Electric Conductivity, Elasticity, and Optical Spectra in Blend Gels of Polydiacetylenes: P(3BCMU)/P(4BCMU)/Mixed Solvent System

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ABSTRACT: Alternating current conductivity σ_{ac}, shear moduli G', and ultraviolet-spectra (UV) were studied for gels consisting of two polydiacetylenes *i.e.*, 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 carbonyl methylurethane)] abbreviated as P(4BCMU). As a common solvent of these polydiacetylenes, a mixed solvent *p*-dichlorobenzene (*p*-DCB)/toluene (TOL) (62/38) was used. Shear moduli G' of blend gels decreased stepwise around 340 and 385 K which coincided with the gel-to-sol transition temperatures of pure P(4BCMU) and P(3BCMU) gels, respectively. At 385 K the blend gels transformed completely into sol. Observed G' of blend gels conformed approximately to the additivity law with respect to the weight fraction of P(3BCMU) and P(4BCMU). This indicates that in the range of $T < 340$ the gel network is composed of both the P(4BCMU) and P(3BCMU) molecules but above 340 K the network is composed only of the P(3BCMU) molecules. Temperature dependence of σ_{ac} at 1 kHz exhibited two maxima around 330 and 360 K. σ_{ac} observed around 360 K was *ca.* ten times higher than σ_{ac} expected from the additivity. The UV spectra of the blend gels exhibited abosorption bands not seen in pure gels of the components. It is speculated that the P(3BCMU) and P(4BCMU) chains partially form a charge transfer complex in blend gels.
KEY WORDS Gel / Electric Conductivity / Elasticity / UV Spectra / Blend / Polydiacetylene / P(3BCMU) / P(4BCMU) / Gel-to-Sol Transition

In our previous papers,[1-3] we reported the electric conductivity, sol–gel transition behavior and ultraviolet and visible (UV) spectra in gels of polydiacetylenes. Specifically they were 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 carbonyl methylurethane)] abbreviated as P(4BCMU). These polydiacetylens are soluble in a variety of solvents and form gels in poor solvents such as *o*-dichlorobenzene (*o*-DCB) and toluene (TOL) at concentration as low as 0.1 wt%.[4,5] The electronic conduction in P(3BCMU) and P(4BCMU) cast films,[6,7] and that in the single crystal of P(4BCMU)[8] were studied throughly but the conduction behavior and physical properties in the gel state have not been studied fully.

Although the structures of the side groups of P(3BCMU) and P(4BCMU) are similar their properties differ greatly.[1-3,9] For example, the color of P(4BCMU) gel is red but that of P(3BCMU) is blue indicating a different electronic state of the conjugated backbone. Gels of P(4BCMU) in *p*-DCB/TOL mixed solvent exhibit the gel-to-sol transition around 345 K and those of P(3BCMU) around 387 K.[3] The transition temperatures of these gels are almost independent of polymer concentration and weakly depend on solvent quality and molecular weight.[1-3]

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The alternating current (AC) conductivity σ_{ac} in the gel state is higher than that in the sol state. The enhancement of σ_{ac} by a dopant iodine and the photoconduction can be observed. Thus the conduction mechanism in P(3BCMU) and P(4BCMU) gels is mainly electronic rather than ionic.

In our preliminary study we found that P(3BCMU) and P(4BCMU) are miscible in a mixed solvent p-DCB/TOL above 385 K. On cooling, the solution transformed into a gel having no turbidity. This indicates that both components are miscible even in the gel state at least in the macroscopic scale. In this paper we report the effects of blending on the electric conductivity, sol–gel transition and UV spectra in such blend gels.

There were two objectives. One was to investigate the effect of blending on the gel-to-sol transition temperature. In gels of pure P(3BCMU) and P(4BCMU), the conformational transformation from rod to random coil occurres at the gel-to-sol transition temperature indicating that the confomational change and the formation of gel network are closely correlated.[1,3] It is interesting to see at what temperature the P(3BCMU) and P(4BCMU) molecules transform from rod to coil in blend gels. For this purpose, measurements of shear moduli G' and UV spectra have been made.

The second objective was to examine the electric conductivity and the electronic state of P(3BCMU) and P(4BCMU) in the blends. Although a vast number of studies on the electronic conduction of conjugated polymers have been reported,[10] there are few reports on conductivity in polymer blends consisting of two chemically different conducting polymers. The influence of blending on the conductivity in blend gels has been studied by comparing the behavior of blend gel with that of the pure gels reported previously.

EXPERIMENTAL

Samples

The details of preparation of P(4BCMU) and P(3BCMU) polymers were reported previously.[6,7] P(4BCMU) with a weight average molecular weight M_w of 4.5×10^5, and P(3BCMU) with M_w of 4.0×10^5 were used. Mixed solvent composed of p-dichlorobenzene (p-DCB) and toluene (TOL) with a mixing ratio of 62/38 (by weight) was dried with calcium hydride and filtered with teflon millipore film of 0.2 µm mesh.

The gel samples were prepared as follows. First P(3BCMU) and P(4BCMU) were dissolved in p-DCB/TOL(62/38) with a prescribed mixing ratio. Then the system was heated to 390 K followed by stiring until it became a homogeneous solution. By cooling, a gel was formed accompanied by color change from yellow to purple. We observed blend gels with an optical microscope but did not find any macroscopic phase separation.

Method

The cell used for electrical measurement was the condenser cell reported previously.[1] The electrodes had an area of 5 cm^2 and about 0.2 mm separated. AC conductivities σ_{ac} were measured with an automatic capacitance bridge (Yokogawa–Hewlett-Packard 4270A) at 5 V in the frequency range from 1 to 100 kHz. All conductivity measurements were made under an argon atmosphere at a heating rate of *ca.* 0.3 K min^{-1}.

UV absorption spectra were obtained with a spectrometer (Shimadzu model UV-200). The temperature dependence of absorbance was measured using monochromatized (530 nm) light from a high power xenon lamp (Nihon Bunko Co., model LH-X500).[1] The transmitted light through the sample sealed in an ampule was measured with a photodiode.
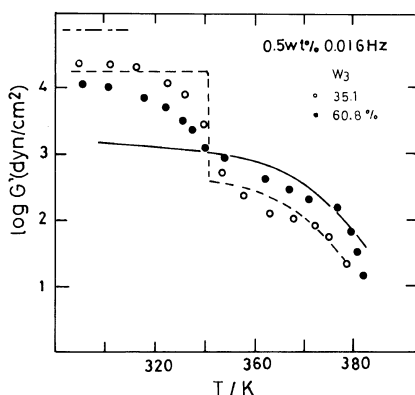
Elastic moduli G' of gels were measured with a coaxial cylinder type rheometer (Iwamoto Seisakusho Co., Autoviscometer IR-200).

RESULTS AND DISCUSSION

Gel-to-Sol Transition Temperature and Shear Moduli

Figure 1 shows the temperature dependence of shear moduli G' of blend gels in which total polymer concentration is 0.50 wt%. The weight fractions w_3 of P(3BCMU) in the total polymer are 0.35 and 0.61. The solid line indicates G' of pure P(3BCMU) gel in the mixed solvent. The dash-dot line shows the G' of pure P(4BCMU) gel estimated from the tensile modulus E as follows. First E for a gel of P(4BCMU)/[p-DCB/TOL(62/38)] was determined to be $1.50 \times 10^6 \, dyn \cdot cm^{-2}$ at concentration C of 4.6 wt% by the method reported previously.[2] Then the value was converted to G' at 0.50 wt% using the relation $E = 3G'$ and assuming $E \propto C.^2$

It is noted that the P(4BCMU)/[p-DCB/TOL(62/38)] system is in the sol state above 345 K and hence G' vanishes above *ca.* 340 K. We see that G' of blend gels are intermediate of those of pure P(4BCMU) and P(3BCMU) in the range of $T < 340$ K. If we assume the

additivity of G', the values of log G' of the blend gels at $w_3 = 0.35$ and 0.61 become 4.2 and 3.9, respectively at 300 K which agree approximately with the observed G' as shown in Figure 1. Therefore, we conclude that the network below 340 K is composed of both the P(3BCMU) and P(4BCMU) molecules.

The shear modulus G' of blend gels changes stepwise around 340 ± 3 K which corresponds to the gel-to-sol transition temperature $T_{tr}(4)$ ($= 345$ K) of pure P(4BCMU) gel. On further heating, the gels transform completely to sols at 385 ± 3 K which corresponds to the transition temperature $T_{tr}(3)$ ($= 387$ K) of pure P(3BCMU) gel. These transition temperatures are slightly lower than those of pure gels. In the range of $T_{tr}(4) < T < T_{tr}(3)$, observed G' is approximately equal to w_3 times the G' of pure P(3BCMU) as indicated by the dashed line for the gel of $w_3 = 0.35$. Thus, the P(4BCMU) molecules do not contribute to elasticity in the range of $T > T_{tr}(4)$.

Network structures below and above $T_{tr}(4)$ are speculated as shown schematically in Figures 2a and 2b, where the thick and thin lines indicate P(4BCMU) and P(3BCMU), respectively. In the range of $T < T_{tr}(4)$, the network of the blend gel is formed by both the rod-like P(3BCMU) and P(4BCMU) molecules. Two types of cross-links are considered. One is linkage between molecules of the same kind and the other is between the P(3BCMU) and P(4BCMU) molecules. It is difficult, however, to conclude which or whether both
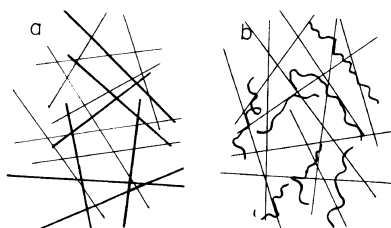

Figure 1. Temperature dependence of storage shear moduli G' at 0.016 Hz of blend gel with polymer concentration of 0.5 wt% and blend ratio w_3 of P(3BCMU) against the total polymer is 0.351 and 0.608. The dash-dot line and solid line indicate G' of pure P(4BCMU) and P(3BCMU) gel, respectively. The dashed line represents G' calculated from observed moduli of components by assuming additivity.


Figure 2. Schematic representation of the structure of blend gel in the temperature T ranges of (a) $T < T_{tr}(4)$ and (b) $T_{tr}(4) < T < T_{tr}(3)$. Thick and thin lines indicate P(4BCMU) and P(3BCMU), respectively.

are formed. Above $T_{tr}(4)$, only the P(3BCMU) molecules preserve the rod-like conformation and form a network but P(4BCMU) molecules with the random coil conformation locate in the mesh as shown in Figure 2b. Probably crosslinks between the rod-like P(3BCMU) molecules and coil-like P(4BCMU) molecules may be formed by hydrogen bonding of the urethane groups[11] but the P(4BCMU) chains do not contribute to the G' since the entropy elasticity of the flexible chains is much smaller than the energetic (enthalpy) elasticity due to bending of the rod-like P(3BCMU) molecules.

Electric Conductivity

In Figure 3, σ_{ac} *vs.* temperature curves for the blend gels with various P(3BCMU) contents are shown. Total polymer concentra-
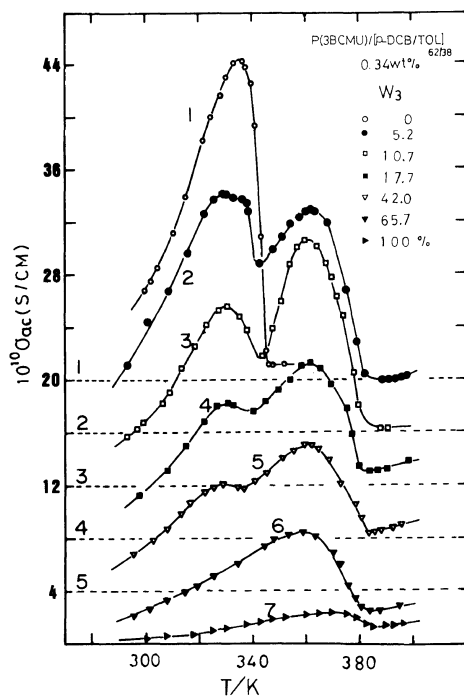

Figure 3. Temperature dependence of alternating current conductivity σ_{ac} at 1 kHz for blend gels with total polymer concentration of 0.34 wt%. The weight fraction w_3 of P(3BCMU) in the total polymer is indicated in the figure. Curves 1 to 5 have been shifted upward. The dashed lines indicate the base lines for the σ_{ac} curves of the same number.

tion was fixed at 0.345 wt%. The data for pure P(4BCMU) and P(3BCMU) gels in the same mixed solvent are also shown.

It is seen that pure P(4BCMU) and P(3BCMU) gels exhibit a single peak around 330 and 360 K, respectively. Above the each peak temperature, σ_{ac} decreases steeply and then becomes minimum at the gel-to-sol transition temperature T_r: $T_{tr}(4) = 345$ K and $T_{tr}(3) = 387$ K. In our previous paper we demonstrated that the peak of σ_{ac} in pure P(3BCMU) and P(4BCMU) corresponds to the incipience of the gel-to-sol transition and above the peak temperature the network structure degrades with increasing temperature. At temperatures of minimum σ_{ac}, the gels transform completely to sols.[1,3]

In the blend gels, two peaks are seen at temperatures corresponding to the peak temperatures of the pure gels. We see that the first peak around 330 K decreases with increasing P(3BCMU) content indicating that the peak is due to P(4BCMU). On the other hand, the intensity of the second peak around 360 K shows a peculiar w_3 dependence. Figure 4 shows the w_3 dependence of σ_{ac} at 330 and 360 K. We see that σ_{ac} at 330 K near the first peak decreases approximately in proportion to w_3. The conductivity σ_{ac} at 360 K around the second peak increases steeply in the range of $w_3 < 0.1$ and decreases gradually beyond $w_3 = 0.1$.
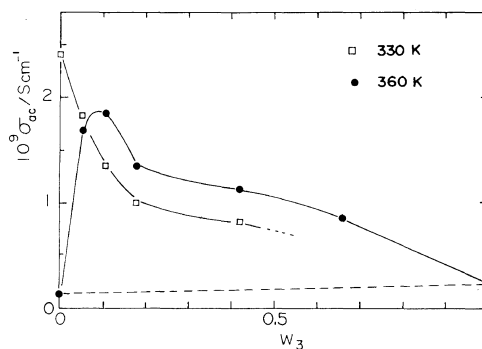
Figure 4. σ_{ac} at 330 K and 360 K plotted against the weight fraction w_3 of P(3BCMU) in the total polymer. The dashed line indicates σ_{ac} at 360 K expected from additivity.
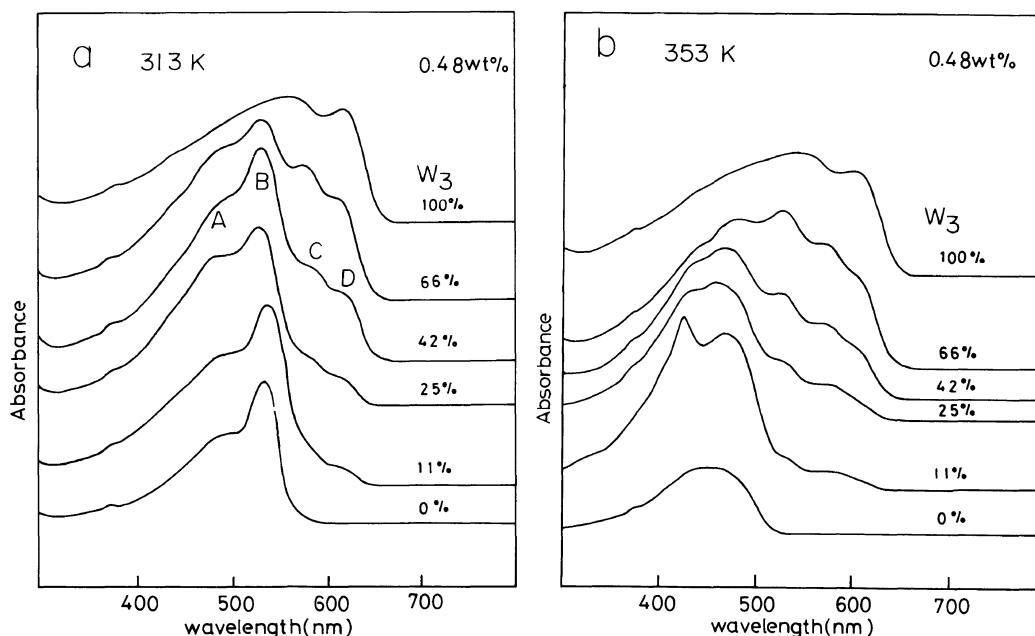
Figure 5. Ultraviolet and visible spectra of blend gels at (a) 313 K and (b) 353 K for gels with various P(3BCMU) content w_3. Total polymer concentration is 0.48 wt%. Base lines have been shifted. Absorbance around 700 nm indicates approximately zero absorbance.

We recognize that in the temperature range $T_{tr}(4) < T < T_{tr}(3)$, σ_{ac} deviates strongly from additivity as typically shown by the dashed line in Figure 4. The level of σ_{ac} of the blend is much higher than those of the components. We speculate that the coil-like P(4BCMU) molecules act as a dopant against the P(3BCMU) molecules and that a charge transfer complex is formed partially between the P(3BCMU) and P(4BCMU) chains.

UV Spectra and Color Change

The UV spectra of blend gels at 313 K and 353 K are shown in Figures 5a and 5b, respectively, in which the polymer concentration was fixed at 0.48 wt% and the blend ratio changed widely. For comparison, the spectra of pure P(3BCMU) and P(4BCMU) are also shown. As mentioned above, both the P(3BCMU) and P(4BCMU) chains contribute to elasticity at 313 K but only P(3BCMU) does so at 353 K.

The spectrum of the blend gel at 313 K con-

sists of four absorption bands at 470 (A), 530 (B), 560 (C), and 630 nm (D). The bands A and B are seen in pure P(4BCMU) gel and hence are due to P(4BCMU) but C and D are due to P(3BCMU). Bands B and D were previously assigned to photo excited $\pi-\pi^*$ excitons along the extended rod-like chains for P(3BCMU) and P(4BCMU) molecules, respectively.[12] Bands A and C are due to the $\pi-\pi^*$ transition of the coiled chains.

In the pure P(4BCMU) system, band B disappears completely at 353 K since it is in the sol state in which the P(4BCMU) chains assume random coil conformation $(T_{tr}(4) = 345 K)$. However in blend gels, this band still remains at 353 K as shown in Figure 5b indicating that the rod-like parts still exist even above $T_{tr}(4)$.
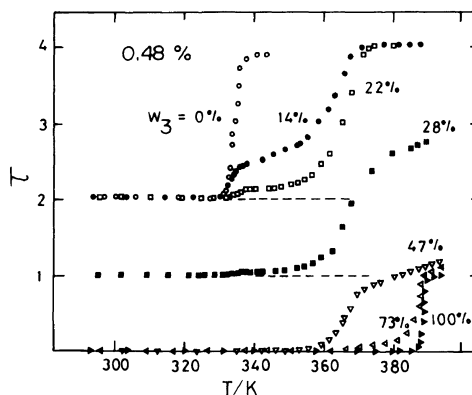
The difference in the spectra at 353 K between blend gels and a hypothetical gel in which the P(3BCMU) and P(4BCMU) molecules do not interact each other was estimated as follows. First, we calculated hypothetical absorbance α_{calc} from the absorbances of pure
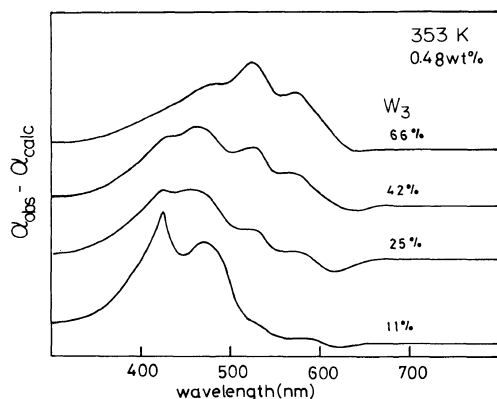
Figure 6. Difference of absorbance α_{obs} of the blend gel and calculated absorbance α_{calc} by assuming additivity at 353 K.

Figure 7. Temperature dependence of transmittance in an arbitrary scale at 530 nm for blends with various P(3BCMU) content w_3. Total polymer concentration is 0.48 wt%. The base lines have been shifted upward as indicated by the dashed lines.

P(3BCMU) gel and P(4BCMU) sol at 353 K by assuming additivity. Then α_{calc} was subtracted from the observed absorbance α_{obs}. The result is shown in Figure 6. We see that the intensity of the band at 530 nm (peak B) increases with the P(3BCMU) content. In addition, a relatively sharp band not seen in the pure gels is seen at 425 nm. We cannot assign this band at the present stage. However, this indicates that the electronic states of the P(3BCMU) and P(4BCMU) molecules differ from the pure state and this is consistent with the speculation that a charge transfer complex is formed partly between these molecules.

In order to investigate the conformational change of P(4BCMU) molecules in more detail, we measured the temperature dependence of transmittance τ at 530 nm. It is noted that the band at this wave length reflects a conjugated electronic state. Figure 7 shows plots of τ vs. T for 0.5 wt% gels with several P(3BCMU) contents. In the range of P(3BCMU) content below 30%, there is a sharp increase of the transmittance at 340 K as seen for the pure P(4BCMU) gel. This is obviously due to the partial rod-to-coil transition of the P(4BCMU) chains. However, in the blend gels above 340 K, transmittance is much lower than the pure P(4BCMU) gel reflecting the presence of band B. Transmit-

tance gradually increases with temperature and reaches the level of pure P(4BCMU) around 370 K. At higher concentrations the transition at 340 K becomes less clear.

In pure P(3BCMU), transmittance changes stepwise at 385 K but in blend gels transmittance increases rather gradually in the range of 360 to 380 K. This indicates that in blend gels, the P(3BCMU) molecules commence to transform from rod to coil at lower temperature than the pure P(3BCMU) gel. This suggests that interaction between the P(4BCMU) and P(3BCMU) molecules, which has been assumed in the former section, weakens the network of the gel.

CONCLUSIONS

1. In the blend gel of P(3BCMU) and P(4BCMU), both components contribute to elasticity in the range of $T < 340$ K, but only P(3BCMU) contributes in the range of $340 < T < 385$ K. UV spectra indicate that the conformation of the P(4BCMU) molecules in blend gels changes from rod to random coil at 340 K but conformation of the P(3BCMU) molecules changes at 385 K.

2. Two maxima are observed in the

alternating current conductivity σ_{ac} *vs.* T curves of blend gels at 330 and 360 K which correspond to σ_{ac} maximum temperatures of pure P(4BCMU) and P(3BCMU) gels, respectively.

3. In the temperature range of $340 < T < 385$, σ_{ac} is *ca.* 10 times higher than the value expected from σ_{ac} of the components. In this range, UV spectra indicate the presence of the rod-like conformation of the P(4BCMU) chains. A new band not seen in pure gels is also observed. There is the possibility that a charge transfer complex is formed between the P(3BCMU) and P(4BCMU) molecules.

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