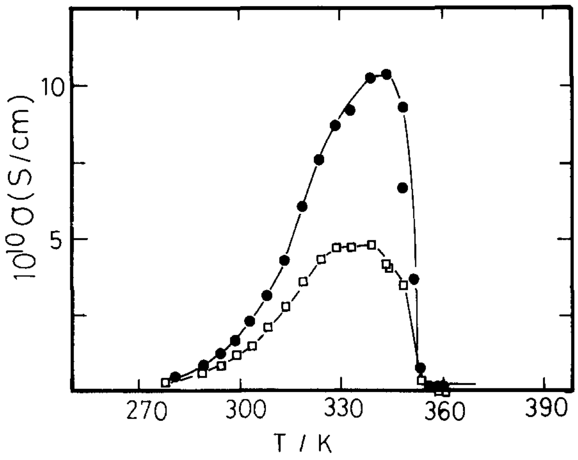

Figure 3 Temperature dependence of d.c. conductivity σ_{dc} (□) and a.c. conductivity σ_{ac} at 1 kHz (●) for P(4BCMU)-180/TOL gel with concentration of 0.88 wt%

Figure 3 compares the temperature dependence of d.c. conductivity σ_{dc} with σ_{ac} for 0.88 wt% P(4BCMU)-180 gel. The temperature T_{dc}(I) of maximum σ_{dc} coincides with T_{ac}(I). The crossover temperatures T_{dc}(II) for σ_{dc} are defined in the same way as for σ_{ac}. As seen in *Figure 3*, T_{dc}(I) and T_{dc}(II) coincide with T_{ac}(I) and T_{ac}(II), respectively.

For P(4BCMU)-180 gel, we observed that T_{ac}(II) was 354 K and was 3 K higher than the value for P(4BCMU)-28 gel. On the other hand, the a.c. conductivity of P(4BCMU)-8 gel exhibited T_{ac}(II) at 348 K which is 3 K lower than the value for P(4BCMU)-28. *Figure 4* shows a plot of T_{ac}(II) *versus* log M_w for the five samples examined. The plot is approximately linear against log M_w which reads:

$$T_{ac}(\mathrm{II}) = 328 + 4.2 \log M_w \qquad (1)$$

For T_{ac}(I), however, we did not find any systematic M_w dependence.

Mechanical and calorimetric measurements. To measure mechanical strength of the gel, we monitored the temperature dependence of the height of a steel ball in the P(4BCMU)-44/TOL gel as the gel temperature was increased. The temperature at which the ball fell abruptly was defined as the falling temperature T_f and is plotted against the weight of the ball in *Figure 5*. The mechanical sol–gel transition point T_M was defined as the value of T_f extrapolated to zero weight. By extrapolation, we determined T_M to be 349.1, 348.7, and 348.9 K at concentrations C of 0.37, 0.61 and 0.92 wt%, respectively. Thus T_M was almost independent of concentration C of the gel and is 349 ± 0.3 K.

We estimate T_M for P(4BCMU)-28 gel to be 348 K assuming that T_M is proportional to log M_w with the slope dT_M/d log M_w = 4.2 as given by equation (1).

The d.s.c. thermogram of 5 wt% P(4BCMU)-28/TOL gel exhibited a small endothermic peak at around 346 K. For the gel below 5 wt%, the endothermic peak was not clear, presumably because of the limited sensitivity of the apparatus. The peak temperature was defined as the calorimetric transition temperature T_{cal}.

Colour change. Figure 6 shows the temperature dependence of the transmittance at 530 nm for P(4BCMU)-8/TOL and P(4BCMU)-201/TOL systems. The wavelength of 530 nm was chosen because the absorbance at

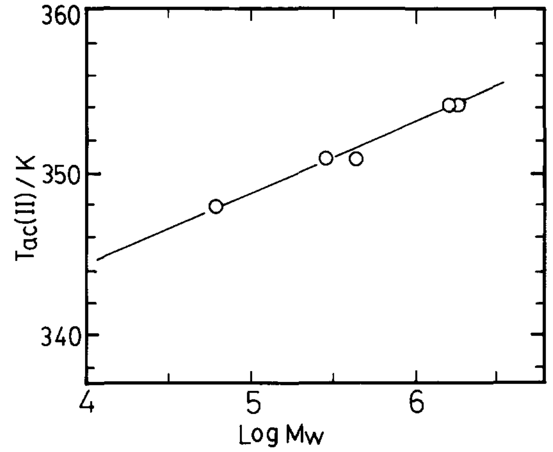

Figure 4 Molecular weight M_w dependence of T_{ac}(II)

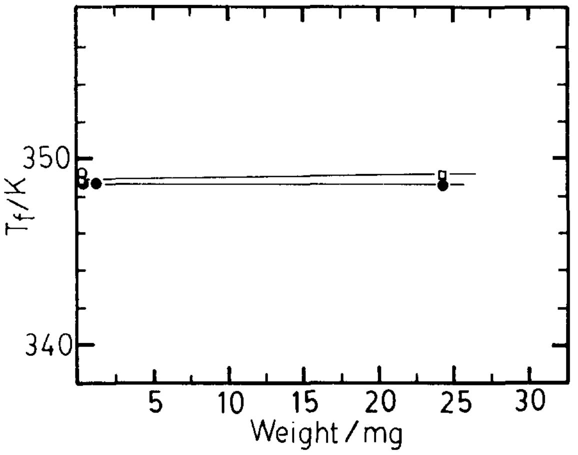

Figure 5 The sol–gel transition temperature measured by the falling ball method for P(4BCMU)-44/TOL gel. Temperature T_f at which the ball falls suddenly is plotted against the weight of steel balls. Gel concentration: ○, 0.37 wt%; ●, 0.61 wt%; □, 0.92 wt%

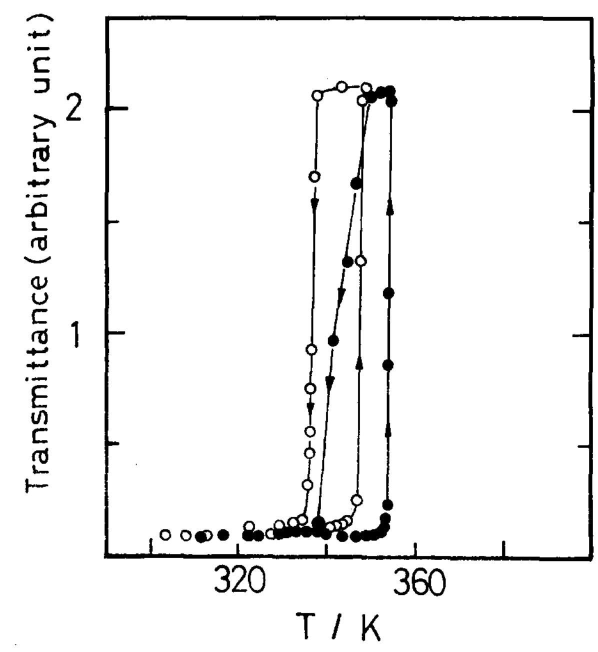

Figure 6 Temperature dependence of the transmittance at 530 nm light for P(4BCMU)-8/TOL gel with concentration of 0.18 wt% (○) and P(4BCMU)-201/TOL gel with concentration of 0.14 wt% (●)

530 nm changed drastically around the transition temperature, as described later. On heating, the intensity of the transmitted light increased sharply at 347 ± 0.5 K for P(4BCMU)-8 and 354 ± 0.5 K for P(4BCMU)-201. These temperatures were defined as the colour change temperature T_{ch}.

The slope $dT_{ch}/d \log M_w$ determined from these two data was 5.0 ± 1 in agreement with the value of $dT_{ac}/d \log M_w$ within experimental error. Upon cooling the transmittance decreased sharply at ~340 K. This hysteresis phenomenon in the colour change will also be discussed later. It is seen that T_{ch} increases with M_w. Thus we assume again that T_{ch} is proportional to log M_w with a slope of 4.2 and T_{ch} for P(4BCMU)-28 is 350 ± 1 K.

Comparison of transition temperatures detected with various probes. The characteristic temperatures T_{ac}(I), T_{ac}(II), T_{dc}(II) and T_{cal} for P(4BCMU)-28/TOL are summarized in *Figure 7*, in which the values of T_{dc}(I), T_{dc}(II), T_M and T_{ch} measured for gels of P(4BCMU) with M_w other than 280000 are also plotted after being reduced to the values for P(4BCMU)-28 gel. The T_{ac}(II), T_{dc}(II) and T_{ch} agree within ±1 K and their average value is 351 ± 1 K. T_M is 348 K and is 3 K below this average. We also note that the transition temperatures are almost independent of concentration.

The T_{ac}(I) is, however, lower than the others by as much as 15 K. This low temperature σ_{ac} peak is considered to be a pretransition phenomenon as discussed later.

Conductivity of P(4BCMU)-28/TOL gel

Effect of dopant. If the conduction mechanism in P(4BCMU)/TOL gels is electronic conduction through the gel network, we expect that σ increases strongly by doping with iodine (I_2). Thus we examined the effect of I_2 on the a.c. conductivity of P(4BCMU) gels. A prescribed amount of I_2 was dissolved in toluene, and then P(4BCMU)-28 was dissolved in this solution to make a gel.

Figure 8 shows the temperature dependence curves of σ_{ac} at 1 kHz and σ_{dc} for I_2-doped P(4BCMU)-180/TOL gels in which the σ_{ac} is enhanced by a factor of ~20. Here the dopant concentration Y is defined as the molar ratio I_3^- to the monomer unit of P(4BCMU) by presuming that all iodine exists as I_3. On the other hand, toluene solution of I_2 exhibited conductivity of an order of 10^{-11} S cm^{-1}, that is 100 times smaller than in doped gels. This result implies that the conduction mechanism in P(4BCMU) gels is electronic rather than ionic: iodine forms a charge transfer complex with P(4BCMU) and creates a hole as in other conductive polymers[19].

Activation energy. The temperature dependence of σ_{ac} and σ_{dc} shown in *Figures 2* and *3* is explained by

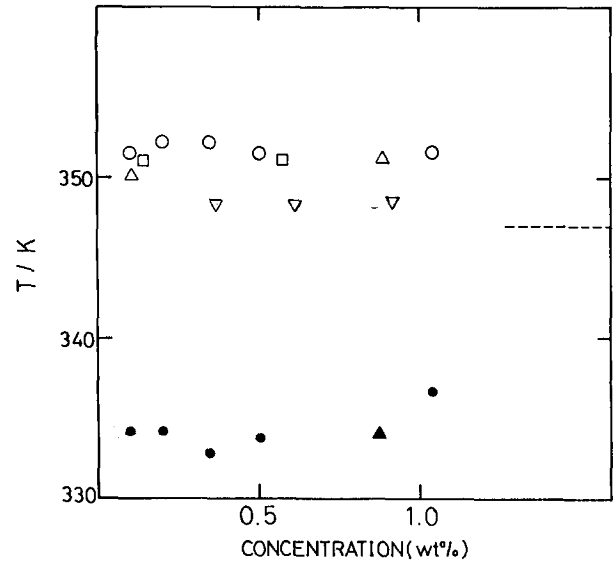

Figure 7 Concentration dependence of the transition temperatures for P(4BCMU)-28/TOL gel: ●, T_{ac}(I); ○, T_{ac}(II); △, T_{dc}(II); ▲, T_{dc}(I); □, T_{ch}; ▽, T_M. Dashed line indicates T_{cal} at 5 wt% concentration

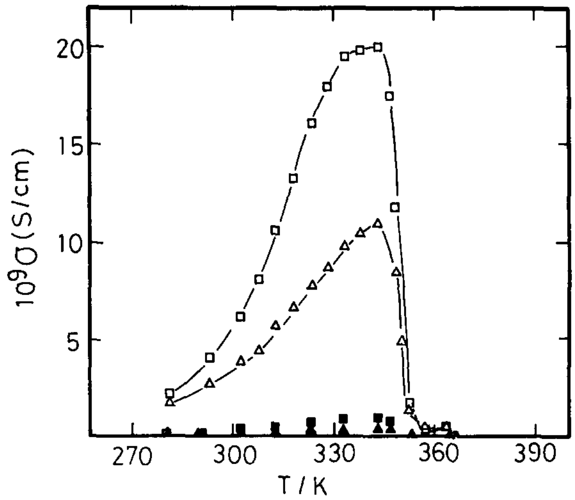

Figure 8 Temperature dependence of a.c. conductivity σ_{ac} at 1 kHz and d.c. conductivity σ_{dc} for P(4BCMU)-180/TOL gel of concentration 0.651 wt% doped with iodine: ■, σ_{ac} at $Y = 0$; □, σ_{ac} at $Y = 0.16$; ▲, σ_{dc} at $Y = 0$; △, σ_{dc} at $Y = 0.16$

Table 1 Activation energy for a.c. conductivity, E(ac), and d.c. conductivity, E(dc), in P(4BCMU)-180 gels doped with iodine

C (wt%)	Y^a	E(ac) (eV mol^{-1})	E(dc) (eV mol^{-1})
0.294	0	0.59	0.42
0.461	0	0.58	0.51
0.651	0	0.54	0.55
0.651	0.16	0.46	0.33
0.868	0	0.46	0.56

[a] Y = molar ratio of I_3 to the monomeric unit of P(4BCMU)

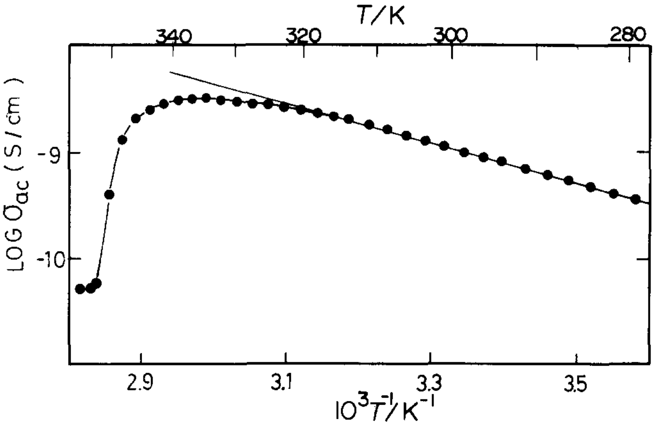

Figure 9 Log σ_{ac} *versus* $1/T$ plots at 1 kHz for P(4BCMU)-28 gel of concentration 1.04 wt%

considering two factors. One is the increase in the number n and the mobility μ of the carriers with temperature through an activation process, and the other is the decrease of the conductivity due to deterioration of the gel structure around the sol–gel transition temperature. From a balance between these two factors, the temperature dependence curve of σ_{ac} should exhibit a maximum.

We assume a hypothetical conductivity σ^0 which could be observed if the gel structure does not change with temperature. $\sigma^0 = q\mu n$ where q is the charge of the carrier. Both μ and n may be given by an Arrhenius type equation:

$$\mu = \mu_0 \exp(-E_\mu/k_B T) \qquad (2)$$

$$n = n_0 \exp(-E_n/k_B T) \qquad (3)$$

where E_μ is the activation energy for the charge mobility, k_0 is the Boltzmann constant and E_n is the energy gap between the conduction and valence levels.

Deterioration of the gel structure should cause a decrease in the conductivity. We simply assume that σ is given by $F\sigma^0$, where F is an order parameter with value unity at a temperature far below the transition temperature but zero in the sol state. *Figure 9* shows the log σ_{ac} *versus* $1/T$ plots for P(4BCMU)-28 gel. We see that the plots conform well to straight lines in the range of $1/T > 0.0032$. This suggests that below 310 K we may assume F is unity. Thus the observed σ_{ac} and σ_{dc} are equal to σ^0_{ac} and σ^0_{dc}, respectively. The values of the activation energy E ($=E_\mu + E_n$) determined in this temperature region are given in *Table 1*. It is seen that the values of E of the doped and undoped gels are of the same order.

A solid film cast from chloroform solution[20] exhibited E(dc) of 1.5 eV mol^{-1}. We note that E(dc) in the gel is only one third of the values in solid P(4BCMU) films[4]. At present it is difficult to explain the C dependence of E until we separately determine the temperature dependence of the carrier density and the mobility. However, we speculate that the conduction mechanisms and hence the values of E_μ in the solid ($C = 100\%$) and in the gel ($C = 1\%$) differ greatly. In the solid film, one P(4BCMU) chain is always surrounded by the neighbouring chains and hence the carriers can frequently migrate through intermolecular hopping. On the other hand the chain in the gel is almost surrounded by the solvent molecules and hence intermolecular hopping is allowed only at junction points of the gel network. We estimated the number of junctions; the results are described elsewhere[21].

Figure 10 shows the parameter F ($=\sigma/\sigma^0$) in which σ^0 was estimated by extrapolating the straight portion of the Arrhenius plot of σ_{ac} and σ_{dc} (see *Figure 9*). It is seen that F starts to decrease at ~310 K. Thus 310 K is considered to be the temperature at which the sol–gel transition commences. In *Figure 10a*, we see that F for undoped gels depends slightly on concentration at ~340 K. This is reflected in the change of T_{ac}(I) shown in *Figure 7*. The F curves for σ_{ac} and σ_{dc} also coincide approximately. Comparing the F curves for doped and undoped gels, we do not see an appreciable difference. This suggests that the structure of gel is hardly affected by doping.

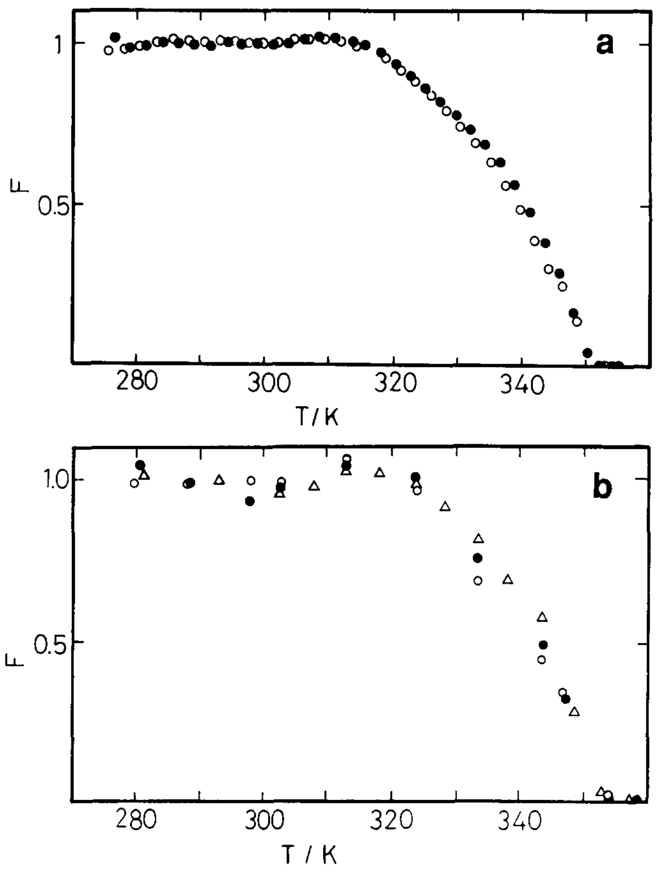

Figure 10 Temperature dependence of the parameter F representing the structural disordering of gel around the sol–gel transition temperature determined from σ_{dc} and σ_{ac} at 1 kHz. (a) σ_{ac} for undoped P(4BCMU)-28/TOL gel: ○, 0.501 wt%; ●, 1.04 wt%. (b) Doped P(4BCMU)-180/TOL gel with concentration of 0.651 wt%: ●, σ_{ac} at $Y = 0$; △, σ_{ac} at $Y = 0.16$; ○, σ_{dc} at $Y = 0$

Effect of syneresis. Finally the effect of syneresis on the apparent conductivity is commented upon briefly. The rate of syneresis increased with increasing M_w and with decreasing concentration. In P(4BCMU)-180 gels, syneresis occurred rapidly and hence reliable data were obtained only with cell-II. In contrast to P(4BCMU)-180, gels of P(4BCMU)-28 exhibited a very slow rate of syneresis. When syneresis caused bad contact between the electrodes and the gel, the apparent σ_{ac} *versus* temperature curves exhibited a sharp secondary peak around T_{ac}(II) besides a broad peak around T_{ac}(I). When syneresis occurred, the σ_{dc} *versus* temperature curves also exhibited a sharp peak at ~349 K. We speculate that although gels begin to shrink by syneresis in the temperature range below ~330 K, they start to swell again as the temperature is raised above 340 K. When a good contact between the sample gel and electrode is made before the gel dissociates into sol, a sharp peak appears in the σ *versus* temperature curve.

U.v. spectra and photoconduction in the gel

U.v. spectra. Figure 11 shows u.v.-vis. spectra at various temperatures of P(4BCMU)-28/TOL system with $C = 0.20$ wt%. Although not shown in this figure, spectra below 328 K were essentially the same as a spectrum at 328 K. For the sake of comparison, the spectrum for a chloroform solution of 0.24 wt% and that for a bulk film of P(4BCMU) are shown. In chloroform solutions, the P(4BCMU) molecules have a random coil conformation. We note that the spectrum of the gel resembles the solid film, while that of the sol resembles the chloroform solution. The peak wavelength of the gel spectrum shifts from 530 nm (red phase) to 450 nm of the sol spectrum (yellow phase) within a relatively narrow range from 347 to 349 K corresponding to the temperature of colour change which occurred simultaneously with the sol–gel transition.

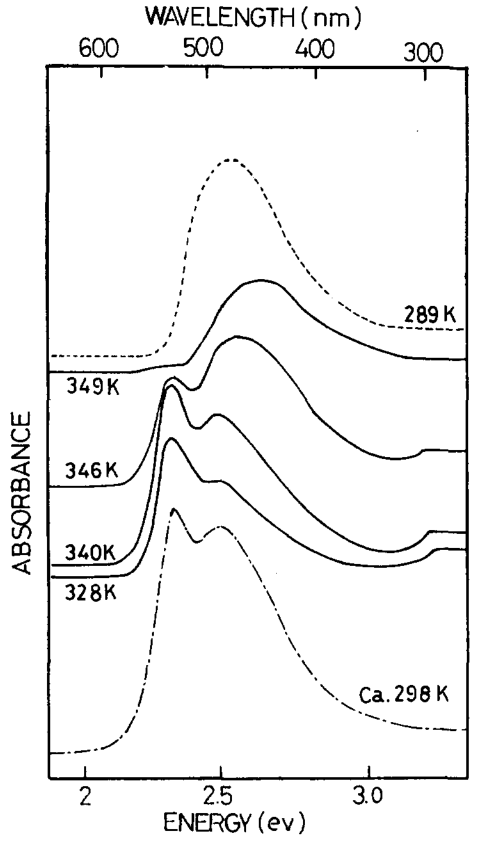

Figure 11 Absorption spectra for P(4BCMU)-28/TOL gel of concentration 0.2 wt% at various temperatures. ----, Spectrum of P(4BCMU)-28 chloroform solution of 0.24 wt%; —·—·, spectrum of undiluted bulk film

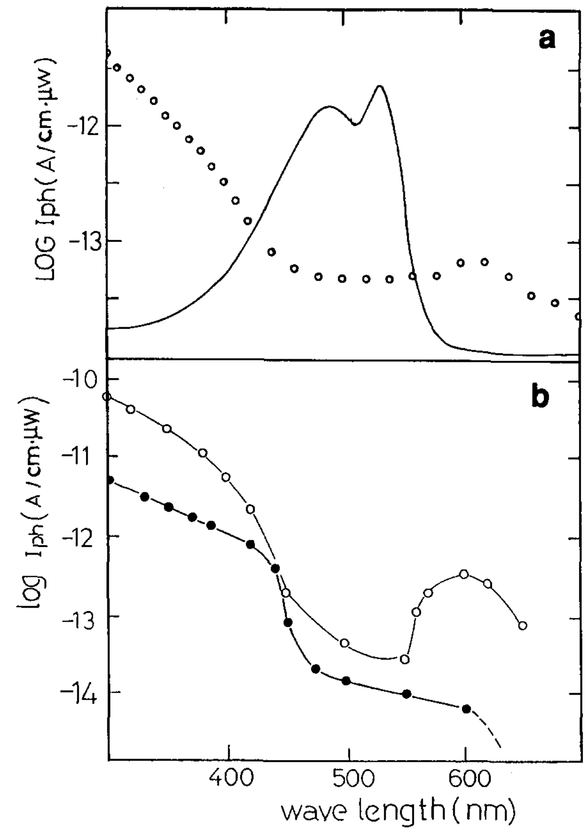

Figure 12 (a) ○, Photocurrent action spectrum and ——, absorption spectrum of the solid P(4BCMU)-28 film cast from chloroform solution. (b) Comparison of the photocurrent action spectra for the 0.50 wt% P(4BCMU)/TOL gel: ○, doped with iodine with $Y = 0.27$; ●, undoped gel

The characteristic spectral change of P(4BCMU) solutions was explained by Kanetake *et al.*[13] in terms of a π–π^* exciton model for the conjugated polymer chains[22]. The spectrum of the red phase shows a sharp peak at the lower energy due to the delocalized photo-excited π–π^* excitons along the extended rod-like linear chain of polymer. In the case of yellow solutions, however, the excitons will be more or less localized on the coil-like backbone chains.

Photoconductivity. Figure 12a shows comparison of the photoconductivity σ_{ph} and the u.v.-vis. spectrum of P(4BCMU)-28 solid film cast from chloroform solution. *Figure 12b* shows the σ_{ph} for doped and undoped gels. We see that the photocurrent action spectra for the solid film and the gel are quite similar. Interestingly the photocurrent is not proportional to the absorbance. As discussed above, the absorbance around 530 nm is due to π–π^* transition[22] and hence does not contribute to creating carriers by exciting electrons from the valence band level.

In the short wavelength region below 450 nm the photocurrent was relatively high. In this region, the photocurrent is considered to be caused by direct excitation of electrons to the conduction band or by an

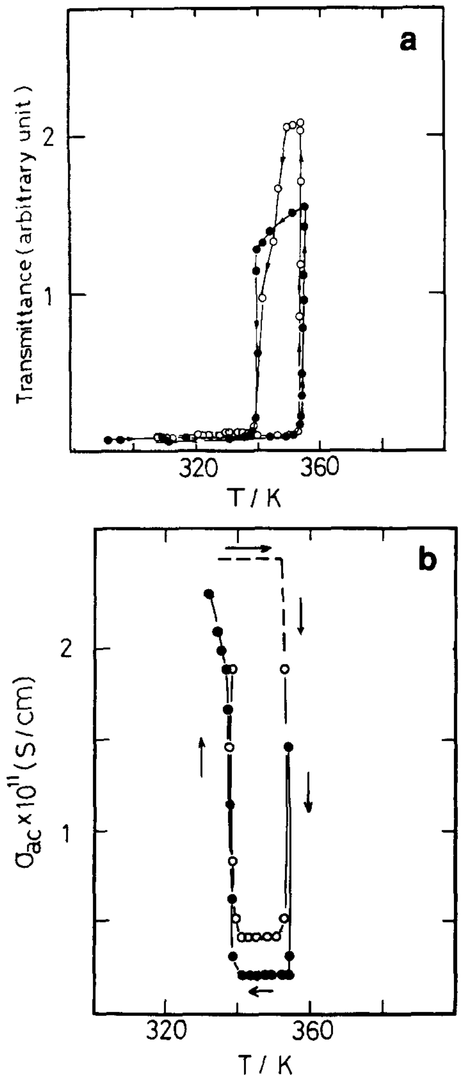

Figure 13 Temperature dependence of (a) transmittance at 530 nm and (b) a.c. conductivity of P(4BCMU)-201/TOL gels with concentration of 0.14 wt% (○) and 0.47 wt% (●)

autoionization of an exciton to the levels with higher energy than the conduction band as in P(3BCMU)[20].

Rod–coil transition

Colour change. As is seen in *Figure 11*, the P(4BCMU) gels exhibit a characteristic absorption band at 530 nm which disappears in the sol phase. Thus the red colour of the gel turns into yellow above the transition temperature. Since the 530 nm band reflects the presence of a long conjugated backbone[1,2], we attempted to clarify the correlation between the conjugation length and the conductivity by measuring the temperature dependence of the conductivity and the 530 nm transmittance of the P(4BCMU)/TOL system.

Figure 13a shows the temperature dependence of the transmittance for the P(4BCMU)-201 gel. Upon heating, the transmittance increased at 354 K (T_{ch}) but upon cooling at the rate of -0.1 K min^{-1}, a sharp decrease in the transmittance was observed ~20 K below T_{ch}. *Figure 13b* shows σ_{ac} measured for the same gels under the same condition. It is seen that σ_{ac} decreased sharply at T_{ch} in measurements in the heating direction. On cooling the transmittance decreased at 338 K and at the same temperature σ_{ac} increased sharply. This result indicates that for electrical conduction to occur, the conformation resulting in the 530 nm absorption is necessary.

A model for the colour change has already been proposed by Berlinsky *et al.*[23] who assigned the colour change to a planar–non-planar conformational transition of the P(4BCMU) chain involving a change of the average conjugation length from three to four repeat units in the yellow to essentially infinite length in the red solution. The backbone with the conjugated electronic structure is stiff and rod-like but that with non-conjugated structure is flexible.

CONCLUSIONS

The sol–gel transition temperature was determined through the measurements of a.c. conductivity, d.c. conductivity, transmittance at 530 nm, d.s.c. thermograms and elasticity. The sol–gel transition temperature detected by these methods for P(4BCMU)-28 is 351 K and agreed within ±1 K. The transition temperature increases with molecular weight.

The sol–gel transition of P(4BCMU)-28 commences around 310 K. The gel completely transforms into sol at 351 ± 1 K.

When the gel is doped with I_2, the conductivity strongly increases by one order of magnitude indicating that the conduction is electronic rather than ionic. The photocurrent observed in gels also supports this conclusion.

Hysteresis in the transition was observed in the temperature dependence of the transmittance at 530 nm and the conductivity. The sharp changes in the conductivity and transmittance occurred simultaneously.

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