

## Urethane Substituted Polydiacetylene: Synthesis and Characterization of Poly[4,6-decadiyn-1,10-diol-bis(*n*-butoxy-carbonyl-methyl-urethane)]

Kazunori SE,\* Hiroshi OHNUMA, and Tadao KOTAKA\*\*

*Department of Macromolecular Science, Faculty of Science,  
Osaka University, Toyonaka, Osaka 560, Japan*

(Received July 12, 1982)

**ABSTRACT:** A diacetylene having 3-methyl-*n*-butoxy-carbonylmethyl-urethane (3BCMU) as a substituent was synthesized and exposed to  $^{60}\text{Co}$ - $\gamma$  ray at various doses to obtain a polymer, poly3BCMU. The polymers obtained at low doses were of fairly high molecular weight and narrow distribution and those at high doses were of relatively low molecular weight and broad distribution. Changes in color of high and low-dose samples in  $\text{CHCl}_3$  and *n*-hexane were compared. The critical solvent compositions ( $\text{CHCl}_3$  content) at which yellow-to-blue or blue-to-yellow changes occurred were independent of polymer concentration but varied with molecular weight and temperature. Visible absorption spectra and Raman spectra were compared for yellow  $\text{CHCl}_3$  and blue  $\text{CHCl}_3$ /*n*-hexane solutions of a high dose sample. Non-Newtonian intrinsic viscosities of these solutions were also compared. The results all suggested that poly3BCMU assumes a more extended, planar conformation in a poor solvent  $\text{CHCl}_3$ /*n*-hexane than in a good solvent  $\text{CHCl}_3$ , in contrast to flexible polymers in these solvents.

**KEY WORDS** Diacetylene Derivative / Solid State Polymerization / Polydiacetylene / Conductive Polymer / Color Change / Conformational Transition / Raman Spectrum / Dilute Solution Characteristics / Intrinsic Viscosity /

Recently, several polymeric materials having electric conductivity or semiconductivity were discovered.<sup>1</sup> The intriguing features of these polymeric conductors are fairly high conductivity and anisotropy of the conductivity. Therefore, these materials may be called linear-chain or one-dimensional conductors.<sup>2</sup> A well-known example is polyacetylene doped with halogens or  $\text{AsF}_5$ .<sup>3-8</sup> However, because of the insolubility and infusibility, it was difficult to characterize this polymer in regard to molecular weight and its distribution. Shirakawa *et al.*<sup>9</sup> attempted to hydrogenize a polyacetylene film to polyethylene and characterize the product by the dilute solution technique. The insolubility and infusibility of polyacetylene also hampers preparation of solvent-cast films or oriented fibrous specimens to be used for measuring

the anisotropic conductivity. All these are examples of the difficulties encountered in elucidating the nature and mechanism of electric conductivity of linear-chain conductors.

Diacetylenes  $\text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$ , where R is a substituent group, are a unique class of monomers which can be polymerized in the solid state by high energy radiation or simply by thermal annealing.<sup>10-12</sup> Polydiacetylenes produced possess conjugated main-chains which exhibit electric and photoconductive properties similar to those of polyacetylene. The major difference between polyacetylenes and polydiacetylenes lies in the backbone structure, the former being the conjugated ethene  $(-\text{CH}=\text{CH})_n$ , and the latter being a resonance admixture of acetylenic  $(-\text{CR}-\text{C}\equiv\text{C}-\text{CR})_n$  and butatriene  $(-\text{CR}=\text{C}=\text{C}=\text{CR})_n$ .<sup>10</sup> Although the poly-

\* Present address: *Department of Materials Engineering, The Technological University of Nagaoka, Nagaoka, Niigata 949-54, Japan.*

\*\* To whom correspondence should be addressed.

merization of a large number of diacetylenes has been reported, especially by Wegner<sup>10</sup> and by Baughman,<sup>11,12</sup> most of the products were insoluble and infusible, and hence not feasible for molecular characterization.

Recently, Patel *et al.*<sup>13,14</sup> succeeded in synthesizing several soluble polydiacetylenes, in which  $R = (\text{CH}_2)_n\text{OCONHCH}_2\text{-COO}(\text{CH}_2)_m\text{CH}_3$  with  $n = 1-4$  and  $m = 1$  and  $3$ . They referred to this new class of diacetylenes as ACMU (standing for alkoxy carbonyl methylurethane; the side chain) and the polymer as polynACMU.<sup>15</sup> As a first step in studying the physical properties of linear-chain conductors, we synthesized 4,6-decadiyn-1,10-diol bis(butoxy carbonyl methyl urethane), and nACMU in which  $n = 3$  and  $A = \text{butoxy}$  ( $m = 3$ ) and hence may be abbreviated as 3BCMU, polymerized it with <sup>60</sup>Co- $\gamma$  irradiation at various doses, and subjected the products poly3BCMU to molecular characterization and dilute solution studies.<sup>16-18</sup>

Since the conjugated main-chains of polydiacetylenes absorb visible light, poly3BCMU exhibits a unique color change both in solutions and in the solid state, following the change in the main-chain conformation.<sup>18,19-22</sup> This phenomenon as well as the dilute solution characteristics of poly3BCMU were studied in some detail by Patel *et al.*<sup>15,18-22</sup> In order to establish the molecular characteristics-electric property relationship of this model linear-chain conductor, we prepared several samples of poly3BCMU with different molecular weight and distribution, and investigated their dilute solution behavior including spectroscopic behavior. Our results were not always in agreement with those of Patel *et al.*<sup>13-15,19-22</sup> This article reports these results along with some additional findings on poly3BCMU.

## EXPERIMENTAL

### Synthesis of 3BCMU Monomer

The 3BCMU monomer was prepared by the following four steps. (i) Tetrahydrofurfuryl alcohol (THF-OH) was chlorinated with thionyl chloride in pyridine at 0°C to obtain tetrahydrofurfuryl chloride (THF-Cl)<sup>23</sup>: bp was 57°C/25 torr and the yield was 70%. (ii) THF-Cl was allowed to react with sodium amide in anhydrous ammonia at -34°C, and ammonium chloride was added to the mixture. After removing the ammonia, the residue

was extracted with ether to recover 4-pentyn-1-ol<sup>23,24</sup>: bp was 66°C/20 torr and the yield was 74%. (iii) 4-pentyn-1-ol ( $\text{HO}-(\text{CH}_2)_3\equiv\text{CH}$ ) was subjected to oxidative coupling by Hay's method<sup>25</sup> to obtain 4,6-decadiyn-1,10-diol: mp was 46°C and the yield was 79%. (iv) The diol was allowed to react at 23°C with *n*-butylisocyanate acetate using triethylamine and dibutyl-tin-di-2-ethylhexanoate as the catalyst in purified THF to obtain 3BCMU monomers: mp was 62°C and the yield was 100%. All the intermediates and the 3BCMU monomer were checked for purity by infrared spectroscopy, NMR, DSC, and elemental analysis.

### Solid State Polymerization

The powder-form monomers obtained were sealed in several ampules after degassing under high vacuum ( $10^{-5}$  torr). The monomer in each ampule was exposed to <sup>60</sup>Co  $\gamma$  irradiation of varying doses from 0.09 to 45 Mrad at room temperature, and powder-form mixed monomer-poly3BCMU crystallites were obtained. The unreacted monomers were removed by extracting with acetone. The polymer was dissolved in  $\text{CHCl}_3$  and precipitated in excess hexane. Finally, the powder-form polymer was recovered by drying under high vacuum.

### Methods

All the polymer samples were tested on a gel permeation chromatograph (GPC: Model 801A, Toyo Soda Mfg. Co.) to estimate their average molecular weights and molecular weight distributions. The carrier solvent was  $\text{CHCl}_3$ . Narrow distribution polystyrenes (TSK polystyrenes, Toyo Soda Mfg. Co.) were used as elution standards. The 45 Mrad sample was examined by low-angle laser-light scattering (LALLS), Raman scattering, and viscometry. The LALLS measurements were made with an LALLS photometer (Model LS-8, Toyo Soda Mfg. Co.) at 633 nm on yellow colored  $\text{CHCl}_3$  solutions at 25°C. Refractive index increments  $dn/dc$  of the same solutions at 25°C were determined by a differential refractometer (Model RF-600, G. N. Wood Mfg. Co.) with a 633 nm helium-neon laser as the light source.

Raman spectra were obtained by a JASCO R-500 double monochromator, with the 514.5 nm line from an argon-ion laser as the source and light scattered at right angles to the direction of the

plane-polarized incident beam. Absorption spectra of the 0.09 and 45 Mrad samples in  $\text{CHCl}_3/n$ -hexane mixtures were obtained by a JASCO spectrophotometer (Model UVDEC-5A, Nihon Bunko Co.). Interest was directed to the spectral changes accompanying the addition of  $n$ -hexane to  $\text{CHCl}_3$  solutions and also the addition of  $\text{CHCl}_3$  to  $\text{CHCl}_3/n$ -hexane mixtures.

Intrinsic viscosities as a function of shear rate were determined for the 45 Mrad sample in  $\text{CHCl}_3$  and  $\text{CHCl}_3/n$ -hexane mixtures at  $30^\circ\text{C}$ . Three conventional Ubbelohde viscometers of different bore sizes and a four-bulb spiral capillary viscometer were used.

## RESULTS AND DISCUSSION

### Molecular Characterization

Polymer conversions at various doses were calculated from the weight of the polymerization mixture and that of the residual polymer found after careful extraction of the monomers with acetone. The conversions were also checked by visible absorption spectroscopy and by differential scanning calorimetry (DSC). The results obtained by these methods agreed with one another reasonably well. Figure 1 shows the plot of polymer conversion vs. total dose or exposure time. The curve consists of two steps. The first step terminates at about 40% conversion or at about 1 Mrad dose, and the second step at about 60% conversion or above 45 Mrad dose.

Each of the polymerization mixtures was dissolved in  $\text{CHCl}_3$  for GPC tests. The chromatogram showed two major peaks corresponding to

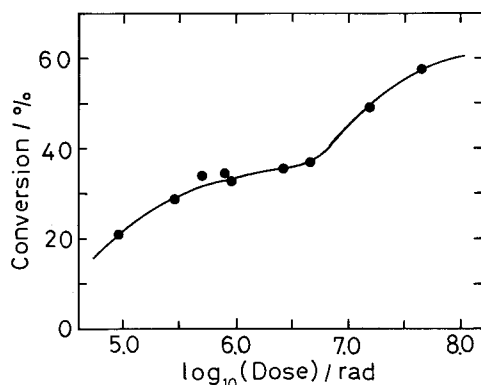


Figure 1. Polymer conversion as a function of  $^{60}\text{Co}$   $\gamma$ -ray dose for 3BCMU.

the unreacted monomer and polymer. Figure 2 shows the peaks for the polymers obtained at various doses. The polymers obtained below a 1 Mrad dose or below 40% conversion showed fairly sharp chromatograms, and those obtained above these limits showed broad chromatograms tailing at low molecular weight. By means of the polystyrene elution standards, the PS-reduced weight-average molecular weight  $M_w$  and polydispersity index (the ratio of the number to weight-average molecular weight  $M_w/M_n$ ) for all samples were determined. The results for GPC measurements are summarized in Table I.

The 45 Mrad sample was subjected to  $M_w$  determination by LALLS. The 633 nm refractive index increment of its  $\text{CHCl}_3$  solution at  $25^\circ\text{C}$  was  $0.168 \text{ cm}^3 \text{ g}^{-1}$ . With this value of  $dn/dc$ ,  $M_w$  and  $A_2$  (second virial coefficient) were found to be

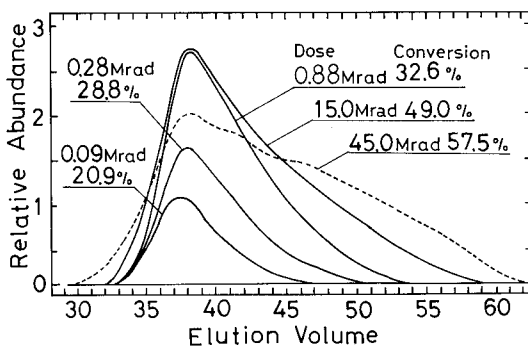


Figure 2. GPC chromatograms of poly3BCMU specimens obtained at different doses.

Table I. Polymer conversions and molecular characteristics of poly3BCMU samples obtained at various doses

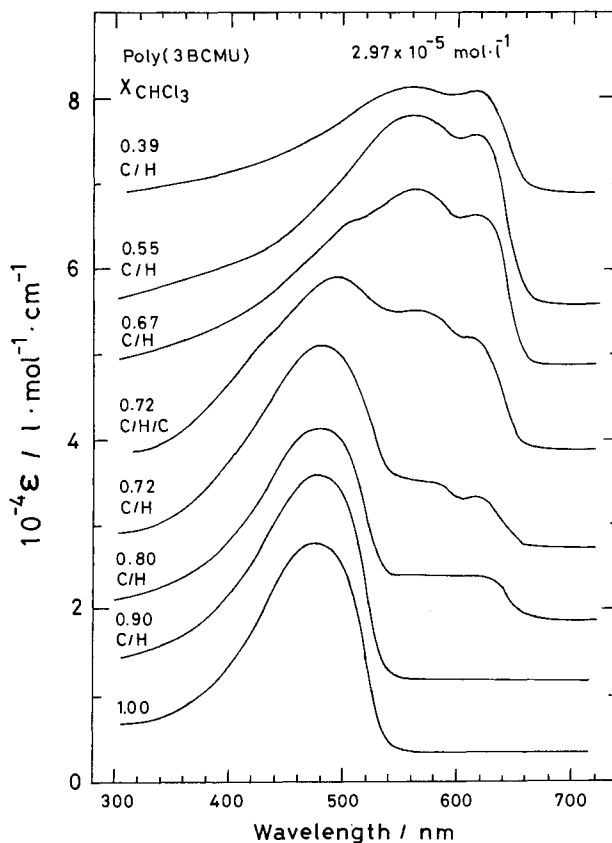
Dose/Mrad	Polymer conversion %	PS-reduced molecular weights		
		$10^{-6}M_n$	$10^{-6}M_w$	$M_w/M_n$
0.09	20.9	1.33	3.90	2.93
0.28	28.8	0.810	2.46	3.04
0.50	34.1	0.734	2.49	3.39
0.80	34.5	0.509	2.57	5.06
0.88	32.6	0.648	2.32	3.59
2.60	35.6	0.465	1.99	4.28
4.50	36.8	0.466	2.25	4.82
15.0	49.0	0.179	2.31	12.8
45.0	57.5	0.0802	3.18	39.7

$10.7 \times 10^6$  and  $0.34 \times 10^{-4}$  mol cm<sup>3</sup> g<sup>-2</sup>, respectively. This value of  $M_w$  was about 3.4 times as large as the PS reduced GPC value. If the difference in monomer molecular weight per unit contour length between PS and poly3BCMU is taken into account, the GPC value may be multiplied by 2.51. However, the corrected GPC value is still about 35% smaller than the LALLS value. This difference may be attributed to the permeability limit and the imperfect resolving power of our GPC columns for high molecular weight components.

Patel *et al.*<sup>14,15</sup> reported that the conversion in synthesizing poly3BCMU increased steadily with increasing radiation dose and that the polymers at various doses had essentially similar average molecular weights and distributions. The conversions obtained by Patel *et al.* are about half or less than our values at low doses, but nearly the same as ours

at high doses. Probably in Patel's experiment, the monomer was exposed to  $\gamma$ -ray in the air, in contrast to our experiment in which the monomer was vacuum-sealed.

In the early stage of the polymerization of 3BCMU, the reaction proceeds *via* 1,4 addition in the reactive monomer crystalline phase, yielding high-molecular weight and narrow distribution components. In the later stage, however, the monomer remaining in the mixed monomer-polymer crystalline phase undergoes polymerization. Some degradation of polymer chains also may take place by prolonged exposure to high energy radiation. These two effects seem to be responsible for the production of low-molecular weight components in the later stage of the reaction.



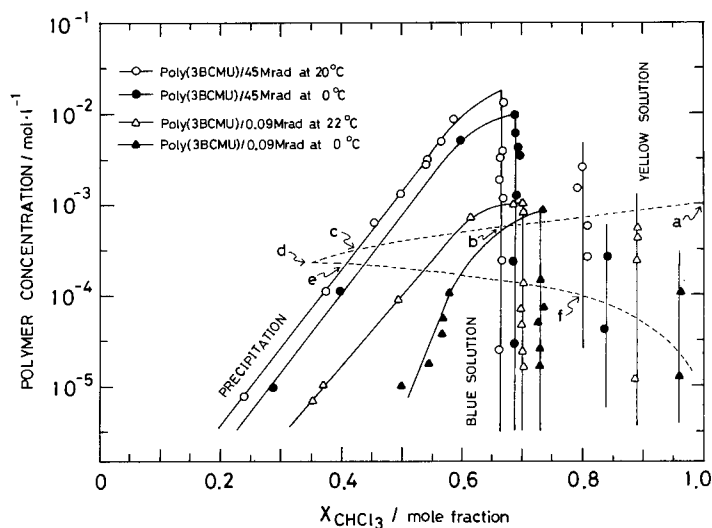
**Figure 3.** Visible absorption spectra of poly3BCMU in mixtures of CHCl<sub>3</sub> and *n*-hexane at 16°C. The spectra are progressively displaced by arbitrary amounts. The polymer concentration is  $2.97 \times 10^{-5}$  mol l<sup>-1</sup>. C/H/C implies that the solution in CHCl<sub>3</sub>/*n*-hexane is back titrated with CHCl<sub>3</sub> to  $X_{\text{CHCl}_3} = 0.72$ .

*Color Change in the Solution*

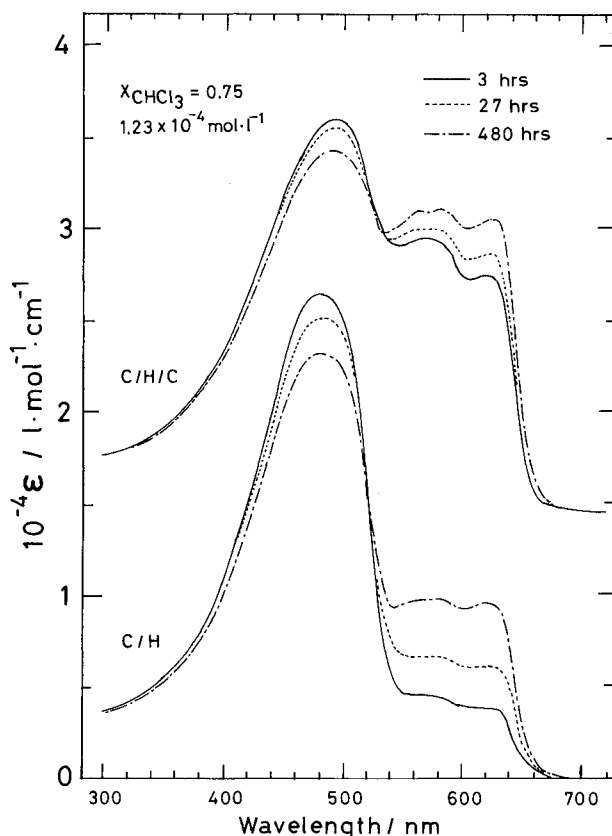
Patel *et al.*<sup>19,20</sup> reported that poly3BCMU dissolved in a good solvent exhibits a yellow color, while that in a poor solvent exhibits a blue color. In a non-solvent, the polymer sediments as a dark blue precipitate. The transitions between these different colors are fairly sharp and reversible. By titrating a  $\text{CHCl}_3$  solution of poly3-BCMU with *n*-hexane, Patel *et al.*<sup>19</sup> established a phase diagram showing these transitions as a function of polymer concentration  $c$  and solvent composition  $X$ . Visible absorption spectra of the 0.09 and 45 Mrad samples were determined by forward and back titrating them with  $\text{CHCl}_3$  and *n*-hexane. Figure 3 shows the typical spectra obtained. The results gave similar phase diagrams at  $0^\circ\text{C}$  and about  $20^\circ\text{C}$ . The general features and the change with  $X$  of the spectra were similar for the two samples, except for the critical solvent compositions at which the transitions take place. Figure 4 shows the phase diagrams obtained and their features as follows: (i) The solvent compositions  $X_c$  and  $X_c'$  (in the mole fraction of  $\text{CHCl}_3$ ), at which the yellow-to-blue and the blue-to-yellow transitions take place, respectively, do not coincide, and always  $X_c < X_c'$ . (ii) Neither  $X_c$  nor

$X_c'$  depends on the polymer concentration. However, (iii) the transition from precipitation to dissolution takes place reversibly at the same composition  $X_p$ , which depends on the polymer concentration. The dashed line in Figure 4 indicates the locus of the transition compositions a, b,  $\cdots$ , d,  $\cdots$ , f determined from the titration of the 45 Mrad sample at  $20^\circ\text{C}$ . Beside these features already pointed out by Patel *et al.*,<sup>19</sup> the following results were also obtained. (iv) By lowering the temperature from  $20^\circ\text{C}$  or  $22^\circ\text{C}$  to  $0^\circ\text{C}$ , the phase boundaries shifted to the good solvent side. Particularly, the shift of  $X_c'$  for the 0.09 Mrad sample was substantial. Comparison of the phase diagrams of the two samples shows that (v) the diagram of the 0.09 Mrad sample is located more on the better solvent side than that of the 45 Mrad sample, but that the difference between the  $X_c$  of the two samples is not as large as either that between their  $X_c'$  or that between their  $X_p$ .

The spectra of the solutions with concentrations between  $X_c$  and  $X_c'$  changed gradually with the period of annealing. Figure 5 shows that the spectrum of a visibly yellow solution of the 45 Mrad sample obtained by adding hexane to the  $\text{CHCl}_3$  solution to  $X=0.75$  underwent a blue shift, al-



**Figure 4.** Phase diagrams for poly3BCMU obtained at 45 Mrad dose (circles) and 0.09 Mrad dose (triangles) in  $\text{CHCl}_3$ /*n*-hexane mixture. The closed and open marks (circles and triangles) represent the results at  $20^\circ\text{C}$  and  $0^\circ\text{C}$ , respectively. The vertical lines in the range  $X_{\text{CHCl}_3} = 0.65\text{--}0.75$  and the slants are the results from titration of *n*-hexane. The vertical lines in the range  $X_{\text{CHCl}_3} = 0.80\text{--}0.95$  are the results from back titration of blue solutions with  $\text{CHCl}_3$ . The dashed curve represents one of the routes of forward and backward titrations.



**Figure 5.** Changes in spectra with time for two solutions of poly3BCMU with  $X_{\text{CHCl}_3} = 0.75$ : The C/H coded solutions were obtained by titrating the  $\text{CHCl}_3$  solution with *n*-hexane, and the C/H/C coded solutions by back titrating the  $\text{CHCl}_3$ /*n*-hexane solution with  $\text{CHCl}_3$ .

though the solution remained visibly yellow after 480 h annealing. The spectrum of a visibly blue solution of the same sample of  $X = 0.75$  ( $X_c' = 0.80$ ) obtained by back titrating the mixture of  $X = 0.66$  with  $\text{CHCl}_3$  also showed a blue shift. These blue shifts suggest that at  $X = 0.75$ , the blue colored solution is more stable than the yellow colored one. However, the change was so slow as to be impossible to estimate the time required for these solutions to reach equilibrium. Actually, it was beyond our means of estimation whether or not such an equilibrium exists.

From the Fourier transform infrared spectra, Patel *et al.*<sup>19-22</sup> suggest that the color changes arise from the planar-nonplanar conformational transition of the polynACMU backbone and that the planar, fully conjugated conformation is stabilized by intramolecular hydrogen bonding of urethane

**Table II.** Critical solvent compositions for the color transition in poly3BCMU solutions<sup>a</sup>

Code	Temp	$X_c$	$X_c'$
	°C		
45 Mrad	20	0.66	0.80
45 Mrad	0	0.68	0.84
0.09 Mrad	22	0.70	0.89
0.09 Mrad	0	0.73	0.96

<sup>a</sup>  $X_c$  and  $X_c'$ , the mole fractions of  $\text{CHCl}_3$  at the color transition points, were determined by titration of a  $\text{CHCl}_3$  solutions with *n*-hexane and titration of a blue solution with  $\text{CHCl}_3$ , respectively.

moieties on the adjacent substituent groups. The disruption of the planarity or the shortening of the conjugation length  $l_c$  of the backbone is com-

compensated for by an increase in the entropy of the substituent groups due to breaking of the hydrogen bonds in the  $\text{CHCl}_3$  solution. On the other hand, a decrease in the entropy of the side groups enhances the planarity of the backbone, giving rise to an increase in the critical solvent compositions  $X_c$  and  $X_c'$  (*i.e.*, shift to the  $\text{CHCl}_3$  rich side). The values  $X_c$  and  $X_c'$  are summarized in Table II, and indicate that as the temperature is lowered, *i.e.*, the contribution of entropy is decreased and both  $X_c$  and  $X_c'$  increase, especially the latter substantially.

On the basis of a modified free electron theory of Kuhn,<sup>26</sup> Patel<sup>19,20</sup> calculated the effective con-

jugation length  $l_c$  from the wavelength of the visible absorption peak. For the yellow solution with an absorption peak at 475 nm,  $l_c$  was estimated to be 6 to 7 repeat units or 12 to 14 conjugated multiple bonds. For blue solutions,  $l_c$  exceeded 30 repeat units.

#### Raman Spectra

Raman spectra were determined on  $0.297 \mu\text{mol dm}^{-3}$  solutions. Figure 6 shows typical results. The spectrum of the yellow solution excited by 514.5 nm radiation exhibits two strong bands due to the resonance Raman effect.<sup>27</sup> According to Baughman

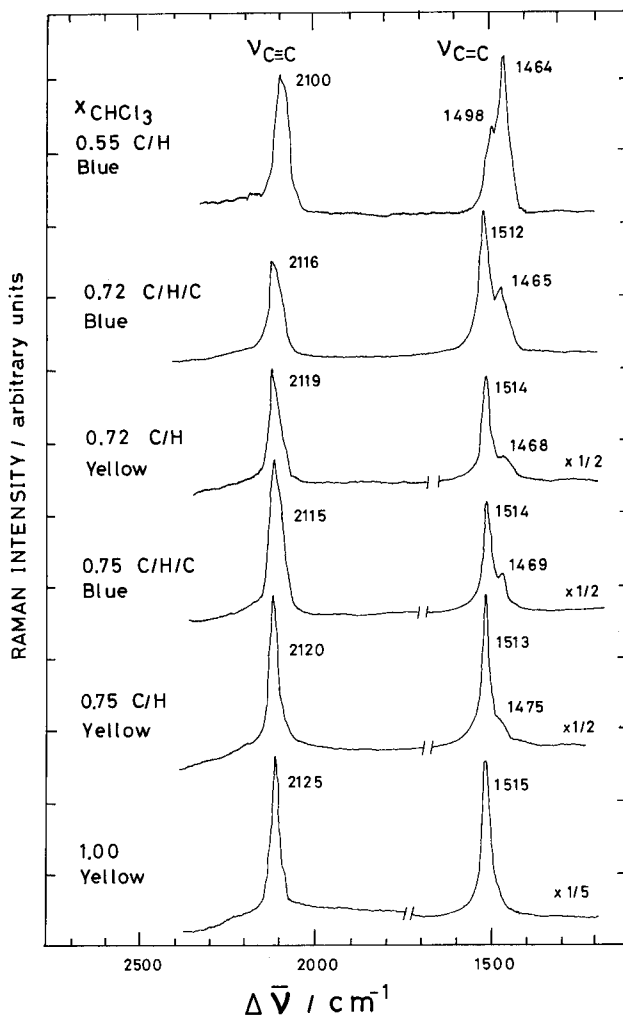


Figure 6. Raman spectra for  $0.297 \mu\text{mol dm}^{-3}$  solutions of poly3BCMU (45 Mrad dose) at  $25^\circ\text{C}$  in  $\text{CHCl}_3/n$ -hexane mixture.

*et al.*,<sup>28,29</sup> the band at 2125 cm<sup>-1</sup> may be assigned to -C≡C- vibration and the one at 1515 cm<sup>-1</sup> to -C=C- vibration. For the blue solution of  $X=0.55$ , the -C≡C- band shifts to 2100 cm<sup>-1</sup> and the -C=C- band to 1464 cm<sup>-1</sup>, accompanied with a small band at 1498 cm<sup>-1</sup>. It should be noted that visibly blue and yellow solutions obtained at the same solvent compositions ( $X=0.72$  and  $0.75$ ) exhibit somewhat different Raman spectra. This difference suggests that, in the solutions between  $X_c$  and  $X_c'$ , the intramolecular hydrogen bonds between adjacent urethane moieties which influence the planarity of the molecule, are unstable.

Probably, electron delocalization in conjugated backbone chains is responsible for the above-mentioned lowering of -C≡C- and -C=C- vibration frequencies as well as for the yellow-to-blue color transition. In order to evaluate the difference in the concentration of delocalized electrons between the yellow and blue solutions, a preliminary electron spin resonance (ESR) measurement was carried out, using a Japan Electron Optics Lab. Model JES-FE 1X apparatus provided with a 100 kHz modulator. However, no significant difference was detected between the ESR spectra of the two solutions. Therefore, the color changes result from changes in the effective conjugation length, and not from changes in the number of delocalized electrons.

#### Shear-Rate Dependent Intrinsic Viscosity

Poly3BCMUs are likely to assume an extended chain conformation because of its conjugated backbone, and its dimensions may differ in yellow and blue (or purple) solutions. In order to check this consideration, a study of intrinsic viscosity on the 45 Mrad sample in CHCl<sub>3</sub> and CHCl<sub>3</sub>/*n*-hexane mixtures as a function of shear-rate was started and attempts were made to measure the viscosity of completely blue solutions of  $X < 0.55$ . However, it was found that these solutions always left precipitates deposited on the capillary wall of the viscometer after each experimental run. For this reason the present viscosity measurement was limited to a yellowish brown solution of  $X=0.70$ , which was apparently more stable than the blue solution as well as the yellow solution in CHCl<sub>3</sub>.

For flexible macromolecules as well as rigid ellipsoids, the dependence of  $[\eta]$  on shear-rate has been theoretically elucidated,<sup>30,31</sup> and tested by experi-

ments.<sup>32,33</sup> The available theories all may be cast into the form

$$[\eta] = [\eta]_0 (1 - A\beta^2 + \text{higher terms in even powers of } \beta) \quad (1)$$

with

$$\beta = (M[\eta]_0 \eta_s / RT) \dot{\gamma} \quad (2)$$

where  $[\eta]$  and  $[\eta]_0$  are the intrinsic viscosities at an apparent shear-rate  $\dot{\gamma}$  and the limit of zero shear-rate, respectively;  $A$ , a factor depending on the shape of the polymer (*e.g.*, the axial ratio for ellipsoids);  $\beta$ , the reduced shear-rate defined by eq 2;  $\eta_s$ , the solvent viscosity;  $M$ , the solute molecular weight; and  $RT$  has the usual meaning.

The value of  $[\eta]$  was determined by the usual procedure. The corresponding value of  $\dot{\gamma}$  was calculated using the Hagen-Poiseuille law:

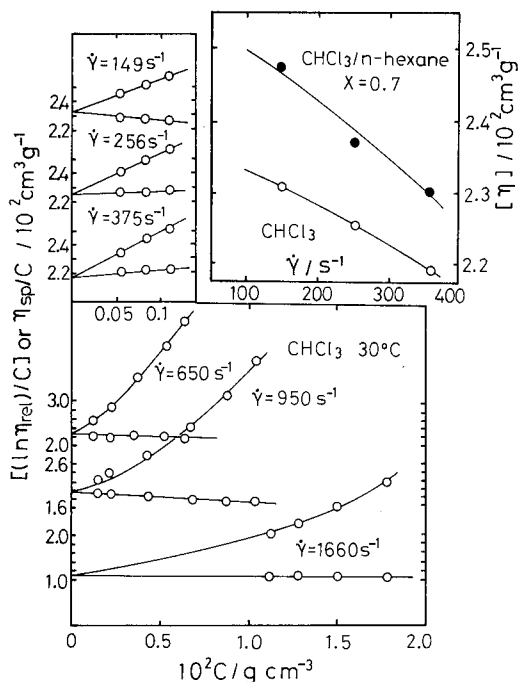
$$\dot{\gamma} = \frac{\rho g h a}{2\eta_s l} \quad (3)$$

where  $a$  and  $l$  are the radius and length of the capillary, respectively;  $h$  is the height of the midpoint between the upper and lower marks of the bulb above the meniscus of the liquid column;  $g$  is the acceleration due to gravity; and  $\rho$  is the solvent density. The values of  $\dot{\gamma}$  for CHCl<sub>3</sub> at 30°C were 650, 950, and 1660 s<sup>-1</sup> for the three Ubbelohde viscometers, and 53.6, 148.5, 256.4, and 357.3 s<sup>-1</sup> for the four bulbs of the spiral capillary viscometer.

Figure 7 shows typical viscosity vs. concentration plots for the 45 Mrad sample in CHCl<sub>3</sub> at 30°C. The insert in the figure compares the  $[\eta]$  vs.  $\dot{\gamma}$  curve for the CHCl<sub>3</sub> solution with that for the CHCl<sub>3</sub>/*n*-hexane ( $X=0.7$ ) solution. From these data, the zero-shear intrinsic viscosities  $[\eta]_0$  were estimated to be 236 and 254 cm<sup>3</sup> g<sup>-1</sup> for CHCl<sub>3</sub> and the mixture, respectively. It can be seen that  $[\eta]_0$  and its decrease with an increase in  $\dot{\gamma}$  are larger for the latter system than for the former one. This tendency is opposite that observed for solutions of ordinary flexible polymers, in which  $[\eta]_0$  is larger and non-Newtonian behavior more pronounced in good solvents than in poor solvents.

The  $[\eta]$  of the 45 Mrad sample in CHCl<sub>3</sub> at finite  $\dot{\gamma}$  are plotted as  $[\eta]/[\eta]_0$  vs.  $\log \beta$  in Figure 8. For comparison, theoretical curves for prolate ellipsoids<sup>30,31</sup> and earlier experimental results on polystyrene solutions<sup>33</sup> are also shown in the figure. The



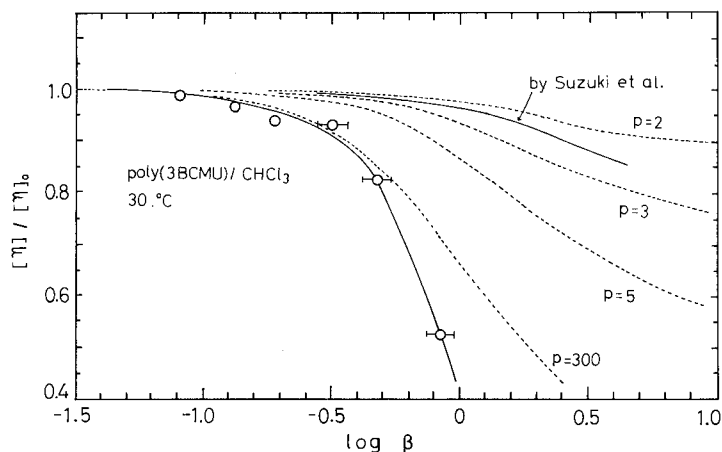


**Figure 7.** Viscosity-concentration plots for the 45 Mrad sample in  $\text{CHCl}_3$  at  $30^\circ\text{C}$ . The plots of  $\eta_{sp}/c$  and of  $\ln(\eta_r)/c$  vs.  $c$  are shown for data obtained by three Ubbelohde viscometers and by three bulbs of the four-bulb viscometer. The shear-rate for  $\text{CHCl}_3$  are indicated in the figure. The insert shows the  $[\eta]$  vs.  $\dot{\gamma}$  curves for the  $\text{CHCl}_3$  and  $\text{CHCl}_3/n$ -hexane ( $X=0.7$ ) solutions.

poly3BCMU data fall in the region of ellipsoids with very large axial ratios, suggesting that poly3BCMU in  $\text{CHCl}_3$  assumes a highly extended conformation.

The data in the insert of Figure 7 shows that  $[\eta]$  of the 45 Mrad sample undergoes a larger shear-rate dependence in the  $\text{CHCl}_3/n$ -hexane mixture than in  $\text{CHCl}_3$ . Thus it seems that the conformation of this sample is more extended in a poor solvent  $\text{CHCl}_3/n$ -hexane mixture than in a good solvent  $\text{CHCl}_3$ , in contrast to the behavior of flexible polymers.

It is known that lyotropic liquid-crystalline solutions exhibit a characteristic rheological behavior when the phase changes from isotropic to anisotropic. For example, at the phase transition usually called the A point, an abrupt change in viscosity occurs. Since poly3BCMU appears to assume a highly extended conformation, viscosity measurements were carried out to examine whether the expected liquid crystalline behavior appears in the  $\eta_r$  (relative viscosity) vs.  $c$  curve for the 45 Mrad sample in  $\text{CHCl}_3$  at  $30^\circ\text{C}$ . For the solutions of  $c$  below 3.16 wt%,  $\eta_r$  increased in proportion to  $c^{2.5}$  and reached 63 at the 3.16 wt% solution. For solutions of  $c$  between 3.16 and 5.37 wt%,  $\eta_r$  was proportional to  $c^{7.5}$ . Above 5.37 wt% the polymer did not dissolve completely in  $\text{CHCl}_3$ . If the break at  $c=3.16$  wt% on the  $\log \eta_r$  vs.  $\log c$  curve corresponds to the A point for this system, a sudden drop in  $\eta_r$  should be seen at or in the vicinity of this



**Figure 8.** Non-Newtonian intrinsic viscosity of the 45 Mrad sample in  $\text{CHCl}_3$  at  $30^\circ\text{C}$ . The ratios of  $[\eta]$  at  $\dot{\gamma}$  to  $[\eta]_0$  at  $\dot{\gamma} \rightarrow 0$  are plotted against reduced shear-rate  $\beta = (M[\eta]_0 \eta_s / RT) \dot{\gamma}$ . Theoretical curves for prolate ellipsoids with various axial ratios are indicated by the broken lines. The solid curve indicates the data for polystyrene in various poor solvents obtained by Suzuki *et al.*<sup>33</sup>

point. However, for solutions with  $c$  below 5.37 wt%, no such drop in viscosity was observed.

According to Flory,<sup>35</sup> the polymer volume fraction  $v_2$  at the A point of a solution of rodlike macromolecules is given by

$$v_2 \cong (8/p)(1 - 2/p) \quad (4)$$

where  $p$  is the axial ratio of the rod. For the 45 Mrad sample, the axial ratio  $p$  may be estimated to be as large as 300 from the data in Figure 8. Assuming the specific volume of the polymer to be  $1 \text{ cm}^3 \text{ g}^{-1}$  and substituting  $p = 300$  into eq 4, we obtain  $v_2 \cong 2.65\%$ , which is somewhat lower than the volume fraction at the above-mentioned break point. Furthermore, within the solubility limit, no evidence was obtained for the liquid crystal formation of poly3BCMU. These findings appear to be due partly to a partial flexibility of the polymer chain.

Another interesting observation on moderately concentrated ( $c > 4 \text{ wt}\%$ ) solutions of poly3BCMU in  $\text{CHCl}_3$  was that they exhibit a significant Weissenberg effect. This fact also suggests that the poly3BCMU chain assumes a highly extended (but not rigid rodlike) conformation in  $\text{CHCl}_3$ .

*Acknowledgements.* The authors are deeply grateful to many colleagues for valuable comments given in carrying out this research. Special thanks are extended to Professor Emeritus M. Nakagawa and Dr. M. Iyoda for the diacetylene synthesis; Professor K. Hayashi and Dr. S. Yamamoto for the radiation polymerization; Professors A. Takahashi and T. Kato for the measurement of refractive index increments of colored solutions; Dr. T. Norisuye and Dr. Y. Einaga for the viscometry; Professors M. Kobayashi and M. Kamachi for the spectroscopic characterization; and Dr. G. N. Patel for his valuable discussion on the occasion of his visit to our laboratory in 1980. The authors appreciate the assistance of Mr. S. Yamao in carrying out the experiments.

## REFERENCES

- G. B. Street and T. C. Clarke, "IBM Symposium on Highly Conducting Polymers and Graphite," San Jose, March, 1979 [*Synthetic Metals*, **1**, 99 (1980)].
- A. J. Epstein and J. S. Miller, *Sci. Am.*, **241**, No. 4, 48 (1979).
- H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc. Commun.*, 578 (1977).
- C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, and A. J. Heeger, *Phys. Rev. Lett.*, **39**, 1098 (1977).
- C. K. Chiang, M. A. Druy, S. C. Gaw, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, *J. Am. Chem. Soc.*, 1013 (1978).
- H. Shirakawa and S. Ikeda, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 103 (1979).
- C. K. Chiang, A. J. Heeger, and A. G. MacDiarmid, *Ber. Bunsenges. Phys. Chem.*, **83**, 107 (1979).
- Y. W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, *J. Chem. Phys.*, **73**, 946 (1980).
- H. Shirakawa, M. Sato, A. Hamano, S. Kawakami, K. Soga, and S. Ikeda, *Macromolecules*, **13**, 457 (1980).
- G. Wegner, *Makromol. Chem.*, **145**, 85 (1971); *ibid.*, **154**, 35 (1972).
- R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1511 (1974).
- R. H. Baughman and K. C. Yee, *J. Polym. Sci., Macromolecular Rev.*, **13**, 219 (1978).
- G. N. Patel, *Polym. Prepr., J. Am. Chem. Soc., Div. Polym. Chem.*, **19**(2) 154 (1978).
- G. N. Patel, Y. P. Khanna, D. M. Ivory, J. M. Sowa, and R. R. Chance, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 899 (1979).
- G. N. Patel and E. K. Walsh, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 203 (1979).
- K. Se, H. Ohnuma, and T. Kotaka, *Rep. Prog. Polym. Phys. Jpn.*, **23**, 3 (1980).
- K. Se, H. Ohnuma, and T. Kotaka, *Rep. Prog. Polym. Phys. Jpn.*, **24**, 409 (1981).
- T. Kotaka, K. Se, H. Ohnuma, and G. N. Patel, *Kagaku*, **36**, No. 10, 811 (1981).
- G. N. Patel, R. R. Chance, and J. D. Witt, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 607 (1978).
- G. N. Patel, R. R. Chance, and J. D. Witt, *J. Chem. Phys.*, **70**, 4387 (1979).
- R. R. Chance, G. N. Patel, and J. D. Witt, *J. Chem. Phys.*, **71**, 206 (1979).
- G. N. Patel, J. D. Witt, and Y. P. Khanna, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1383 (1980).
- Org. Synthesis Coll. Vol., **3**, 698 (1955).
- Org. Synthesis Coll. Vol., **3**, 778 (1955).
- A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962).
- H. Kuhn, *Frostschi. Chem. Org. Naturstoffe*, **16**, 169 (1958); *ibid.*, **17**, 404 (1959).
- H. J. Bernstein, Resonance Raman Spectra: in "Advances in Raman Spectroscopy," J. P. Mathieu, Ed., Heyden, 1973.
- A. J. Melveger and R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 603 (1973).
- R. H. Baughman, J. D. Witt, and K. C. Yee, *J. Chem. Phys.*, **60**, 4755 (1974).
- N. Saito, *J. Phys. Soc. Jpn.*, **6**, 197 (1951).
- H. A. Scheragea, *J. Chem. Phys.*, **23**, 1526 (1955).

### Urethane Substituted Polydiacetylenes

32. See, for example: J. T. Yang, *J. Am. Chem. Soc.*, **81**, 1783 (1958); *ibid.*, **82**, 1902 (1959).
33. T. Kotaka, H. Suzuki, and H. Inagaki, *J. Chem. Phys.*, **45**, 2770 (1966); *ibid.*, **51**, 1279 (1969).
34. C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
35. P. J. Flory, *Proc. R. Soc., London Ser. A*, **234**, 73 (1956).