NOTES

Titration and Color Change in Poly(deca-4,6-diynedioic acid) in KCl Solution

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(Received May 26, 1989)

KEY WORDS Polydiacetylene / Poly(electrolytic diacetylene) / Water soluble polydiacetylene / Poly(deca-4,6-diynedioic acid) / Poly[4,6-decadiyne-1,10-diol-bis([urethane]methyl-carboxylic acid)] / Titration / Conformational Change / Color Change /

In our previous papers,^{1,2} we reported color change upon titration of a water soluble poly-(diacetylene) with substituent group $R = -(CH_2)_3-OCONH-CH_2COOH$ in aqueous KCl solution, *i.e.*, poly[4,6-decadiyn-1,10-diol-bis([urethane]methylcarboxylic acid)]. The polymer abbreviated as poly(3HAU) was a hydrolyzate of a urethane substituted polydiacetylene, poly[4,6-decadiyn-1,10-diol-bis-([*n*-butoxycarbonyl)methyl]urethane)] [poly-(3BCMU)]. The color change of poly(3HAU) solutions was attributable to conformational transition accompanying change in the effective conjugation length of the backbone π electrons.³ At low pH, the planar conformation of the polymer backbones was maintained with hydrogen bonds between neighboring urethane groups, while at high pH, the poly-(3HAU) chains assumed a non-planar conformation due to dissociation of the hydrogen bonds and electrostatic repulsion between the dissociated COO^- groups. However, this interpretation is ambiguous for the relative contribution of the two effects: hydrogen bonds

and/or electrostatic repulsion. We thus synthesized poly(deca-4,6-diynedioic acid) [abbreviated as poly(2HA)] with $R = -(CH_2)_2-COOH$ which contains no urethane groups and is incapable of forming hydrogen bonds. Then we examined the titration behavior and color change of poly(2HA) in KCl solution by absorption spectroscopy and potentiometric titration together with intrinsic viscosity measurement to elucidate the effect of electrostatic interaction on the conformation of poly-(diacetylene) chains.

EXPERIMENTAL

Materials

The monomer, deca-4,6-diynedioic (2HA), was prepared by the method of Patel,⁴ and was allowed to polymerize through exposure under 10^{-5} Torr to ^{60}Co γ rays of 0.3 Mrad h^{-1} dose rate for 170 h. The unreacted monomer was removed from the crude product by washing it with $80^\circ C$ hot water for 24 h. The color of the obtained poly(2HA) powder was blue.

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Methods

Visible absorption spectra of poly(2HA) in 10^{-2} M KCl aqueous solution were measured at various degrees of neutralization α' . The measurement was carried out on a Jasco spectrophotometer (Nihon Bunko Co., Model UVDEC-5A) with quartz cell of 1 cm optical path length.

Potentiometric titration was conducted for dilute poly(2HA) solution in 10^{-2} M KCl at 25 and 55°C under CO_2 free nitrogen atmosphere with 0.2 M HCl standard solution on a Beckman Select Ion Analyzer (Beckman Instrument Co., Type 5000). The details are described elsewhere.² The degree of dissociation α was estimated from the degree of neutralization α' according to the equation:

$$\alpha = \alpha' + ([\text{H}^+]_{\text{BL}} - [\text{OH}^-]_{\text{BL}}) / [\text{COOH}] \quad (1)$$

where $[\text{H}^+]_{\text{BL}}$, $[\text{OH}^-]_{\text{BL}}$, and $[\text{COOH}]$ refer to the molar concentrations (mol l^{-1}) of free hydrogen and hydroxyl ions and carboxylic acid group, respectively. The former two were determined by blank titration of the salt solution containing no polymer. Intrinsic viscosities $[\eta]$ of poly(2HA) in KCl solution were determined as a function of α' at 25°C with a Ubbelohde viscometer.

RESULTS AND DISCUSSION

Figure 1 shows visible absorption spectra of 2.55×10^{-5} monomer mol l^{-1} poly(2HA) in 10^{-2} M KCl solution at various degrees of neutralization α' . Color of the solution changed from yellow (the absorption maximum λ_m of 475 nm) to red ($\lambda_m = 535$ nm) upon titration corresponding to the decreasing of α' . This behavior is in sharp contrast to that of poly(3HAU) solution, which exhibited color change from yellow ($\lambda_m = 475$ nm) to violet ($\lambda_m = 580$ nm) when α' was decreased.

Figure 2 compares potentiometric titration curves, $\text{p}K = \text{pH} - \log[\alpha/(1-\alpha)]$ versus the degree of dissociation α , of 10^{-2} M KCl solution of poly(2HA) at 25 and 55°C (the left panel)

Figure 1. Absorption spectra of poly(2HA) in 10^{-2} M KCl solutions.

Figure 2. Titration curves of poly(2HA) (the left panel) and poly(3HAU) (the right panel) solutions at various temperatures.

and of poly(3HAU) at 25, 35, 45 and 55°C (the right panel). Their polymer concentrations were 7.0×10^{-3} and 7.4×10^{-3} monomer mol l^{-1} , respectively. The titration curves of the poly(3HAU) solution show distinct anomaly similar to that found in poly(α -glutamic

Figure 3. Henderson-Hasselbalch plots for poly(2HA) solution at 25 and 55°C.

acid) solution, which shows helix-coil transition.^{5,6} The curves for the poly(2HA) solution show monotonous increase with α with a small inflection, this being often observed for ordinary flexible-chain polyelectrolyte solutions. The pK value at $\alpha=0$ for poly(2HA) solution is about 5.3 and is larger by a factor of about 1 than that for poly(3HAU). This suggests that dissociation of COOH groups in poly(2HA) chains is strongly affected by the conjugated main chains, because each COOH group is separated by only two methylene units from the main chain but that of poly(3HAU) by a bulky trimethyl-urethane-methyl group.

To examine the titration behavior of poly(2HA) solution more closely, we replotted the data as a Henderson-Hasselbalch plot,^{7,8} pH versus $\log[\alpha/(1-\alpha)]$, as shown in Figure 3. As pH decreased, the curve at 25°C changed its slope from 1.8 to 1.6 at $\alpha=0.7$, where a conformational change took place. However, this change in the poly(2HA) solution was much smaller than that in poly(3HAU) solutions.²

The titration curve of poly(2HA) solution at 55°C has a constant slope of 1.8 and exhibits no bending point. This is similar to that of common polyelectrolyte solution, which often yields a Henderson-Hasselbalch plot with a slope of 2. The conformation of poly(2HA) chains at 25°C in the low α region appears to become less stable as temperature is raised to 55°C.

Figure 4. Dependence of $[\eta]$ of poly(2HA) (the upper panel) and poly(3HAU) (the lower panel) solutions on the degree of neutralization α' at 25°C.

The change observed at 25°C upon titration with HCl of poly(2HA) solution thus involves only a small change in the conformation from a slightly more expanded to less expanded conformation. This change may arise from decrease in electrostatic repulsion as well as in the affinity of the side groups to the aqueous medium due to protonation with decreasing degree of dissociation α .

To check this conformational change of poly(2HA) chains, we examined the intrinsic viscosity $[\eta]$ in 10^{-2} M KCl solution at various degrees of neutralization α' . In Figure 4,

the results are compared with those of poly(3HAU) in KCl solution. The $[\eta]$ of poly(2HA) in KCl solution decreases monotonously as α' decreases upon titration, this suggesting only moderate decrease in the chain dimension with decreasing α' , as anticipated. $[\eta]$ of poly(3HAU) in 10^{-2} M KCl solution at 25°C exhibited, upon titration with HCl, an initial decrease to a minimum at around $\alpha' = 0.8$, followed by a sharp upturn with further decreasing of α' to 0.6. The final rapid increase in $[\eta]$ corresponds to formation of hydrogen bonds. Upon titration, the poly(3HAU) chain changes its conformation from the expanded random-coil form at high α' through slightly twisted non-planar conformation to the planar conformation stabilized with hydrogen bonds between neighboring urethane moieties. This corresponds to the case of titration of

poly(3BCMU) in a good solvent CHCl_3 with a nonsolvent hexane.

Acknowledgement. This work was supported in part by a Grant from the Naoji Iwatani Memorial Foundation during 1982.

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