Electric Conductivity and Phase Transition of a Polydiacetylene Gel: Poly[4,6-decadiyn-1,10-diol-bis(n-butoxy-carbonylmethyl urethane)] P(3BCMU)

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ABSTRACT: Electric conductivity and sol–gel transition behavior were studied for gels of a polydiacetylene poly[4,6-decadiyn-1,10-diol-bis(n-butoxy-carbonylmethyl urethane)] abbreviated to P(3BCMU). Two solvents with different dielectric constant were used, *i.e.*, *o*-dichlorobenzene (*o*-DCB) and a mixed solvent of *p*-dichlorobenzene (*p*-DCB) and toluene (TOL). Temperature dependence of the shear moduli G' was measured to determine the gel-to-sol transition temperatures T_t at which the moduli decreased steeply. The T_t was 378 K in *o*-DCB and 387 K in *p*-DCB/TOL (62/38). Both direct current (DC) conductivity σ_{dc} and alternating current (AC) conductivity σ_{ac} at 1 kHz exhibited a maximum around 368 and 362 K in *o*-DCB and *p*-DCB/TOL, respectively. Dopant effects of an electron acceptor iodine and a donor tetrathiafulvalene TTF on σ_{dc} and σ_{ac} were also studied. σ_{ac} was enhanced approximately by 100 times with iodine but only by 5 times with TTF. The pronounced dopant effect indicates that the conduction in the gel state is partly due to electronic conduction through the P(3BCMU) chains. We also observed an appreciable strength of ionic conductivity in the sol and gel phases. The ionic conductivity in the gel phase was estimated from σ_{ac} of the solvent containing the ions extracted from the gel phase. Then observed σ_{ac} and σ_{dc} were separated into the contributions of ionic and electronic conductions. Electronic conductivity increased with increasing dielectric constant of the solvent. Transition temperature T_t where the color changed from blue to yellow was also determined by measuring the transmittance at 630 nm wave length. The temperature dependence of the transmittance indicated a hysteresis.
KEY WORDS Electric Conductivity / Sol–Gel Transition / Polydiacetylene / Gel / Poly[4,6-decadiyn-1,10-diol-bis(n-butoxycarbonylmethyl urethane)] / P(3BCMU) /

Among conducting polymers, derivatives of polydiacetylene with a relatively long side group are unique in a sense that they are soluble in a variety of organic solvents and form gel in poor solvents.[1-4] In our previous papers,[1,2] we reported behavior of the reversible sol–gel transition and electric conduction in toluene (TOL) solution of poly[5,7-dodecadiyn-1,12-diol-bis(n-butoxy carbonyl methylurethane)] abbreviated to P(4BCMU). The alternating current (AC) conductivity σ_{ac} at 1 kHz and the direct current (DC) conductivity σ_{dc} of P(4BCMU)/TOL gel exhibited a broad maximum around 336 K. Above this temperature, the σ_{ac} and σ_{dc} decreased steeply with increasing temperature and reached to a level of an insulator. The σ_{ac} and σ_{dc} were enhanced approximately 20 times by doping with iodine.

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Reflecting a change in conjugation length, a sudden color change from dark red to yellow was observed as the gel phase transformed into the sol phase. A weak photo-conductivity was also observed in the gel state. From these results we concluded that the conduction mechanism in P(4BCMU)/TOL gel was dominantly due to the electronic origins through the gel networks rather than ionic ones in the toluene medium.

There exists a derivative very similar to P(4BCMU) namely poly[4,6-decadiyn-1,10-diol-bis(n-butoxy-carbonylmethyl urethane)] abbreviated to P(3BCMU). The electrical properties of the solid films of P(3BCMU) were studied extensively by Se et al.[5,6] and others[7-12] as well as those of P(4BCMU). Patel et al.[13] reported that P(3BCMU) forms gel in a suitable solvent such as o-dichlorobenzene (o-DCB). However, the electrical properties in the gel have not been studied thoroughly.

In this paper, we report the phase behavior and conductivity of P(3BCMU) gel and compare the properties with those of P(4BCMU)/TOL gel. Although the difference in the structure between P(4BCMU) and P(3BCMU) is that the number of methylene group of the side group differs by only one, the physical properties of them differ remarkably.[5-14] For example, P(3BCMU) does not form gel in toluene and furthermore the color of P(3BCMU) gel is blue in contrast to red of P(4BCMU) gel indicating the difference in the band structure. Thus we expect the conduction behavior of P(3BCMU) gel is also different from P(4BCMU). The objective of the present study is to clarify the difference of the electric properties and transition behavior between them.

In study of electric properties of conducting polymers, it is necessary to separate observed conductivity into the contributions of electronic and ionic conductions. This is important in case of the both contributions are of the same order as in P(3BCMU) gel. Since it is known that ionic conductivity due to impurity ions increases with increasing dielectric constant ε of the medium, we used two solvents to clarify the effect of ε on the conductivity in P(3BCMU) gel. One was o-dichlorobenzene (o-DCB) with the dielectric constant $\varepsilon = 9.9$ at 298 K and the other was a mixed solvent of p-dichlorobenzene (p-DCB) and toluene (TOL) with $\varepsilon = 2.4$ at 320 K.

Nowak et al.[15] demonstrated using ESR that the number of polarons or bipolarons depends on ε of the medium in solution of poly(3-hexyl thienilene). This result suggests that ε affects the electronic conductivity as well as ionic one. We attempted to investigate the effect of ε on the conductivity in gel of P(3BCMU).

Besides conductivity, we also measured the temperature dependence of shear modulus and the transmittance of ultraviolet (UV) light to investigate the gel-to-sol transition temperature. The shear modulus reflects the higher order network structure of the gel and the UV transmittance the conformational structure. These information on the structure of gel were used to understand the electrical properties of gel.

EXPERIMENTAL

Samples

P(3BCMU) was prepared previously by Se et al.[5,6] from 4,6-decadiyn-1,10-diol bis(n-butoxycarbonylmethyl urethane) (3BCMU) which has the structure $R-C \equiv C-C \equiv C-R$ with $R = -(CH_2)_3OCONHCH_2COOC_4H_9$. Crystalline 3BCMU was sealed in ampules in vacuum and irradiated by ^{60}Co γ-rays of 45 Mrd. Unreacted monomer was extracted from the reaction products by acetone. The P(3BCMU) sample thus prepared was further purified by repeated reprecipitation with a good solvent chloroform and a non-solvent methanol and then dried for 24 h under vacuum of 5×10^{-2} Pa at room temperature.

The weight-average-molecular weight $\bar{M}_w$ was determined to be 4.0×10^5 on a gel permeation chromatograph equipped with a

low angle light scattering detector (TOSOH LS-8000). To prepare gel samples, a prescribed amount of P(3BCMU) was dissolved in either o-DCB or a mixed solvent p-DCB/TOL at 390 K. By cooling the solution, a gel was formed accompanied by a color change from yellow to dark blue. To prepare doped gel samples, solutions of dopant with a prescribed concentration were prepared and then P(3BCMU) was dissolved in them at 390 K. The concentration of P(3BCMU) was controlled in the range from 0.2 to 2 wt%. The gel in o-DCB was coded in a way P(3BCMU)-(1.5)/o-DCB which indicates the polymer concentration is 1.5%. On the other hand gels in mixed solvent are coded in a way P(3BCMU)(1.5)/[p-DCB/TOL(62/38)] which indicates that the polymer concentration is 1.5 wt% and that the mixing ratio of p-DCB/TOL is 62/38 by weight. We used the mixed solvents in which p-DCB content ranges from 34 to 62 % since below p-DCB content of 34%, P(3BCMU) did not dissolve in the mixed solvent, and above 62% p-DCB crystallized at room temperature.

Method

A condenser cell of the type-I reported previously[1] was used. The electrodes with area of 5 cm^2 were about 1.0 mm separated. Before measurements argon was filled in the cell to prevent moisture.

The AC conductivity σ_{ac} was measured with an automatic capacitance bridge (Yokogawa-Hewlett-Packard 4270A) at 50 V cm^{-1} in the frequency range from 1 to 100 kHz. The DC conductivity σ_{dc} was measured with an electrometer (Keithley 640) under electric fields from 0.1 to 1000 V cm^{-1}. We observed time dependence of the current after a constant DC voltage was applied: The current decreased rapidly during the initial 100 seconds to a level of ca. 1/2 of the value just after the application of the DC voltage, and then it gradually decreased. We defined σ_{dc} after 15 minutes as the equilibrium current. Temperature de-

pendence of the σ was measured at the heating or cooling rates of ca. 0.3 K min.$^{-1}$

Measurements of ultraviolet and visible light (UV-Vis) spectra were made by a spectrometer (Shimadzu UV-200). Details of the measurements of transmittance of monochromatized light were described previously.[1]

Dynamic shear moduli G' of P(3BCMU) gel were measured with a coaxial cylinder type rheometer (Iwamoto Seisakusho Auto-viscometer IR-200). The amplitude of shear was ca. 0.2 and frequency was varied from 0.0159 to 0.159 Hz.

RESULTS AND DISCUSSION

Gel-to-Sol Transition

The gel-to-sol transition temperature was measured by a mechanical method. Figure 1 shows the temperature dependence curves of storage shear modulus G' at 0.16 Hz for P(3BCMU)/o-DCB and P(3BCMU)/[p-DCB/TOL(62/38)]. Below 340 K, the G' remained almost constant, while above 340 K the G' decreased with increasing temperature. Temperatures at which G' became almost zero were assigned to the gel-to-sol transition temperature T_t which was 378 K for gels in o-DCB and 387 K in p-DCB/TOL.
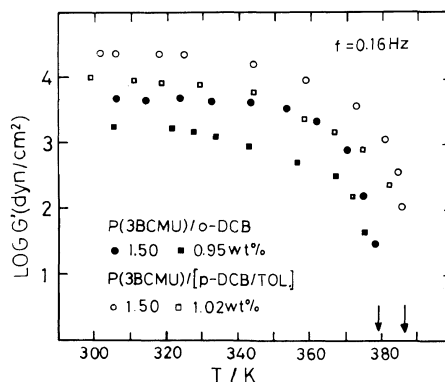

Figure 1. Temperature dependence of dynamic shear moduli G' at 0.16 Hz for P(3BCMU)/o-DCB and P(3BCMU)/[p-DCB/TOL(62/38)] gels. Concentration is indicated in the figure. The arrows indicate the gel-to-sol transition temperatures.

The Lissajou's diagrams for the stress *vs.* strain relation were almost straight in the range below 340 K, indicating that the gels were elastic. The value of $\tan \delta$ was less than 0.001 over whole temperature range.

Temperature Dependence of Conductivity

Figure 2 shows the temperature dependence of σ_{ac} at 1 kHz for P(3BCMU)/*o*-DCB gels with concentrations of 0.90, 0.66, and 0.30 wt%. For comparison, the σ_{ac} of the solvent *o*-DCB is also shown with open keys. The σ_{ac} of *o*-DCB denoted as "extracted" is explained later.

As is seen in Figure 2, σ_{ac} *vs.* temperature curve showed a maximum σ_{ac}(max) around 369 K and minimum σ_{ac}(min) at 378 K. We note that the temperature of σ_{ac}(min) coincides with T_t determined by the mechanical method. Above T_t, σ_{ac} increased again with temperature. This behavior is qualitatively the same as that of P(4BCMU)/TOL gel. However, we note that the ratio of σ_{ac}(max) and σ_{ac} (min) in P(3BCMU)/*o*-DCB gel was smaller than that of P(4BCMU)/TOL *i.e.*, σ_{ac} (max)/σ_{ac}(min) equals 1.15 for P(3BCMU)/*o*-DCB and 50 for P(4BCMU)/TOL.

The difference mentioned above may be ascribed to the difference of ionic conductivities of the both systems as discussed in detail later. When concentration of salts in the gel is the same, the ionic conductivity increases with increasing dielectric constant ε of the solvent since the Coulombic energy for dissociation of salts is proportional to $1/\varepsilon$. Since the ε of *o*-DCB 9.9 is much higher than that of TOL 2.3, *o*-DCB solutions of P(3BCMU) contains more impurity ions than P(4BCMU)/TOL system. We expect that the impurity concentration is of the same order. Thus ionic conductivity in P(3BCMU)/*o*-DCB is higher than that in P(4BCMU)/TOL.

In order to test the effect of ε on the medium, σ_{ac} of P(3BCMU)/[*p*-DCB/TOL] was investigated where ε of the mixed solvent was almost independent of the composition and was *ca.* 2.4. Figure 3 shows σ_{ac} and σ_{dc} of P(3BCMU)/
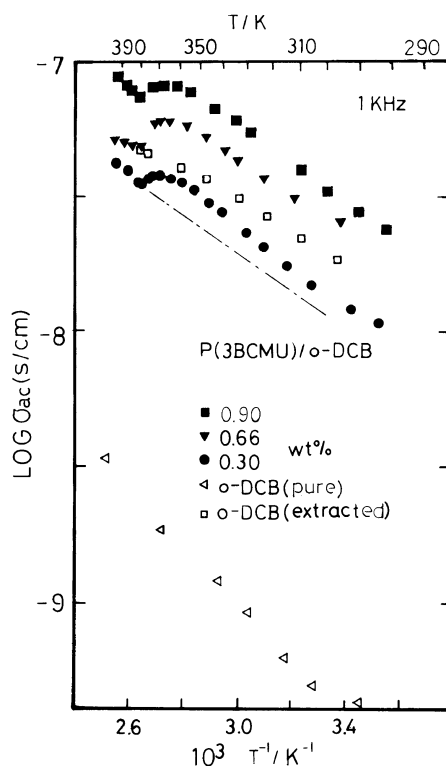
Figure 2. Temperature dependence of σ_{ac} at 1 kHz for P(3BCMU)/*o*-DCB with concentrations of 0.90, 0.66, and 0.30 wt%. The open keys indicate σ_{ac} at 1 kHz for pure *o*-DCB (triangle) and the extract (o-DCB) (square) containing ions extracted from the 50/50 (in volume) mixture of the gel with $C = 0.90$ wt% and pure *o*-DCB (see the text).

[*p*-DCB/TOL(62/38)] with concentrations C of 0.30, 0.61, and 1.21 wt%.

Three features are noted in Figure 3. Firstly the value of σ_{ac} in the sol state is order of 10^{-10} S cm^{-1} and is *ca.* 1/100 of σ_{ac} in *o*-DCB. Secondly, the ratio of σ_{ac}(max)/σ_{ac}(min) amounts to 2.0 which is higher than that in *o*-DCB ($= 1.15$). Thirdly σ_{dc} is of the same order as σ_{ac}. The first and second features are obviously due to the ionic conductivity which prevails in P(3BCMU)/*o*-DCB but does not so much in P(3BCMU)/[*p*-DCB/TOL].

Next we compare σ_{ac} between P(3BCMU)/[*p*-DCB/TOL] and P(4BCMU)/TOL gels in which the ε of the solvents in the both systems
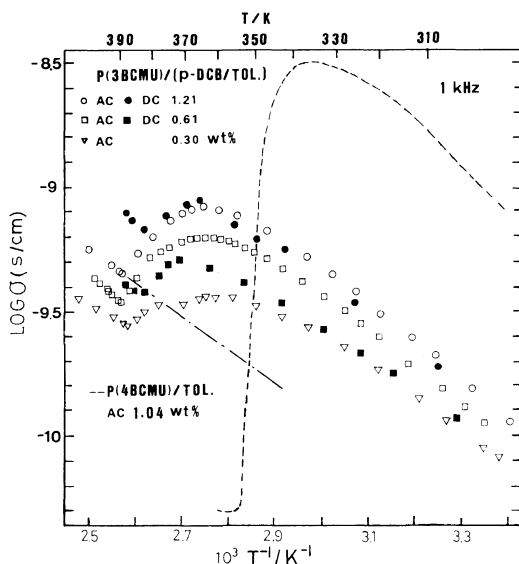
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Figure 3. Temperature dependences of σ_{dc} and σ_{ac} at 1 kHz for P(3BCMU)/[p-DCB/TOL (62/38)]. The concentrations are given in the figure. The dashed line shows σ_{ac} of P(4BCMU)(1.04)/TOL gel. The dash-dot line shows the estimated ionic conductivity for P(3BCMU)(1.21)/[p-DCB/TOL(62/38)].

Figure 4. Filled keys show the temperature dependence of σ_{ac} of P(3BCMU)(0.3)/[p-DCB/TOL] in varying ratio of p-DCB and TOL. Open key shows σ_{ac} of the mixed solvent with p-DCB/TOL = 52/48.

are approximately the same. The dashed line in Figure 3 represents the σ_{ac} of P(4BCMU)-(1.0)/TOL reported previously.

First we compare σ_{ac} in the sol states of the both systems. If the σ_{ac} is due to ionic conduction, we expect that they are of the same order. In order to examine whether this expectation is fulfilled, we compare σ_{ac} of the both systems at same temperature. For this purpose we exptrapolated the σ_{ac} curve of P(3BCMU)/[p-DCB/TOL] assuming the Arrhenius type dependence of σ_{ac}. Specifically the portion of log σ_{ac} vs. $1/T$ curve in the range of $1/T < 2.6 \times 10^{-3}$ was extrapolated to higher $1/T$ side as indicated by a dash–dot line. As is seen in Figure 3, thus extrapolated σ_{ac} in the P(3BCMU) sol phase is ca. three times higher than that of P(4BCMU)/TOL. However, we note that the σ_{ac} of the both systems are of the same order. Therefore we conclude that the contributions of ionic conduction in the both systems are approximately the same.
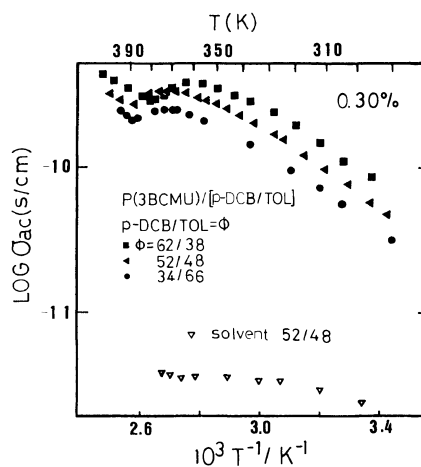
Figure 4 shows the σ_{ac} curves at 1 kHz for P(3BCMU)(0.3)/[p-DCB/TOL] with three different compositions of the mixed solvent. We see that σ_{ac} depends weakly on the composition. Thus we mostly used a mixed solvent with the composition of p-DCB/TOL = 62/38.

Effect of Dopant on Conductivity

In our previous study, we found that the σ_{ac} and σ_{dc} of P(4BCMU)/TOL gel increased more than ten times by doping with iodine. Se et al.[5] reported that σ_{dc} of P(3BCMU) films doped with iodine increased by a factor of 10^3 to 10^5 compared with the undoped ones. They suggested the formation of a charge transfer complex between P(3BCMU) and I_3^- which created holes on the P(3BCMU) chains.

The doping effect on the conductivity in gels of P(3BCMU) was examined by using iodine as an acceptor and tetrathiafulvalene TTF as a donor. We expect that the σ_{ac} of P(3BCMU) gel also increases by doping if the conduction in P(3BCMU) gel is due to electronic conduction through the gel network.

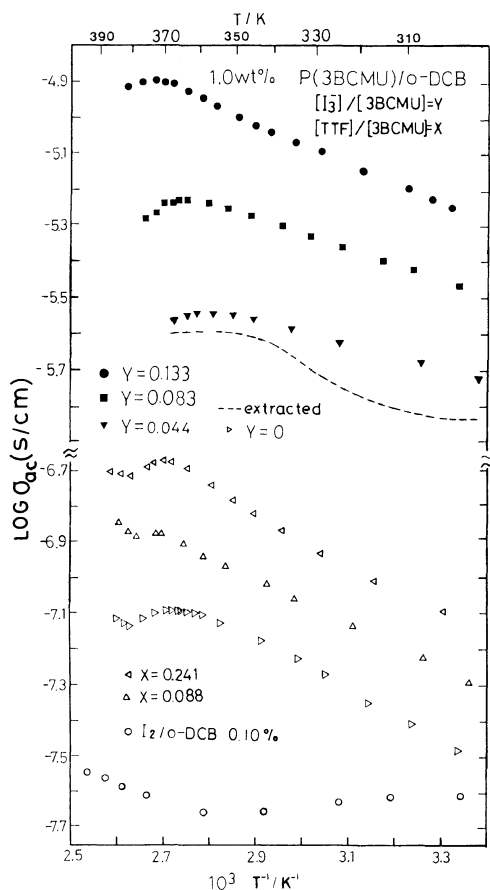Figures 5 and 6 show σ_{ac} vs. temperature curves for P(3BCMU)/o-DCB and P(3BCMU)/

Figure 5. Temperature dependence of σ_{ac} at 1 kHz for P(3BCMU)/o-DCB gel doped with iodine and TTF. The molar ratios $Y = [I_3]/[3BCMU]$ and $X = [TTF]/[3BCMU]$ are indicated in the figure.

Figure 6. Temperature dependence of σ_{ac} at 1 kHz for P(3BCMU)/[p-DCB/TOL(62/38)] with concentration of 0.501 wt% doped with iodine. The molar ratio $Y = I_3^-/3BCMU$ is indicated in the figure.

[p-DCB/TOL] gels, respectively. The dopant content was represented by molar ratio $Y \equiv [I_3]/[3BCMU]$ or $X \equiv [TTF]/[3BCMU]$ where [ ] indicates the molar concentration of I_3, TTF and the monomeric unit 3BCMU. The σ_{ac} increased by a factor of *ca.* 100 by doping with iodine as shown in Figures 5 and 6. This factor is greater than that for P(4BCMU)/TOL gel. In the range of $Y \equiv [I_3^-]/[3BCMU] < 0.13$, σ_{ac} increased with increasing Y but in the range of $Y > 0.13$, σ_{ac} became almost independent of Y. This behavior of saturation is quite similar to that of P(4BCMU)/TOL gel and P(3BCMU) film. These results suggest that the conduction
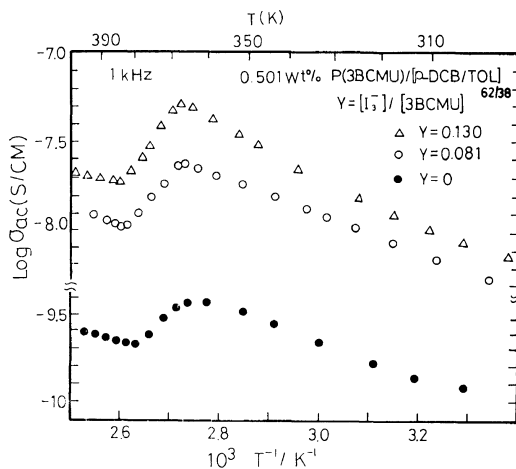
in P(3BCMU) gel is partly due to the electronic conduction.

In contrast to the effect of iodine, the σ_{ac} increased only several times by doping with a donor TTF and saturated at the dopant concentration of $[TTF]/[3BCMU] = 0.64$ where [ ] indicates the moles. This suggests that an acceptor is more effective in enhancement of σ_{ac} than a donor for P(3BCMU) gels.

Concentration Dependence of Transition Temperature

Temperatures T_{max} of maximum σ_{ac} and those T_{min} of minimum σ_{ac} of doped and undoped P(3BCMU) gels are summarized in Figure 7. We note that T_{max} and T_{min} are almost independent of concentration. This behavior was also observed in P(4BCMU)/TOL system.[1] For P(3BCMU)/[p-DCB/TOL] the average values of T_{max} and T_{min} are 362 and 388 K, respectively while T_{max} and T_{min} for P(3BCMU)/o-DCB are 367 and 378 K, respectively. The gel-to-sol transition temperatures T_t determined by measurements of shear moduli are also plotted. T_t agreed well with T_{min}. As is seen in this figure, the T_{max} was 3 K higher when iodine was added, while T_{min} did
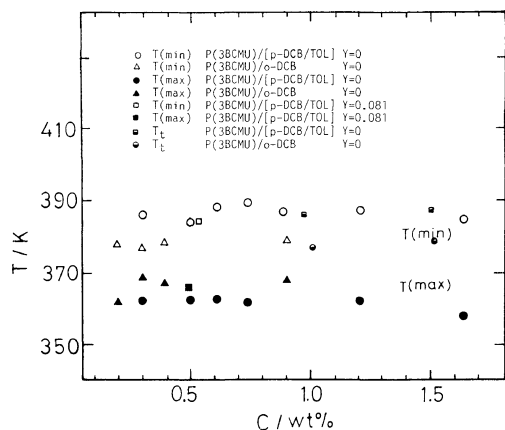
Figure 7. Concentration dependence of the maximum (T(max)) and minimum temperature (T(min)) of the σ vs. temperature curves for doped and undoped P(3BCMU)/[p-DCB/TOL] and P(3BCMU)/o-DCB systems.

Figure 8. Concentration dependence of σ_{dc} in the sol phase at 390 K for P(3BCMU/[p-DCB/TOL(62/38)]. The dashed line indicates the overlapping concentration C^*.

not change by doping.

Estimation of Ionic Conductivity in Gel Phase

We have concluded that the conductivity in the gel phase is due to both the electronic and ionic conductions. In this section we estimate separately the contributions of the electronic and ionic conductivities in P(3BCMU) gel. We have assumed that conductivity in the sol phase is ionic. If this assumption is valid, we can estimate the ionic conductivity in the gel phase by simply extrapolating the conductivity of the sol phase.

First of all, we check this assumption. Although it is not conceivable, there is a possibility that the conduction in the sol phase is still due to migration of electrons or holes along the P(3BCMU) chains with occasional hopping from one chain to another. If this is the case, conductivity must decrease drastically around the overlapping concentration C^* below which carriers hardly hop from one chain to another. C^* is given by

$$C^* = 1/[\eta] \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity. Using eq 1, we estimated C^* of this system to be 0.45% from the data of $[\eta]$ in chloroform (CHCl$_3$)
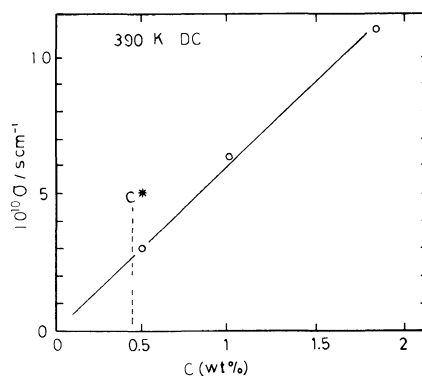
reported by Se et al. for P(3BCMU) prepared by 45 Mrad dose.[6] Here we note that CHCl$_3$ is better solvent than p-DCB and hence C^* in the present system may be slightly higher than 0.45%. Figure 8 shows the concentration dependence of σ_{dc} in the sol phase of P(3BCMU)/[p-DCB/TOL]. As is seen in this figure, σ_{dc} did not vanish around 0.45%. Therefore we conclude that the conduction in the sol state is due to ionic conduction.

Second step is to estimate the ionic conductivity in the gel phase. Since the concentration of the gel in the present study was about 1%, it is reasonable to consider that the mobilities of ions in the gel and pure solvent are nearly the same.

Two methods for estimating ionic conductivity are available. One is to extrapolate the log σ_{ac} vs. $1/T$ curve in the sol phase by assuming the Arrhenius type behavior. The other is to measure conductivity on the solvent containing the same ions as P(3BCMU) gel. However, the former method is less reliable because the measurement of σ_{ac} in the sol phase was limited in the narrow temperature range. Thus we employed the latter method as follows.

First a gel was crashed and a certain amount of the same solvent as the gel was added at room temperature. The system was stirred

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gently for 20 h to extract ions from the gel phase to the solvent phase. Then the system was separated into the solvent and gel phases by filtration with a glass filter. The solvent thus separated is referred to as *extract* and was served for measurements of ionic conductivity.

The σ_{ac} *vs.* T curves at 1 kHz for the solvent containing extracted ions are shown in Figures 2 and 5. Details of the condition of extraction are given in the figure caption. For example, the curve shown in Figure 2 was obtained for the *extract* from a mixture of P(3BCMU)(0.9)/ *o*-DCB and pure *o*-DCB of the volume ratio of 50/50. It is seen that the conductivity of the corresponding gel is higher than the extract. One of the origin is that ions are diluted by addition of pure solvent and the other is that probably it takes long time to achieve an equilibrium partition of ions between the gel and solvent phases. Therefore the concentration of the ions in the extract is lower than that in the gel. In fact we observed that the conductivity of the extract increased with increasing extraction period.

It is needed to find a factor ξ to correct the concentration of ions in the solvent phase. We assumed that ξ is given by the ratio of σ_{ac} of the sol and σ_{ac} of the extract at T_{min}. In Figure 2, the ionic conductivity ($= \xi\sigma_{ac}$(extract)) thus estimated is shown by a dash–dot line. The difference between the gel and thus estimated ionic conductivity was assigned to the electronic conductivity σ_{ac}^{e} in the gel phase.

In the case of gels doped with iodine, the extra ions of I_3^- are formed. We expect that the I_3^- ions are not extracted by the procedure mentioned above due to the condition that both the gel and extract phases must be electrically neutral. Therefore, there is a possibility that the electronic conductivity of the doped gels estimated by the above method still includes the ionic conductivity due to I_3^-. The contribution of I_3^- to the ionic conductivity may be assessed by means of a suitable ion-selective electrode which have an approximately zero contact resitance for electronic con-
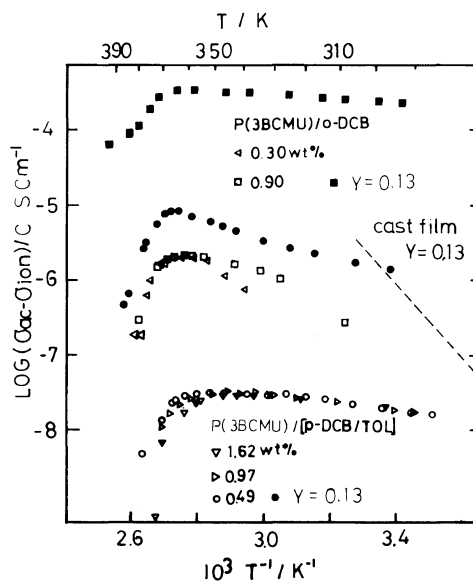

Figure 9. Temperature dependence of the electronic conductivity σ_{ac}^{e} for the doped and undoped P(3BCMU) gels. Dashed line shows the σ_{dc} of bulk P(3BCMU) film ($Y=0.13$) cast from chloroform solution reported by Se *et al.*[5]

duction but have a high resistance for ionic conduction. At present we assume that the binding energy of the charge transfer complex between the I_3^- ion and P(3BCMU) chain is so high that the I_3^- ions hardly migrate.

Electronic Conductivity in Gel

The electronic conductivity σ_{ac}^{e} thus estimated was normalized to 100% concentration by dividing by concentration C and plotted in Figure 9. The σ_{dc} of a P(3BCMU) film doped with iodine at $Y=0.13$ was reported by Se *et al.*[5] The datum is also plotted in Figure 9 by dashed line for the sake of comparison.

First we compare the conductivities between the bulk films and gels. As is seen in Figure 9, the σ_{dc} of the bulk film at $Y=0.13$ approximately agrees with σ_{ac}^{e}/C for P(3BCMU)/[*p*-DCB/TOL] gel doped with iodine at $Y=0.13$. However the slopes and hence activation energy E_a of the bulk and gel are different. The strength of the contribution of ionic conductivity in the bulk films has not been measured.

Se *et al.*[5,6] assumed that the conductivity in bulk P(3BCMU) was mostly due to electronic conduction.

Comparison of σ_{ac}^{e}/C for undoped gels in mixed solvents [*p*-DCB/TOL] and that in *o*-DCB indicates that σ_{ac}^{e} in *o*-DCB is 40 times higher than in [*p*-DCB/TOL]. We also note that σ_{ac}^{e} does not depend on the content of *p*-DCB in the mixed solvent of *p*-DCB/TOL.

In doped gels, σ_{ac}^{e} depends on the content of dopant. When σ_{ac}^{e} of the gels in *o*-DCB and *p*-DCB/TOL are compared at the same doping level, say $Y = 0.13$, σ_{ac}^{e} in *o*-DCB is *ca.* 50 times higher than that in *p*-DCB/TOL. These results indicate that σ_{ac}^{e} increases with increasing dielectric constant of the medium surrounding the conjugated chains.

If the chains surrounding one test chain of bulk P(3BCMU) are regarded as a medium, the medium dielectric constant is 2.8 and is similar to *p*-DCB/TOL.

Effect of dielectric constant of the medium on σ_{ac}^{e} is explained as follows. Either holes or electrons are created by an acceptor or a donor as shown in Figure 10. This model is similar to the polaron model proposed for conducting polymers: Unpaired electrons (free radicals) and charged defects (holes or electrons) are created. Such a charge transfer complex may be also created without dopant by inter- and/or intramolecular interactions probably interactions between the main chain and the side group. Recently we have confirmed the existence of such a radical ion by measurements of electron spin resonance ESR.[16]

Holes or electrons migrate through chains under a constraint due to the Coulombic potential from the radical ions. The constraint obviously decreases with increasing ε of the medium. We also expect that the ions of the acceptor or donor act as trap for carriers. The depth of the trap-potential decreases with increasing ε of the medium. Similar argument was made by Nowak *et al.*[15] to understand creation of polaron and bipolaron in solutions of poly(3-hexylthienylene).
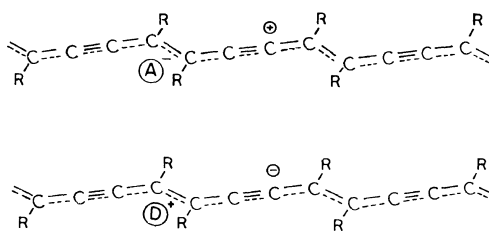

Figure 10. Speculated electronic structure of P(3BCMU) backbone.

Table I. Activation energy E_a of undoped and doped P(3BCMU) gels in *p*-DCB/TOL mixed solvent and in *o*-DCB[a]

Solvent	$C/wt\%$	Y	E_a/eV
p-DCB/TOL	0.49	0	0.13
	0.97	0	0.11
	1.62	0	0.09
	0.50	0.13	0.27
o-DCB	0.90	0	0.19
	0.91	0.13	0.06

[a] Dopant is iodine and $Y = [I_3]/[3BCMU]$.

Activation Energy

From the slope of the log σ_{ac}^{e} *vs.* $1/T$ curves, the activation energy E_a for electronic conduction is determined and listed in Table I. As is seen in this table, values of E_a in P(3BCMU)/*o*-DCB and P(3BCMU)/[*p*-DCB/TOL] gels range from 0.06 to 0.27 eV/mol. These values are *ca.* 1/2 to 1/10 of the E_a of P(4BCMU)/TOL.

We pointed out in our previous paper[1] that E_a of P(4BCMU) film reported by Se *et al.*[5,6] was *ca.* three times higher than that of P(4BCMU)/TOL gel. The same relation is also seen between the film and gels of P(3BCMU). Previously we speculated that the mechanisms of carrier migration for the bulk and gel are different to explain the difference in E_a.

Relationship between Elasticity and Electronic Conduction

In our previous study on P(4BCMU)/TOL gel,[1] we defined an order parameter F characterizing the network structure of the gel.
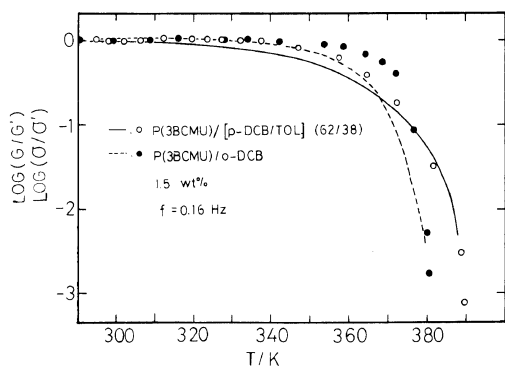
Figure 11. Comparison of the temperature dependence of parameter F and normalized shear moduli (see the text) for P(3BCMU)/[p-DCB/TOL (62/38)] and P(3BCMU)/o-DCB.

Figure 12. Effect of DC bias on σ_{ac} for P(3BCMU)/[p-DCB/TOL(62 /38)] gel.

F is defined as follows. The observed conductivity σ is assumed to be F times hypothetical conductivity σ^0, i.e., $\sigma = F\sigma^0$ where σ^0 is given by the Arrhenius equation of σ in the temperature region in which $\log \sigma$ vs. $1/T$ curve is straight. F is unity if the gel structure at low temperature is preserved and zero in the sol state.

Figure 11 shows the temperature dependence of parameter F (σ/σ^0) in which σ is the observed σ_{ac}^e at 1 kHz. It is seen that F starts to decrease around 350 K. Thus 350 K is considered to be the temperature of the commence of the gel-to-sol transition.

The scaling theory assumes that the conductivity and elasticity in a gel are expressed by the same functional form as the both properties are related to the connectivity of the gel.[18] We note that the temperature dependence of F resembles the shear modulus vs. T curve shown in Figure 1. The normalized G' curves are replotted in Figure 11 with full and dashed lines for P(3BCMU)/[p-DCB/TOL] and P(3BCMU)/o-DCB, respectively. As shown in Figure 11, the temperature dependence of F and G' are similar. This indicates that the elastic modulus can be described by the order parameter determined from conductivity.
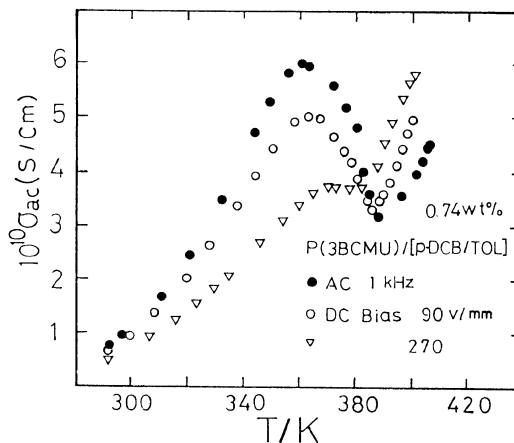
Direct Current Conductivity

In Figure 3, we see that σ_{dc}^e is smaller than σ_{ac}^e as judged from $\sigma_{ac}(\max)/\sigma_{ac}(\min)$. Similar behavior was observed for P(4BCMU)/TOL gels.[1] This may be explained as follows. In P(3BCMU) gels, the physical crosslink and/or contact points exist. Through such junctions carriers can migrate from one electrode to the other. The part of chain from the chain end to the junction point which is nearest from the end is called the dangling chain. When the carriers move in the direction of a DC field, some of the carriers are trapped in the part of dangling chain which acts as a blind lane for the carriers. Due to the applied DC electric field, the carriers hardly return to a junction point to continue their migration.

Based on such a view, we also tested the effect of DC bias on the σ_{ac}. The temperature dependences of σ_{ac} measured at 1 kHz under DC bias of 90, 270 V mm^{-1} and AC voltage of 5 V mm^{-1} are shown in Figure 12. The maximum of the curves became smaller with increasing DC bias, and at 376 K σ_{ac} increased sharply.

Ultraviolet and Visible Light Spectra and Color Change
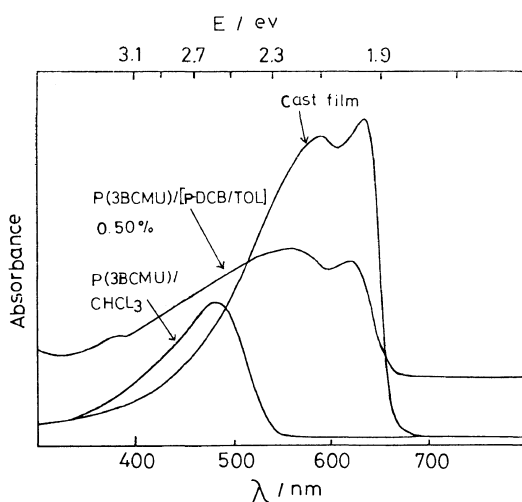
Figure 13 shows the UV spectrum of the

Figure 13. The UV and visble light spectra of P(3BCMU) gel, chloroform solution of P(3BCMU) and a film cast from chloroform solution.
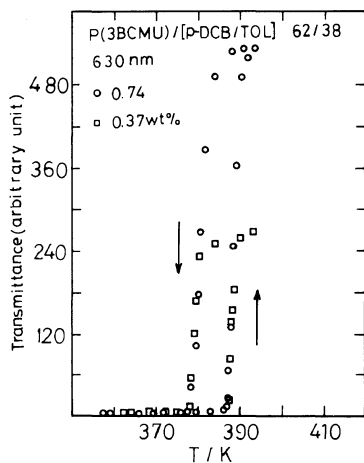

Figure 14. Temperature dependence of the transmittance of 630 nm light for P(3BCMU)/[p-DCB/TOL(62/38)] gel with concentration of 0.740 and 0.37 wt%. The arrows indicate the direction of temperature change.

P(3BCMU)(0.5)/[p-DCB/TOL](62/38) gel. For the sake of comparison, the spectrum for a chloroform solution of 0.24 wt% and that for a bulk film of P(3BCMU) are shown. It is noted that chloroform is a good solvent for P(3BCMU) and hence the P(3BCMU) molecules have a random coil conformation. Previously we reported for the P(4BCMU)/

TOL system that the the spectrum in the sol state is quite similar to that of chloroform solution. In the present study we did not observe the spectrum of P(3BCMU) sol since a spectrometer equiped with temperature regulator around 120°C was not available. Thus we expect that the spectrum in the sol state of P(3BCMU) is similar to the $CHCl_3$ solution.

The characteristic spectral change of P-(3BCMU) solution was explained by Kanetake et al.[17] It is reported that the color change is due to the conformation change of the backbone from rod-like to coil-like accompanied by the change of the conjugation length. The 630 nm wavelength light was used to monitor the color change. From the temperature dependence of the transmittance for the 630 nm light, we determined the temperature of color change. Details of the procedure of the measurements were described previously.[1]

Figure 14 shows a representative result of the transmittance vs. temperature curve for P(3BCMU)/p-DCB/TOL system at two concentrations of 0.74 and 0.37 wt%. The intensity of the transmitted light increases sharply at 388 K on heating, while decreases sharply around 378 K on cooling. The transition temperature on heating agrees well with the temperature of minimum σ_{ac} shown in Figure 3. The color change temperatures were independent of both the P(3BCMU) concentrations and the heating and cooling rates. Similar hysteresis was reported previously for P(4BCMU)/TOL system.

CONCLUSIONS

1. Gel-to-sol transition temperature was determined by measurements of the shear moduli to be 378 K for P(3BCMU)/o-DCB gel and 387 K for P(3BCMU)/[p-DCB/TOL] gel.

2. Alternating current (AC) conductivity σ_{ac} at 1 kHz in the gel state was attributed to the contributions of electronic and ionic conductions.

3. Conductivity in P(3BCMU) gel was enhanced by dopants iodine and tetrathiafulvalene by factors of 100 and 5 times, respectively.

4. Electronic conductivity reduced by concentration in P(3BCMU)/o-DCB gel is *ca.* 40 to 50 times higher than that in P(3BCMU)/[p-DCB/TOL] gel. Thus the mobility of the carrier increases with increasing polarity of the solvent.

5. At the transition temperature, the transmittance at 630 nm changed sharply. This corresponds to the color change from dark blue in the gel to yellow in the sol state.

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