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

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ABSTRACT: A diacetylene having 3-methyl-*n*-butoxy-carbonylmethyl-urethane (3BCMU) as a substituent was synthesized and exposed to ^{60}Co - γ 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 CHCl_3 and *n*-hexane were compared. The critical solvent compositions (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 CHCl_3 and blue 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 CHCl_3 /*n*-hexane than in a good solvent 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.¹ 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.² A well-known example is polyacetylene doped with halogens or AsF_5 .³⁻⁸ 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.*⁹ 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.¹⁰⁻¹² 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 $\text{CR}-\text{C}\equiv\text{C}-\text{CR}$ and butatriene $\text{CR}=\text{C}=\text{C}=\text{CR}$.¹⁰ Although the poly-

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merization of a large number of diacetylenes has been reported, especially by Wegner¹⁰ and by Baughman,^{11,12} most of the products were insoluble and infusible, and hence not feasible for molecular characterization.

Recently, Patel *et al.*^{13,14} 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.¹⁵ 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 $^{60}\text{Co-}\gamma$ irradiation at various doses, and subjected the products poly3BCMU to molecular characterization and dilute solution studies.¹⁶⁻¹⁸

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.^{18,19-22} This phenomenon as well as the dilute solution characteristics of poly3BCMU were studied in some detail by Patel *et al.*^{15,18-22} 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.*^{13-15,19-22} 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)²³: bp was $57^\circ\text{C}/25$ 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^{23,24}: bp was $66^\circ\text{C}/20$ 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 method²⁵ 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 ^{60}Co γ 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 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 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 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 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 CHCl_3 solutions and also the addition of CHCl_3 to CHCl_3/n -hexane mixtures.

Intrinsic viscosities as a function of shear rate were determined for the 45 Mrad sample in CHCl_3 and CHCl_3/n -hexane mixtures at 30°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 CHCl_3 for GPC tests. The chromatogram showed two major peaks corresponding to

Figure 1. Polymer conversion as a function of ^{60}Co γ -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 CHCl_3 solution at 25°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

10.7×10^6 and 0.34×10^{-4} mol cm³ g⁻², 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.*^{14,15} 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 γ -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 CHCl₃ and *n*-hexane at 16°C. The spectra are progressively displaced by arbitrary amounts. The polymer concentration is 2.97×10^{-5} mol l⁻¹. C/H/C implies that the solution in CHCl₃/*n*-hexane is back titrated with CHCl₃ to $X_{\text{CHCl}_3} = 0.72$.

Color Change in the Solution

Patel *et al.*^{19,20} 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 CHCl_3 solution of poly3BCMU with *n*-hexane, Patel *et al.*¹⁹ 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 CHCl_3 and *n*-hexane. Figure 3 shows the typical spectra obtained. The results gave similar phase diagrams at 0°C and about 20°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 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°C . Beside these features already pointed out by Patel *et al.*,¹⁹ the following results were also obtained. (iv) By lowering the temperature from 20°C or 22°C to 0°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 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 CHCl_3 /*n*-hexane mixture. The closed and open marks (circles and triangles) represent the results at 20°C and 0°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 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 CHCl_3 solution with n -hexane, and the C/H/C coded solutions by back titrating the CHCl_3/n -hexane solution with 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 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.*¹⁹⁻²² 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^a

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

^a X_c and X_c' , the mole fractions of CHCl_3 at the color transition points, were determined by titration of a CHCl_3 solutions with n -hexane and titration of a blue solution with 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 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 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,²⁶ Patel^{19,20} 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.²⁷ According to Baughman

Figure 6. Raman spectra for $0.297 \mu\text{mol dm}^{-3}$ solutions of poly3BCMU (45 Mrad dose) at 25°C in CHCl_3/n -hexane mixture.

et al.,^{28,29} the band at 2125 cm^{-1} may be assigned to $-\text{C}\equiv\text{C}-$ vibration and the one at 1515 cm^{-1} to $-\text{C}=\text{C}-$ vibration. For the blue solution of $X=0.55$, the $-\text{C}\equiv\text{C}-$ band shifts to 2100 cm^{-1} and the $-\text{C}=\text{C}-$ band to 1464 cm^{-1} , accompanied with a small band at 1498 cm^{-1} . 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 $-\text{C}\equiv\text{C}-$ and $-\text{C}=\text{C}-$ 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_3 and CHCl_3/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_3 .

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

ments.^{32,33} 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); β , the reduced shear-rate defined by eq 2; η_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 mid-point between the upper and lower marks of the bulb above the meniscus of the liquid column; g is the acceleration due to gravity; and ρ is the solvent density. The values of $\dot{\gamma}$ for CHCl_3 at 30°C were 650, 950, and 1660 s^{-1} for the three Ubbelohde viscometers, and 53.6, 148.5, 256.4, and 357.3 s^{-1} for the four bulbs of the spiral capillary viscometer.

Figure 7 shows typical viscosity vs. concentration plots for the 45 Mrad sample in CHCl_3 at 30°C . The insert in the figure compares the $[\eta]$ vs. $\dot{\gamma}$ curve for the CHCl_3 solution with that for the CHCl_3/n -hexane ($X=0.7$) solution. From these data, the zero-shear intrinsic viscosities $[\eta]_0$ were estimated to be 236 and $254\text{ cm}^3\text{ g}^{-1}$ for CHCl_3 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_3 at finite $\dot{\gamma}$ are plotted as $[\eta]/[\eta]_0$ vs. $\log \beta$ in Figure 8. For comparison, theoretical curves for prolate ellipsoids^{30,31} and earlier experimental results on polystyrene solutions³³ are also shown in the figure. The

Figure 7. Viscosity-concentration plots for the 45 Mrad sample in CHCl_3 at 30°C . The plots of η_{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 CHCl_3 are indicated in the figure. The insert shows the $[\eta]$ vs. $\dot{\gamma}$ curves for the CHCl_3 and $\text{CHCl}_3/n\text{-hexane}$ ($X=0.7$) solutions.

poly3BCMU data fall in the region of ellipsoids with very large axial ratios, suggesting that poly3BCMU in 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 $\text{CHCl}_3/n\text{-hexane}$ mixture than in CHCl_3 . Thus it seems that the conformation of this sample is more extended in a poor solvent $\text{CHCl}_3/n\text{-hexane}$ mixture than in a good solvent 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 η_r (relative viscosity) vs. c curve for the 45 Mrad sample in CHCl_3 at 30°C . For the solutions of c below 3.16 wt%, η_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%, η_r was proportional to $c^{7.5}$. Above 5.37 wt% the polymer did not dissolve completely in 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 η_r should be seen at or in the vicinity of this

Figure 8. Non-Newtonian intrinsic viscosity of the 45 Mrad sample in CHCl_3 at 30°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.*³³

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

According to Flory,³⁵ 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 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 CHCl_3 .

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