Effect of scission of hydrogen bonds by phenol on phase behaviour and physical properties of polydiacetylene gels: P(3BCMU) and P(4BCMU)

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We report the effect of phenol on the phase behaviour and physical properties of polydiacetylene gels. Specifically, they are *o*-dichlorobenzene (*o*-DCB) solution of poly[4,6-decadiyne-1,10-diol-bis(n-butoxycarbonylmethylurethane)], abbreviated as P(3BCMU), and toluene (Tol) solution of poly[5,7-dodecadiyne-1,12-diol-bis(n-butoxycarbonylmethylurethane)], abbreviated as P(4BCMU). The polymer concentration was 0.1 to 2 wt%, and the molar ratio z of phenol to the monomer unit of the polydiacetylenes was regulated within 20.

The gel-to-sol transition temperatures T_t were determined by measurements of shear modulus for the P(3BCMU)/*o*-DCB system and by a falling ball method for the P(4BCMU)/Tol systems. T_t decreased with increasing z and the systems with polymer concentration of 1 wt% turned into a sol at room temperature in the range of $z \gtrsim 10$. The temperature dependence of alternating-current (a.c.) conductivity σ_{ac} at 1 kHz exhibited a maximum at a temperature ca. 20 K below the transition temperature. The value of σ_{ac} decreased steeply at the electrical transition temperature T_σ, which also decreased with increasing z. Ultra-violet and visible-light spectra for the P(3BCMU)/*o*-DCB and P(4BCMU)/Tol systems shifted to the short-wavelength side with increasing z. The infra-red spectra indicate that the intramolecular hydrogen bonds between the N–H and C=O groups of the side groups are cleaved by phenol. These results indicate that the conjugated rod-like conformation is made unstable by phenol. To clarify the mechanism of crosslinks of the gel network, the crystallinity of concentrated P(3BCMU) gels was determined by wide-angle X-ray diffraction. No crystallinity was observed in the gels of C less than 30 wt%.

(Keywords: polydiacetylene gels; gel–sol transition; physical properties)

INTRODUCTION

In our series of papers[1-4], we reported the behaviour of the thermo-reversible sol–gel transition, electronic conductivity and ultra-violet/visible (u.v./vis.) spectra in polydiacetylene gels, poly[4,6-decadiyne-1,10-diol-bis(n-butoxycarbonylmethylurethane)], abbreviated as P(3BCMU), and poly[5,7-dodecadiyne-1,12-diol-bis(n-butoxycarbonylmethylurethane)], abbreviated as P(4BCMU). These polydiacetylenes form gel at a concentration as low as 0.1 wt% in some solvents such as toluene and dichlorobenzene[5]. P(3BCMU) and P(4BCMU) gels are blue and red, respectively, indicating that the chains possess a conjugated electronic structure. However, they turn into yellow in the sol state, where the π electrons are localized.

The conjugated electronic state inevitably requires a planar structure of the backbone atoms. Patel *et al.*[6,7] proposed that the P(3BCMU) and P(4BCMU) molecules have a tape-like structure in which the backbone atoms take a conformation similar to the planar zig-zag structure and the neighbouring side groups are linked by the hydrogen bonding of the urethane groups (see the insert of *Figure 8*). The conjugated structure is thus stabilized by the bridges of the intramolecular hydrogen bonds. On the other hand the chains in the sol state assume a random-coil conformation. The gel-to-sol transition occurs in a narrow temperature range accompanied by the colour change.

Three mechanisms for the formation of gel networks may be considered: (i) intermolecular hydrogen bonding between the urethane groups on the side chains; (ii) the microcrystallites working as crosslinkages; and (iii) the physical entanglement between the tape-like stiff chains as theoretically proposed by Doi and Kuzuu[8]. However, the third mechanism may be ruled out, or at least is not the major origin of the gelation, since the initial slope of the stress *versus* strain of P(4BCMU) gels in toluene was found to be finite, in contrast to the Doi–Kuzuu theory[2]. This indicates that specific intermolecular interactions, i.e. the first or second mechanisms, must play an important role for the formation of the gels.

In this study we first investigated the effect of the hydrogen bonds between the –NH and O=C– groups on the gel-to-sol transition and the physical properties of the gel. Since the NH group is basic, it is easily attacked by acids. We chose phenol as such an acid to cleave the

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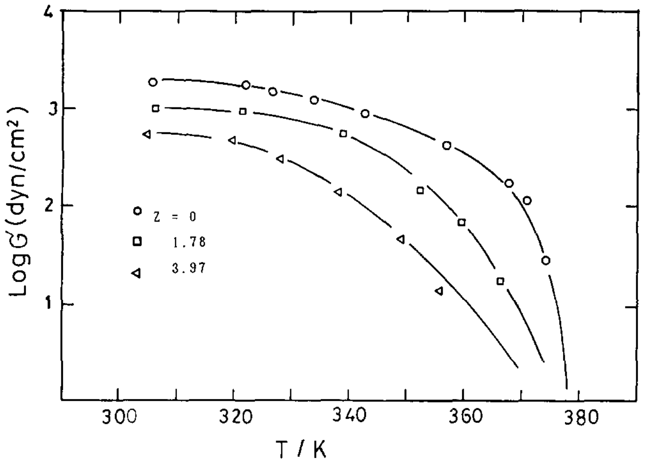

Figure 1 Temperature dependence of dynamic shear modulus G' at 0.16 Hz for P(3BCMU)/[PhOH(z)/o-DCB] gels. The polymer concentration is 0.90 wt% and the molar ratio z of PhOH/3BCMU is given in the figure. The arrows indicate the estimated gel-to-sol transition temperatures

hydrogen bonds[9]. The effects of phenol on the electrical conductivity, ultra-violet/visible spectra and infra-red spectra were examined. Secondly, we estimated the crystallinity of P(3BCMU) gels by wide-angle X-ray scattering to examine whether microcrystallites exist as crosslinks.

EXPERIMENTAL

Samples

Samples of P(3BCMU) and P(4BCMU) were prepared by irradiation of the monomer crystals sealed in glass ampoules by ^{60}Co γ-rays of 40 Mrad. The weight-average molecular weights M_w of P(3BCMU) and P(4BCMU) were 4.5×10^5 and 4.0×10^5, respectively. The details of preparation and characterization of the samples were reported previously by Se *et al.*[10–12]. Toluene (Tol) was purified by distillation with calcium hydride. o-Dichlorobenzene (o-DCB) was dried with CaH_2 and filtered with Millipore film of 0.2 μm mesh. Phenol (PhOH) of reagent grade was purchased from Wako Chemicals Co. and used as received.

Gels were prepared as follows. P(3BCMU) or P(4BCMU) were dissolved together with PhOH in a suitable solvent at temperatures above the gel-to-sol transition temperature. On cooling, gels were formed. These systems are coded as P(3BCMU)/[PhOH(2.5)/o-DCB], which indicates that the molar ratio of PhOH to the 3BCMU monomeric unit is 2.5.

Methods

Measurements of the alternating-current (a.c.) conductivity σ_{ac} were carried out under an argon atmosphere with the condenser cells reported previously[1]. An automatic capacitance bridge (Yokogawa–Hewlett–Packard 4270A) was used to measure σ_{ac} at 50 V cm^{-1} in the frequency range from 1 to 100 kHz. Temperature dependence of σ was measured at the heating or cooling rates of ca. 0.3 K min^{-1}.

Measurements of ultra-violet/visible (u.v./vis.) spectra were made on a Shimadzu UV-200 spectrometer. The sols were introduced at a temperature above the sol–gel transition temperature into a cell with thickness of 0.1 mm. The temperature was raised at a rate of 0.3 K min^{-1}.

The colour change temperatures were observed by measurements of the transmittance at 630 nm. Details 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. The apparatus for observation of a falling ball suspended in gels was also described previously[1].

The infra-red spectra were obtained on a Fourier-transform infra-red spectrometer (Jasco FT/IR-3). The solutions were sandwiched between KBr single crystals together with a spacer 0.2 mm thick.

X-ray diffractograms were taken by a diffractometer (Rigaku, model RAD-ROC) using Cu Kα emission.

RESULTS AND DISCUSSION

Gel-to-sol transition temperature by mechanical measurements

Figure 1 shows the temperature dependence of storage shear modulus G' at 0.16 Hz for P(3BCMU)/[PhOH(z)/o-DCB], where the molar ratio $z = [\mathrm{PhOH}]/[\mathrm{3BCMU}]$ was changed from 0 to 3.97. The polymer concentration was 0.90 wt% for all z. In the system containing no phenol, G' remained almost constant below 340 K, while above 340 K G' decreased with increasing temperature as reported earlier[3]. Previously we defined the temperature at which G' became almost zero as the gel-to-sol transition temperature T_t. For P(3BCMU)/o-DCB system containing no phenol, T_t was 378 ± 2 K. However, as is seen in *Figure 1*, G' of the system containing phenol decreases gradually with temperature and hence T_t of these systems are estimated with relatively large ambiguity: T_t of P(3BCMU)/[PhOH(1.8)/o-DCB] is estimated to be 377 ± 5 K and T_t of P(3BCMU)/[PhOH(4.0)/o-DCB] is 373 ± 5 K. We recognize the tendency that T_t decreases with increasing content of phenol. Measurements on systems with z higher than 4 were difficult owing to the very low modulus.

With increasing phenol concentration, G' decreased and the gel-to-sol transition temperature defined above shifted to the lower-temperature side. The logarithm of G' at 305 K decreased linearly with the slope $\mathrm{d}\log G'/\mathrm{d}z = -0.15$.

For P(4BCMU) gels the temperature dependence of the elastic modulus was examined qualitatively by the falling-ball method. A steel ball was suspended in the gel and its height was observed by a travelling microscope as a function of temperature. Measurements of G' were not made since our apparatus could not prevent evaporation of toluene. *Figure 2* shows the height H plotted against temperature T in P(4BCMU)/[PhOH(1.8)/Tol] gel. The temperature at which the ball fell down is defined as falling temperature T_f. T_f is plotted against the weight w of the ball as shown in the insert of *Figure 2*, and T_f extrapolated to $w = 0$ is adopted as the mechanical gel-to-sol transition temperature T_t. The results are listed in *Table 1*. At $z = 10.8$, the thus-determined gel-to-sol transition temperature is 340 K, which is 9 K below T_t of the system containing no phenol.

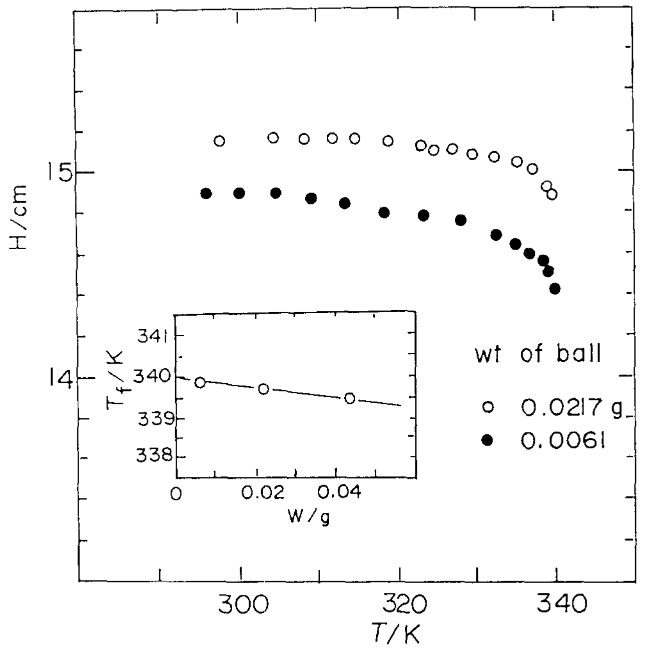

Figure 2 Temperature dependence of the height H of a ball suspended in P(4BCMU)/[PhOH(0.18)/Tol] gel

Table 1 Mechanical (T_t) and electrical (T_σ) transition temperatures and colour change temperature (T_{ch}) in P(3BCMU)/[PhOH(z)/o-DCB] and P(4BCMU)/[PhOH(z)/Tol] systems[a]

System	C (wt%)	w_P (wt%)	z	T_t (K)	T_σ (K)	T_{ch} (K)
P(3BCMU)/o-DCB	0.90	0	0	377	379	378
		0.27	1.78	–	376	376
		0.68	3.97	373	374	371
		1.56	9.12	357	356	362
		2.05	12.0	–	<298	362
P(4BCMU)/Tol	0.50	0	0	349	348	352
		0.50	5.4	–	352	347
		1.00	10.8	340	342	342
		1.50	16.2	–	332	336
		1.70	18.4	–	325	323
		1.89	20.5	–	<298	–
	1.0	0	0	348	351	–
		1.14	6.16	–	340	–
		1.74	9.40	–	331	–
		1.85	10	–	332	–
		2.02	10.9	–	<298	–
	2.0	0	0	348	351	–
		1.70	4.59	–	327	–

[a] C = polymer concentration, w_P = concentration of phenol

Conductivity

As reported in our previous papers[1–4], conduction in polydiacetylene gels is mainly due to electrons and/or holes migrating along the gel network. Thus when the gel transforms into a sol, the electronic conductivity vanishes. Since the frequency dependence of the conductivity was found to be weak above 100 Hz (ref. 2), we measured the conductivity at 1 kHz throughout the present study. *Figure 3* shows the temperature dependence of a.c. conductivy σ_{ac} at 1 kHz for P(4BCMU)/[PhOH(z)/Tol] gels. The polymer concentration was 0.50 wt% and the z value was varied from 0 to 20.5. We see that the σ_{ac} vs. T curves exhibit a maximum, and above the maximum temperature σ_{ac} decreased sharply. The temperature of maximum σ_{ac} is denoted as T_{max}. Previously we proposed a phenomenological equation to represent the temperature dependence of the electronic conductivity σ_{ac}^{el}:

$$\sigma_{ac}^{el}(T)=\sigma_0\exp(-E_a/k_BT)F(T) \qquad (1)$$

where σ_0 is a constant depending on the polymer concentration; E_a is the activation energy; and $F(T)$ is the order parameter representing the temperature dependence of the deterioration of the network structure of the gel. At a temperature far below the transition temperature, $F(T)=1$, but above T_t, $F(T)$ becomes zero. We defined[1] the temperature at which F became 0 as the electrical transition temperature T_σ. As is shown in *Table 1*, T_σ coincides with T_t.

In *Figure 3*, we see that the maximum value of σ_{ac} decreases with increasing phenol content and at the same time the gel-to-sol transition temperature shifts to the low-temperature side. Around 300 K, σ_{ac} is almost independent of the phenol content. This indicates that σ_0 and E_a in P(4BCMU) gel are almost independent of the phenol content in the range of $z<18$. Thus phenol merely lowers T_σ without affecting the conduction mechanism. When $z=20.5$, σ_{ac} is smaller than that in the gel state by a factor of 1/100. For this phenol content the system was in the sol state at room temperature and the contribution of the electronic conduction vanished.

Figure 4a shows the σ_{ac} vs. T curves for P(3BCMU)/[PhOH(z)/o-DCB] gels of 0.90 wt%. In this system the effect of phenol on σ_{ac} is qualitatively the same as for the P(4BCMU)/[PhOH(z)/Tol] system. However, the P(3BCMU) gels exhibited less systematic tendency than the P(4BCMU)/[PhOH(z)/Tol] system. As reported previously the contributions of both electronic and ionic conduction increase with increasing dielectric constant ε' of the solvent. This is because the Coulombic interaction between the carriers with positive and negative charges decreases in proportion to $1/\varepsilon'$ and hence the number of

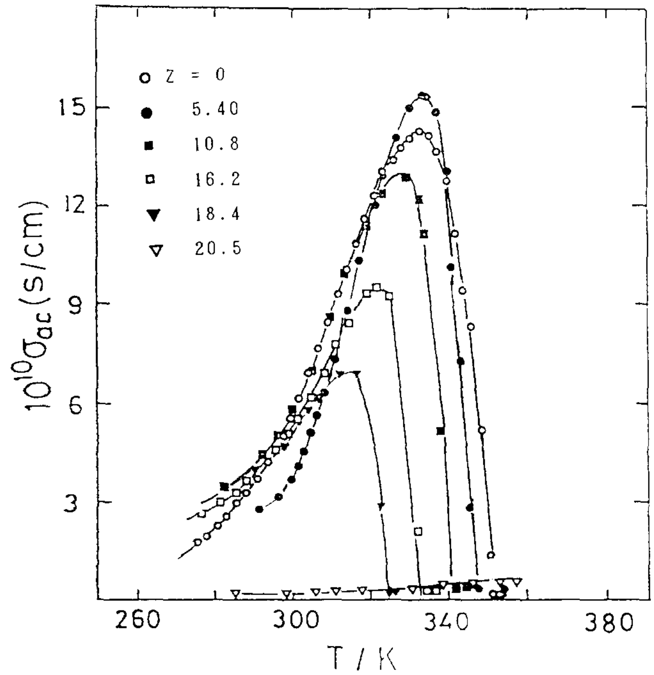

Figure 3 Temperature dependence of σ_{ac} at 1 kHz for P(4BCMU)/[PhOH(z)/Tol] system with total polymer concentration of 0.50 wt%. The molar ratio z of PhOH/4BCMU is given in the figure

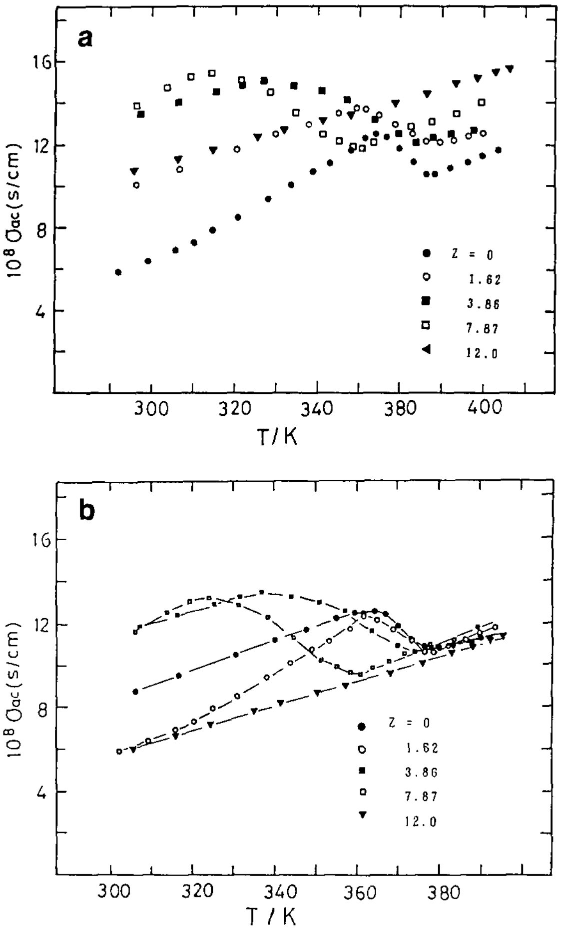

Figure 4 (a) Temperature dependence of σ_{ac} at 1 kHz for P(3BCMU)/[PhOH(z)/o-DCB]. The total polymer concentration is 0.90 wt% and z values are given in the figure. (b) The σ_{ac} curves reduced so that the conductivity in the sol state is the same as that of the curve at $z=0$

carriers dissociated from charge-transfer complexes or salts increases with increasing ε'[3,13]. Since ε' of o-DCB is 9.5 and is higher than that of toluene (2.5), o-DCB enhances dissociation of phenol into proton H^+ and phenoxy PhO^- ions. This causes more complicated conduction behaviour.

In order to see the systematic trend of σ_{ac}^{el}, we have reduced the σ_{ac} curves to an iso-ionic conduction state as follows. Since the conductivity in the sol state can be assigned to ionic conduction[3], we have shifted the σ_{ac} curves so that σ_{ac} in the sol state coincides. Here the σ_{ac} curve at $z=0$ is chosen as the reference. The result is shown in *Figure 4b*.

Comparing this figure with *Figure 3*, we see that T_σ of P(3BCMU) gels also shifts to lower temperature with increasing phenol content. In contrast to P(4BCMU) gels, σ_{ac}^{el} of P(3BCMU) gels appears to increase by addition of phenol. We cannot explain this behaviour at the present stage.

In the P(3BCMU)/o-DCB system, gelation was not observed when z exceeded 10. This critical z value is almost the same as for the P(4BCMU)/[PhOH(z)/Tol] system of polymer concentration 1 wt%. However, we note that the critical z value at which a gel transforms to a sol depends on the polymer concentration as discussed later.

In order to see the temperature dependence of $F(T)$, we extracted the contribution of the electronic conduction based on the method reported previously[3]. In *Figure 5*, the temperature dependence of F for P(3BCMU)/o-DCB gel is shown. The F vs. T curves are very similar to the $\log G'$ vs. T curves in *Figure 1*. This indicates that G' is approximately equal to $G_0 \exp[\alpha F(t)]$ where G_0 and α are constants: α equals 1.5, 1.3 and 1.2 for $z=0$, 1.75 and 4.17, respectively. Previously we demonstrated that the Young's modulus E of P(4BCMU)/Tol gels is proportional to the electric conductivity at room temperature[2]. To a good approximation G equals $E/3$. Thus G_0 is proportional to σ_{ac} at sufficiently low temperature where $F(T)=1$. Since the $F(T)$ dependences of G and σ_{ac} (equation (1)) are different, we expect that the relationship between the conductivity and the elasticity at high temperatures is more complicated than the prediction of the percolation theory[14].

U.v. absorption spectra and rod-to-coil transition

Figures 6a and *6b* show the absorption spectra at 298 K of the P(3BCMU)/[PhOH(z)/o-DCB] and P(4BCMU)/[PhOH(z)/Tol] systems, respectively. The polymer concentrations of the former and latter were 0.15 and 0.17 wt%. We see a general trend in both figures that the spectra shift to the short-wavelength side with increasing z. This change is similar to the temperature dependence of the spectra at $z=0$[1,3]. The colour changes to yellow when z exceeds 24 for P(3BCMU) and 17 for P(4BCMU) gels. Above these phenol contents, the spectra resemble well those in chloroform.

At $z=0$, P(3BCMU) and P(4BCMU) gels exhibit a sharp terminal band at 630 and 530 nm, respectively. These bands weaken with increasing z and disappear above T_t. It is expected that these bands are closely related to the conjugated structure. By addition of phenol the wavelength of these bands shifts only slightly but the intensity decreases.

In order to see the temperature dependence of these absorption bands in more detail, we measured the temperature dependence of the transmittance for P(3BCMU) and P(4BCMU) gels at 630 and 530 nm, respectively. As reported previously[1,3,4] the transmittance increased sharply at the colour change temperatures T_{ch}. As is seen in *Table 1*, T_{ch} approximately coincides with T_t and T_σ of the same gel sample.

Infra-red spectra and hydrogen bonding

Infra-red spectra of the P(3BCMU)/[PhOH(z)/o-DCB] system are shown in *Figure 7*, where the absorptions due to the solvent o-DCB were subtracted as is usually done

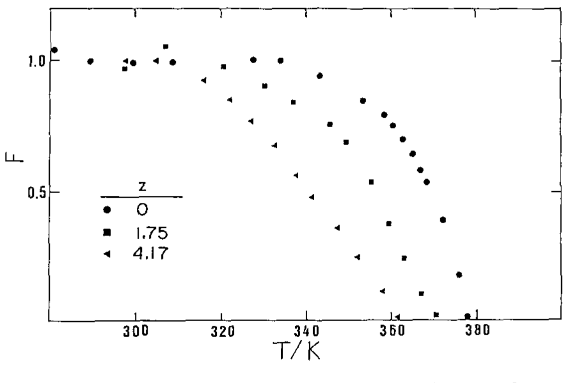

Figure 5 Order parameter F defined by equation (1) for σ_{ac} of P(3BCMU)/[PhOH(z)/o-DCB] and varying z. Polymer concentration is 0.90 wt%

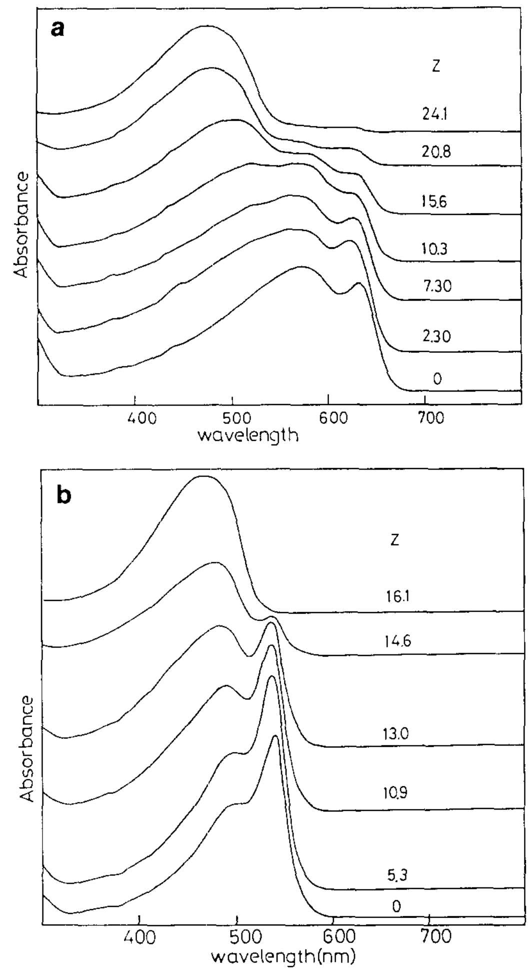

Figure 6 U.v. and visible spectra at 25°C of (a) P(3BCMU)/[PhOH(z)/*o*-DCB] and (b) P(4BCMU)/[PhOH(z)/Tol] systems. Polymer concentrations are 0.15 and 0.17 wt% for (a) and (b), respectively; and the z values are given in the figure

in *FT*i.r. measurements. We examined the effect of phenol on four bands, namely the stretching of the N–H bond of the urethane group (μ_1), the C=O stretching of the ester group (μ_2), the C=O stretching of the urethane group (μ_3), and the band of the mixed N–H bending and the C–N stretching modes (μ_4)[15].

When the phenol content $z = 0$, the widths of the bands μ_1 and μ_4 for the vibration of the N–H group are relatively narrow. This indicates that all of the N–H groups are in an ordered state. With increasing z, the widths of these bands increase suddenly in the range of $1.78 < z < 3.97$, indicating that the N–H groups are in various force fields. This indicates that the tape-like ordered structure (see *Figure 8*) formed by the intramolecular hydrogen bonding of the N–H and C=O bonds is cleaved by phenol. We also see that the widths of the bands μ_2 and μ_4 also broaden in the same way as μ_1. On the other hand the band μ_3 broadens slightly with increasing z.

We see that the band μ_1 at $z = 3.97$ and 9.12 is composed of two peaks as indicated by the broken curves. The peak at 3320 cm^{-1} corresponds to the ordered structure of P(3BCMU) and that at 3410 cm^{-1} to the disordered structure. We also see a new band in the range of wavenumbers between μ_2 and μ_3 with increasing z. This new band may also correspond to a band in the disordered state. When z exceeds 10, the system is in the sol state at room temperature, as mentioned above. In this state the band μ_1 becomes a single peak corresponding to the disordered structure. For the bands μ_2 and μ_4 a similar trend can be seen.

The changes in the spectra due to phenol for the P(4BCMU)/[PhOH(z)/Tol] system are essentially the same as those for the P(3BCMU) system (*Figure 8*). The equilibrium of hydrogen bonding between the urethane group and phenol may be given by either of the following formulae:

$$>\!C{=}O\cdots H{-}N\!< + 2PhOH \rightleftharpoons\; >\!C{=}O\cdots HOPh + PhO^{-}\cdots H_2N^{+}\!<$$

$$>\!C{=}O\cdots H{-}N\!< + 2PhOH \rightleftharpoons\; >\!C{=}O\cdots HOPh + PhHO\cdots HN\!<$$

where dotted lines represent the hydrogen bonds. We found that the transition temperature decreases when organic acids such as dichloroacetic acid, acetic acid and formic acid are added, while alcohols do not cause the transition. These facts suggest that the contribution of the upper formula is dominant.

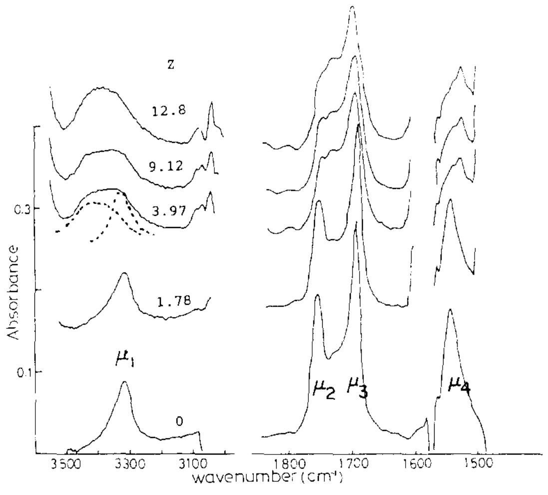

Figure 7 Infra-red difference spectra at 25°C of the P(3BCMU) molecules in the P(3BCMU)/[PhOH(z)/*o*-DCB] system in the ranges of wavenumber of 3100–3500 cm^{-1} and 1500–1800 cm^{-1}. Total polymer concentration is 0.90 wt%. Four bands are denoted as μ_1, μ_2, μ_3 and μ_4 as shown

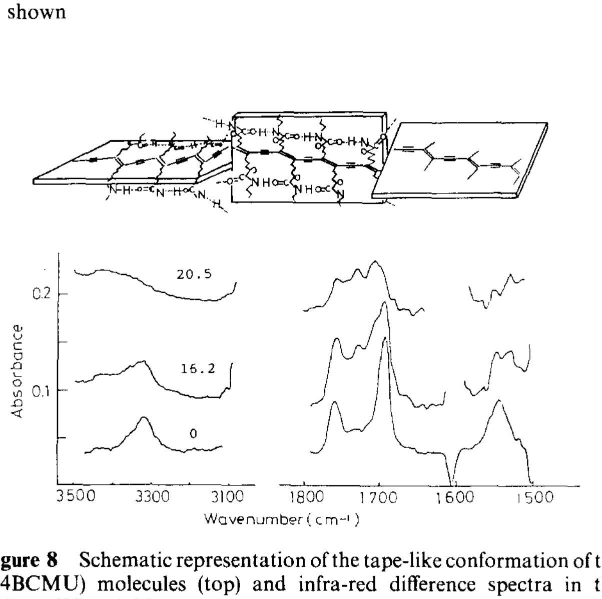

Figure 8 Schematic representation of the tape-like conformation of the P(4BCMU) molecules (top) and infra-red difference spectra in the P(4BCMU)/[PhOH(z)/Tol] system (bottom)

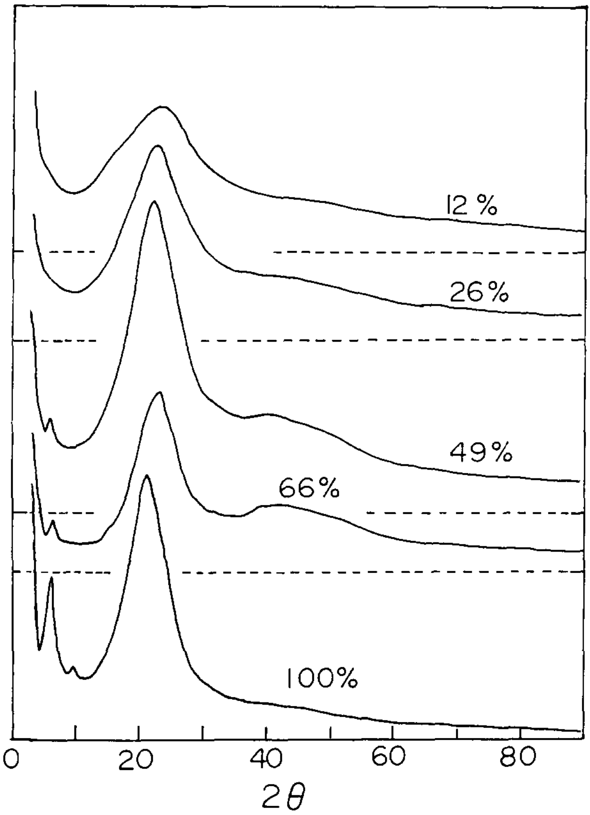

Figure 9 X-ray diffractograms of concentrated P(3BCMU) gels with concentrations 12, 26, 49, 66, and 100 wt%, respectively. Broken lines A, B, C and D indicate the base lines for 12, 26, 49 and 66% gels, respectively

Crystallinity of P(3BCMU)/o-DCB gel

As mentioned in the introductory section, one of the possible origins of the crosslinks of P(3BCMU) and P(4BCMU) gels is microcrystallites of the polydiacetylene molecules. In this section we examine the crystallinity of P(3BCMU)/*o*-DCB gel at $z=0$.

Since the polymer concentration of the gels used in this study was less than 2 wt%, it was difficult to detect scattering from the P(3BCMU) molecules, since scattering from the solvent molecules is overwhelmingly strong. Thus the gel samples were concentrated at room temperature under vacuum. *Figure 9* shows the X-ray diffractograms of P(3BCMU) gels thus concentrated. A small sharp peak is seen around $2\theta=6°$ for gels with C above 49 wt%. This peak is ascribed to the crystalline part of P(3BCMU)[1]. From these X-ray diagrams, the fraction χ of the crystalline part in the total polymer was very roughly estimated:

$$\chi=w_c/C \qquad (2)$$

where w_c is the weight fraction of the crystalline part in a gel. Our purpose here is to estimate χ roughly at C less than 2 wt% by extrapolating the C dependence of χ determined at high concentrations.

The total intensity A of scattered X-rays from a gel is the sum of A_c, A_a and A_{solv} where subscripts c, a and solv indicate crystalline P(3BCMU), amorphous P(3BCMU) and *o*-DCB, respectively. As is seen in *Figure 9*, the crystalline peaks other than that at $2\theta=6°$ are not clear. Therefore we assumed that

$$A_c=KA_c(6°) \qquad (3)$$

where $A_c(6°)$ is the intensity of the peak at $2\theta=6°$ and K is a constant. Then A and A_c were calculated by integrating the observed intensity I:

$$A=\int_0^\infty s^2 I\,\mathrm{d}s \qquad (4)$$

where s is the scattering vector, equal to $4\pi\sin\theta/\lambda$. Similarly, $A_c(6°)$ was determined by integrating the intensity around the peak. In the determination of A, the integration was performed from 0 to 40°. We did not correct for the contribution of incoherent scattering and the polarization factor[16].

In order to calculate χ given by equation (2), it is necessary to estimate the contribution of the solvent A_{solv} in total A. We assumed that the total intensities from P(3BCMU) and *o*-DCB are proportional to the sum B of the square of the atomic scattering factor f. We define B_{3BCMU} and B_{solv} by:

$$B_{3BCMU}=N_{3BCMU}\sum_j n_j\int_0^\infty s^2 f_j^2\,\mathrm{d}s \qquad (5)$$

where N_{3BCMU} is the number of monomeric units of P(3BCMU) in unit volume; j is a label for atoms of different kinds in the monomeric unit; and N_j is the number of j atoms. B_{solv} was calculated in the same way.

Then the value of A_c+A_a is given by:

$$A_c+A_a=A\frac{B_{3BCMU}}{B_{3BCMU}+B_{solv}} \qquad (6)$$

Finally we obtain:

$$\chi=\frac{KA_c(6°)}{A_c+A_a} \qquad (7)$$

Based on equation (7) we determined χ/K from A and $A_c(6°)$. Se estimated χ of bulk P(3BCMU) to be 20% from the heat of fusion[17]. Using this value, we calculated K and then χ for the 49 and 66% gels. *Figure 10* shows the C dependence of χ. If the χ vs. C curve is extrapolated to lower concentration, χ vanishes below 30% concentration. This indicates that there is no crystalline region in gels with concentration less

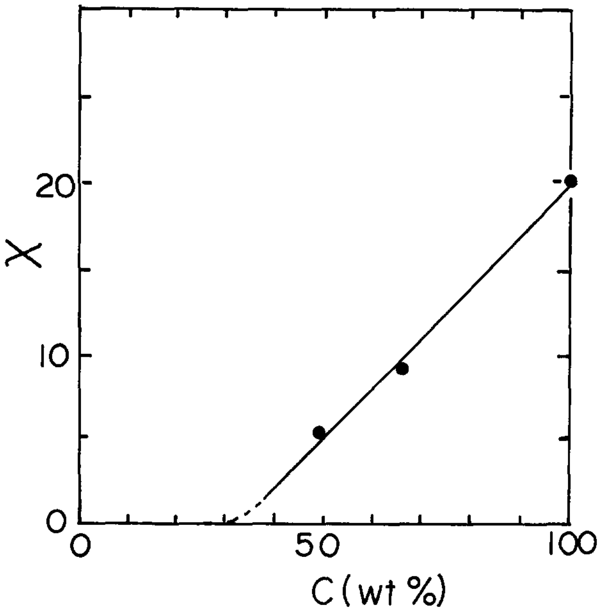

Figure 10 Concentration dependence of crystallinity of P(3BCMU) gels at room temperature

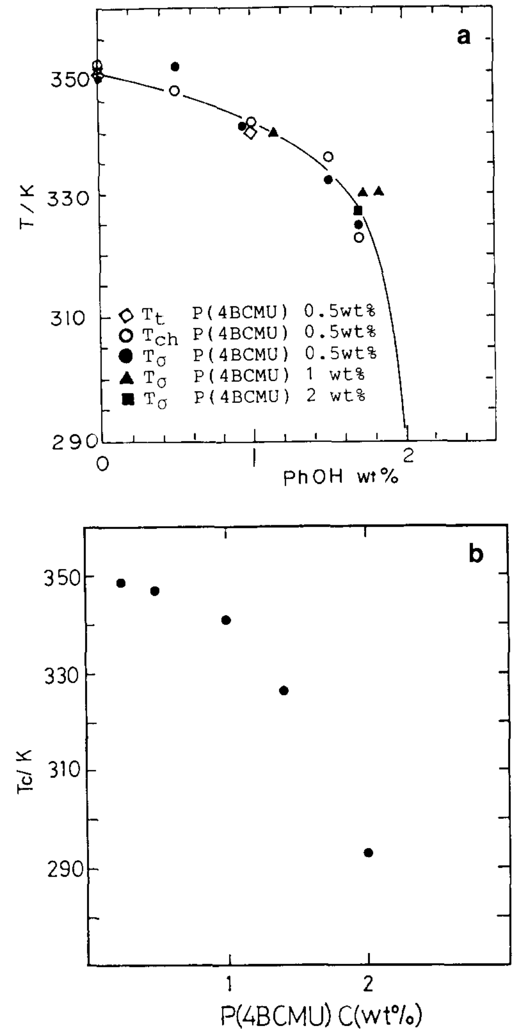

Figure 11 (a) Dependence of T_t, T_σ and T_{ch} in P(4BCMU)/Tol gels on concentration of phenol. (b) Dependence of T_{ch} on P(4BCMU) concentration at constant $z=5.40$

than 2 wt%. We may rule out the possibility of microcrystallites as the crosslinkages of the P(3BCMU) gel network.

Phase diagram and gel structure

Figure 11a shows the dependence of T_t, T_σ and T_{ch} of P(4BCMU) gels on the PhOH concentration. It is seen that T_t, T_σ and T_{ch} fall on a universal curve within the experimental error. Thus the transition temperature is determined by the weight fraction of PhOH rather than z in the system and is independent of polymer concentration. *Figure 11b* shows the dependence of T_{ch} on P(4BCMU) concentration at constant z, i.e. $z=6.4$. As is seen in this figure, T_{ch} decreases with increasing P(4BCMU) concentration. Based on these data, we constructed the phase diagram as shown in *Figure 12*, where we also plotted T_{max} observed in the conduction measurements.

Finally we discuss the structure of polydiacetylene gels. We speculate that the planar tape-like conformation of the chains is disrupted partially at 'defects' where the intramolecular hydrogen bonds are cleaved and the 'tape' is twisted. Such defects have free C=O and NH groups and result in intermolecular hydrogen bonds working as crosslinks. By adding PhOH to the systems, the intermolecular hydrogen bonds are destabilized as well as the intramolecular hydrogen bonds.

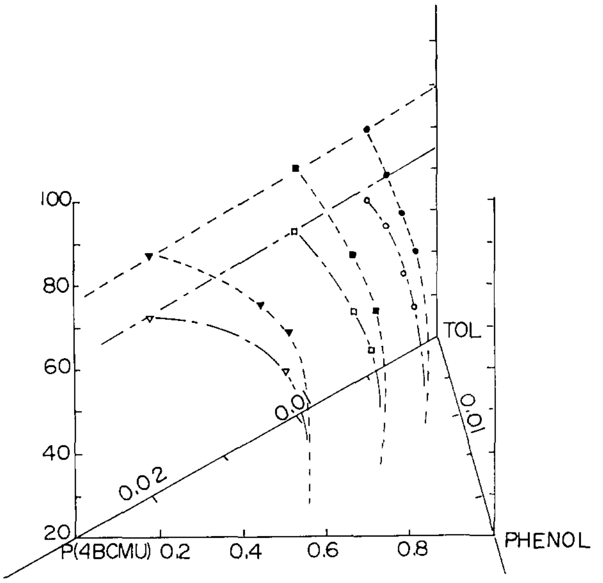

Figure 12 Phase diagram representing gel–sol equilibria for P(4BCMU)/[PhOH(z)/Tol] system

Recently Kobayashi *et al.*[18,19] reported the conformation of syndiotactic and isotactic polystyrene gels. They found by *FT*i.r. measurements that the network strands in the gel state have a highly ordered conformation. This suggests that the occurrence of the ordered conformation in gels does not inevitably require the effect of hydrogen bonds. It is expected that the ordered conformation is realized by various interactions acting cooperatively. However, our results indicate that in the present systems hydrogen bonding is the key factor governing the gel-to-sol transition of P(3BCMU) and P(4BCMU).

CONCLUSIONS

The gel-to-sol transition temperatures of P(3BCMU)/*o*-DCB and P(4BCMU)/Tol gels containing a trace amount of PhOH were determined by mechanical means, electrical conduction and transmittance of visible light. The transition temperature decreased with increasing PhOH concentration. When PhOH concentration exceeded 2% the systems turned into a sol at room temperature.

Infra-red spectra indicate that the hydrogen bonds between the C=O and NH groups of the urethane group are cleaved when a sufficient amount of PhOH is added.

From the data of X-ray scattering for concentrated P(3BCMU) gels, the crystallinity of gels vanishes below 30% concentration. The crosslinkages of the P(3BCMU) gel network are not due to microcrystallites.

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