

# Conformational Change of Poly(ethylene Glycol) near the Critical Point of Isobutyric Acid + Water<sup>†</sup>

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In solutions of isobutyric acid + water, poly(ethylene glycol) (PEG) can assume a helical conformation. [Alessi, M. L.; Norman, A. I.; Knowlton, S. E.; Ho, D. L.; Greer, S. C. *Macromolecules* **2005**, *38*, 9333–9340.] Here we report new measurements of the kinematic viscosity,  $\nu$ , as a function of temperature for a solution of isobutyric acid + water at the critical composition, to which PEG (number average molecular weight =  $1.01 \times 10^3$  g/mol) was added at a concentration of 6.01 mg/mL. The data show that  $\nu$  decreases near the critical point, with a maximum in  $\nu$  at about 0.05 °C above the critical temperature,  $T_c$ . We interpret this change in  $\nu$  in terms of a change in conformation of the polymer from helix to coil. This interpretation is supported by polarimetry measurements on the same mixture doped with (S)-(+)-1,2-propanediol, which indicates the loss of helicity near  $T_c$  and also a second helix-to-coil transition at about 60 °C.

## 1. Introduction

The conformation of a polymer in solution can change when the nature of the solvent changes. A polymer in a dilute solution in a one-component poor solvent that is subjected to change in either temperature or composition, such that the quality of the solvent decreases, can undergo a coil–globule transition: a condensation from a loose coil to a dense globule so as to minimize polymer–solvent interactions in the poorer solvent.<sup>1,2</sup> The coil–globule transition has been observed, for example, in polystyrene + cyclohexane,<sup>3–5</sup> in poly(*N*-isopropylacrylamide) + water,<sup>6</sup> and in poly(methyl methacrylate) + water.<sup>7</sup> For a polymer in a one-component poor solvent at the polymer–solvent critical composition, the polymer conformation may also be affected by the critical point as the critical temperature,  $T_c$ , is approached from the one-phase region: Some theorists predict a partial collapse, and others predict no effect (see references in Melnichenko et al.<sup>8</sup>); an experiment on poly(styrene) + deuterocyclohexane has shown no effect.<sup>8</sup>

A dilute solution of polymer in a mixture of two solvents at the critical composition of that solvent mixture has been considered by de Gennes and Brochard<sup>9,10</sup> and others<sup>11</sup> who predict that, as the temperature is decreased toward the critical point, the polymer will first collapse then re-swell. The collapse is the coil–globule transition. The re-swelling is due to the preferential attraction of one of the solvent components to the polymer near the critical point: As soon as the correlation length of the critical fluctuations exceeds the radius of gyration of the polymer, then the polymer is “within” a droplet of the better solvent and expands. Although the polymer contraction has been seen for poly(ethylene glycol) in tetrahydrofuran + water,<sup>12</sup> for poly(acrylic acid) in water + 2, 6-lutidine,<sup>13</sup> and for poly(*N*-isopropylacrylamide) in methanol + cyclohexane,<sup>14</sup> there has never been an experimental report of the re-swelling. The re-swelling has been seen in simulations.<sup>15,16</sup>

We are interested here in system that is related to, but different from, those discussed above: poly(ethylene glycol) (PEG) in the mixture isobutyric acid + water. Isobutyric acid + water has an upper critical solution point at about 26 °C.<sup>17,18</sup> PEG in water has a coil conformation.<sup>19,20</sup> Recent experimental work in our group has shown that PEG in solutions of isobutyric acid + water can take a helical conformation, including solutions at the critical concentration.<sup>20</sup> At low molecular weights (around  $10^3$  g/mol), the PEG is entirely helical. At higher molecular weights ( $10^4$  –  $10^5$  g/mol), the PEG consists of both coils and helices; whether these conformations exist as different blocks of one molecule or as coexisting forms on different molecules is not clear. At temperatures above about 68 °C for PEG of molecular weight  $2.38 \times 10^4$  g/mol in pure isobutyric acid, the helices all revert to coils; the temperature of this helix–coil transition can be expected to depend on the polymer molecular weight and on the solvent composition. The presence of the helical polymer configuration that unfolds to a coil conformation distinguishes this system from those discussed above. We do not know why the PEG molecules form helices in this solvent, although we postulate<sup>20</sup> that a hydration layer of water may be involved.

We have also shown<sup>21,22</sup> that for PEG in isobutyric acid + water at temperatures below the critical point in the two-phase region, the PEG fractionates quite dramatically between the two phases, with a smaller average molecular weight in the upper, isobutyric acid-rich phase and a larger average molecular weight in the lower, water-rich phase. In addition, there is a greater mass of PEG in the isobutyric acid-rich phase, although PEG is more soluble in water than in isobutyric acid. However, PEG is quite hygroscopic, and even the PEG molecules in the isobutyric acid-rich phase are likely to have adsorbed layers of water.<sup>23</sup>

Our goal in this study was to explore the conformations of PEG near the upper critical solution point of isobutyric acid + water. We have measured the kinematic viscosity,  $\nu$ , of PEG in a solution of isobutyric acid + water that is at the critical concentration, as a function of temperature,  $T$ . We find that the

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addition of the PEG results in a decrease in  $\nu(T)$  as  $T$  is decreased toward the critical point, with a maximum at about 0.05 °C above the critical temperature. We propose that the decrease in the viscosity is evidence of a conformational change in the PEG, from helix to coil, near  $T_c$ . We confirm this hypothesis by a study of the optical rotation as a function of temperature for the same system but with a chiral dopant added. The optical rotation as a function of temperature indicates that PEG in this mixture is a coil at high temperatures, a helix at intermediate temperatures, and a coil again at temperatures near  $T_c$ .

## 2. Methods

**2.1. Materials.** The PEG sample was from Polymer Source Inc., Dorval, Canada, catalog no. PEG2OH-2K, with  $M_w = 1.01 \times 10^3$  g/mol,  $M_n = 9.19 \times 10^2$  g/mol, for a polydispersity index of 1.10, as characterized by size-exclusion chromatography in our laboratory and described previously.<sup>20</sup> This polymer was terminated by hydroxyl groups. The polymer was used without further purification.

The solvents used were isobutyric acid (Aldrich, 99.9%) and freshly distilled, deionized H<sub>2</sub>O from a Nanopure system (Barnstead, 18 M $\Omega$  cm). The isobutyric acid and water mixture for the sample without PEG had a composition of 0.390 mass fraction of isobutyric acid and a phase transition temperature of 26.012 °C. Values of the critical composition in the literature are 0.380–0.395 in mass fraction,<sup>18,24,25</sup> and values of the critical temperature,  $T_c$ , are 25.999–26.300 °C.<sup>17,18</sup> The mixture for the sample with PEG added had a composition of 0.388 mass fraction of isobutyric acid and a phase transition temperature of  $30.528 \pm 0.003$  °C after the PEG was added to a concentration of 6 mg/mL (mass fraction  $6.01 \times 10^{-3}$ ), which is below the overlap concentration.<sup>26</sup> Shresth et al.<sup>21</sup> reported a shift of  $-0.7$  °C in  $T_c$  when PEG with  $M_n = 2.10 \times 10^4$ , polydispersity index = 1.14, and with hydroxyl terminations<sup>20</sup> was added to a critical mixture of isobutyric acid + water to a concentration of 1 mg/mL. We see a shift of  $+4.5$  °C in this work, where we are using six times as much polymer and using polymer that is twenty times smaller in molecular weight. Third components that are equally soluble in both solvents tend to make them more compatible, while third components that prefer one solvent tend to make them less compatible.<sup>27</sup> PEG is more soluble in water than in isobutyric acid, so it is reasonable for the addition of the PEG to make the solvents less compatible and thus to raise the temperature.

For the polarimetry measurements, the sample was 0.3899 mass fraction of isobutyric acid. The PEG concentration was again 6 mg/mL. The chiral dopant concentration was  $2.0 \times 10^{-3}$  in mass fraction. The critical temperature was 30.5–30.6 °C, in agreement with that measured for the viscometry sample. The addition of the dopant did not affect  $T_c$  significantly.

Solutions of PEG in isobutyric acid + water have previously been studied by To et al.,<sup>28</sup> who observed the presence of a third liquid phase at temperatures near  $T_c$ , using PEG of molecular weight  $9 \times 10^5$  g/mol (no polydispersity given) at a concentration of 0.1 mass %. We did not observe such a third phase with this sample. The concentration of polymer in this study was about half that of the To et al. study, and the polymer in our experiments was of much smaller molecular weight and lower polydispersity.

The chiral dopant used in the polarimetry experiments was (S)-(+)-1,2-propanediol (Lancaster Research Chemicals, 98% pure enantiomer).

**2.2. Viscometry.** The kinematic viscosity,  $\nu$ , was measured using the capillary viscometer constructed by Gruner et al.<sup>29</sup>

Run times ( $\tau$ ) were determined using a stopwatch with a resolution of 0.01 s. The viscometer was calibrated<sup>30</sup> with two fluids of known density and viscosity [acetone (0.306 mPa s) and ethanol (1.074 mPa s)] to determine the constants  $k_1$  and  $k_2$  in the equation  $\nu = k_1\tau - k_2/\tau^2$ . The accuracy is about 1%. For each data point, the runtime was measured 15–30 times, and the average and standard deviation of the mean were calculated. The precision is about 0.1%.

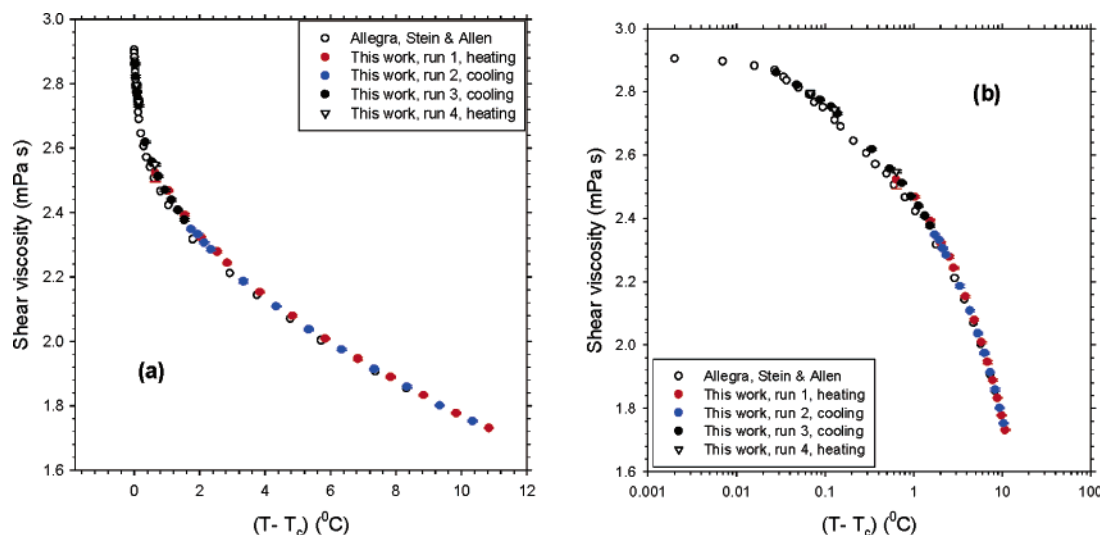
The  $\nu$  measurements for the mixture without PEG were converted to shear viscosities,<sup>30</sup>  $\eta$ , by multiplying by the mass density of a nearly critical mixture of isobutyric acid and water, as given by Greer.<sup>17</sup> We note that there is an error in the equation for the density,  $D$ , as a function of temperature in ref 17; the correct equation is  $D = D_c + A_1t + A_2t^2$ , where  $t = (T - T_c)/T_c$ ,  $T$  is the temperature in K,  $T_c$  is the critical temperature in K,  $D_c = 0.99357 \pm 0.00001$ ,  $A_1 = -0.165 \pm 0.002$ , and  $A_2 = -0.449 \pm 0.065$ . The mass density of isobutyric acid and water as a function of temperature shows only a very small critical anomaly, detectable at the level of 0.1 ppm,<sup>31</sup> and is thus not important in the current study.

The viscometer was held in a stirred water bath with the temperature controlled to a few mK.<sup>32</sup> The temperature was measured using a Hart Scientific 1502A (American Fork, UT) digital thermometer with an accuracy of 0.01 K and a precision of 0.001 K. Typically a day or two was allowed for equilibration at each temperature.

**2.3. Polarimetry.** When the PEG molecules form helices, they can be expected to form left- and right-handed helices in equal number (a racemic mixture), and thus give zero net optical rotation. Indeed, PEG in isobutyric acid + water solutions shows no optical rotation.<sup>20</sup> However, chiral dopants can lead to an “enantiomeric excess,” as we have shown previously.<sup>20</sup> The dopant used here (see above) was (+)-1,2-propanediol.

The Jasco P1010 polarimeter consists of a 10-cm path length glass cell with an interior volume of 8 mL. The P1010 uses a halogen lamp with a wavelength of 589 nm selected by a filter and has an accuracy of 0.002° with a reproducibility of 0.002° or better for measurements less than 1°. To measure the optical rotation,  $\alpha$ , as a function of temperature, the polarimeter was configured with a VWR 1160 bath to circulate temperature-controlled water through a jacketed polarimeter cell (Jasco, 10-cm path length, 3.5 mL volume). Connecting Tygon tubing was insulated tightly with foam to minimize heat loss between the water bath and the sample. The temperature at the sample was measured with a thermistor connected to a Sper Scientific digital thermometer. The temperature was controlled and measured to an accuracy and precision of about 0.1 °C.

The polarimeter was first zeroed with a critical mixture of isobutyric acid and water at room temperature. Background measurements for a sample consisting of a critical mixture of isobutyric acid + water with added dopant (S)-1,2-propanediol (mass fraction  $2.0 \times 10^{-3}$ ) were then made at temperatures between 30 and 60 °C. Then the PEG (6 mg/mL) was added to the sample of the critical mixture with dopant, and measurements were made by repeated integrations (10-s sampling time) of the signal. The first data were recorded at 50 °C, after which the sample was cooled and measurements were taken at several temperature intervals. For each measurement, the sample was allowed to equilibrate at that temperature for at least 30 min or until the reading became stable. The sample was heated again, from 30.6 to 60.0 °C, and more measurements were made. We subtracted the optical rotation of the solvent + dopant mixture from that of the PEG + solvent + dopant mixture to obtain the net optical rotation due to the PEG.



**Figure 1.** Shear viscosity of a critical mixture of isobutyric acid + water, including measurements of Allegra, Stein, and Allen<sup>33</sup> and four runs on the sample under study here, as a function of (a)  $(T - T_c)$  and (b)  $\log(T - T_c)$ , where  $T$  is the temperature and  $T_c$  is the critical temperature. Error bars represent one standard deviation and are usually smaller than the symbols.

### 3. Results and Discussion

Error bars are given as one standard deviation. Error bars are not plotted for the temperature axes.

**3.1. Viscosity of Isobutyric Acid + Water at the Critical Composition without PEG.** Figure 1 shows our measurements of the shear viscosity of isobutyric acid + water, as a function of  $(T - T_c)$  and  $\log(T - T_c)$ , where the four runs agree well with one another. Also plotted are measurements from the literature by Allegra, Stein, and Allen.<sup>33</sup> There are other excellent measurements of the viscosity for this system,<sup>25,34–36</sup> but this data set suffices to give us confidence in our own viscometry.

**3.2. Viscosity of Isobutyric Acid + Water at the Critical Composition with PEG.** The solution with PEG added showed a higher  $T_c$  than the solution without PEG (see section 2.1). The liquid–liquid meniscus appeared first near the top of the sample, after which the top phase slowly grew over 24–48 h until it was, so far as could be determined from the geometry of the cell, near the middle of the sample. The appearance of the meniscus near the middle of the sample indicates that the critical composition was not changed significantly by the addition of the PEG. The evidence is that the effect of small amounts of polymer on critical compositions is small.<sup>13,28,37,38</sup>

Figure 2a shows the measured kinematic viscosity as a function of temperature for the critical mixture of isobutyric acid + water with PEG added, along with the kinematic viscosity for the critical mixture without the PEG. The data for the mixture with PEG are listed in Table 1. We consider the kinematic viscosity for this sample because that is the directly measured quantity; moreover, the conversion to the shear viscosity requires multiplication by the density, and we do not have measurements of the density for the mixture with PEG. The data for the PEG solution extend to higher temperatures than do the data for the solution without PEG.

Figure 2a shows that the addition of the PEG *increases* the kinematic viscosity at a given temperature near  $T_c$  but that this difference decreases as  $T$  increases, away from  $T_c$ , and that the two data sets appear to coincide above about 40 °C. That is, the difference in  $\nu$  between the solution with PEG and the solution without PEG increases near  $T_c$ . Figure 2b shows  $\nu$  very near to  $T_c$ , where a maximum in  $\nu(T)$  can be seen at about 0.05 °C above  $T_c$ . The maximum is reproduced reasonably well on two runs, given that the error bars represent just one standard

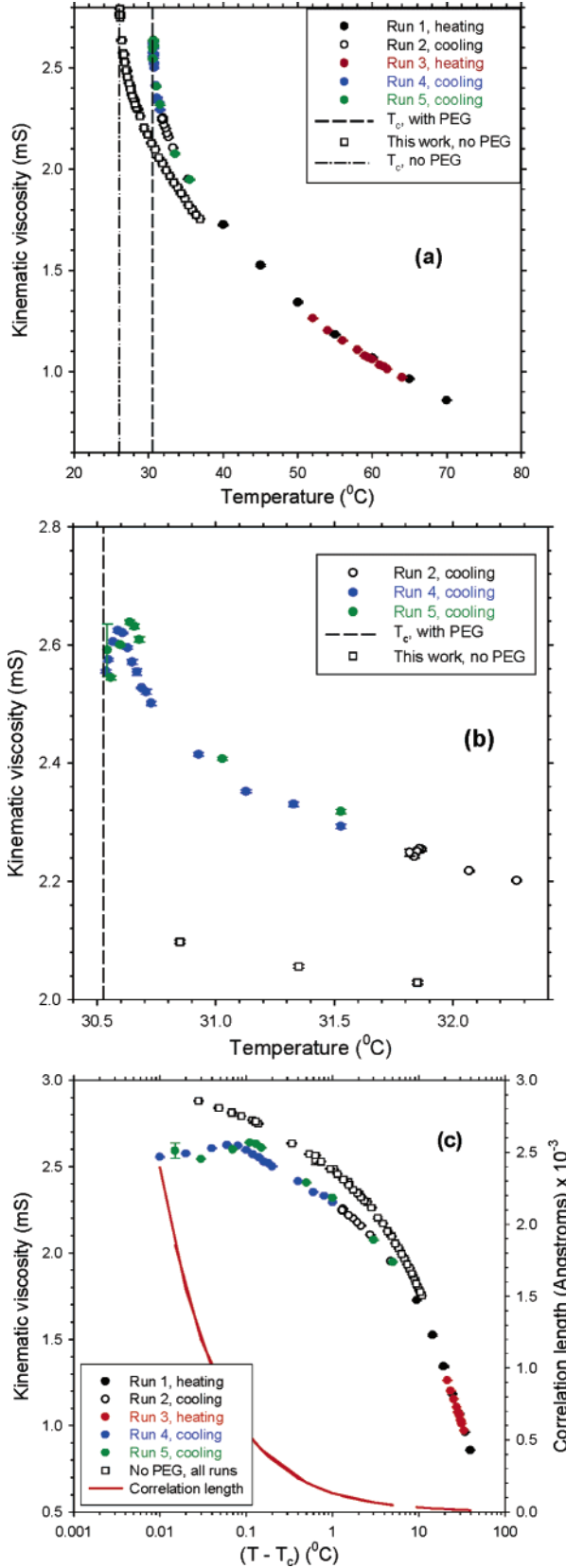
deviation and 99% confidence intervals would be three times the size of the error bars shown.

Figure 2c shows the same data as Figure 2a, now plotted as a function of the logarithm of  $(T - T_c)$ . When plotted against  $(T - T_c)$  in Figure 2c, the kinematic viscosity for the PEG solution is *lower* than for the solution without PEG, whereas it is *higher* when plotted against  $T$  in Figure 2a, but this is just a reflection of the difference in  $T_c$  between the mixture with PEG and without PEG: A given  $(T - T_c)$  will be at a higher  $T$  for the PEG solution, and the viscosity is lower at higher  $T$ . Figure 2c shows: (1) that the difference between the kinematic viscosity with PEG and without PEG increases as  $T_c$  is approached; (2) that  $\nu(T - T_c)$  for the mixture with PEG has a maximum at  $(T - T_c) \cong 0.05$  °C; and (3) that  $\nu(T - T_c)$  for the mixture without PEG does not have a maximum near  $T_c$ .

How do we interpret the behavior of the kinematic viscosity near  $T_c$  for the PEG solution? Recent work on the conformation of PEG in solutions of isobutyric acid + water<sup>20</sup> has shown that, for an  $M_n$  of  $1.73 \times 10^3$  g/mol and methoxyl terminating group, the PEG takes a helical conformation in a mixture of critical composition at temperatures well above  $T_c$ . The  $M_n$  of the PEG used here was  $1.01 \times 10^3$  g/mol (hydroxyl terminating group), so we can assume that the PEG in the present experiment is also entirely in the helical conformation. If it is in the helical conformation, how can its conformation change so as to cause the viscosity to decrease? The viscosity is larger for helical, rod-like species in dilute solution than for coil-like species in solution.<sup>39</sup> Then the only imaginable conformational change is that from helix to coil. Such a change would be contrary to the contraction seen for other polymers near  $T_c$ . However, as discussed in the Introduction, PEG has a coil conformation in water and a helical conformation in isobutyric acid. Near the critical point, the PEG molecules within the waterlike critical fluctuations can have coil configurations, thus leading to the decrease in viscosity.

Figure 2c also shows the correlation length of the critical fluctuations in isobutyric acid + water without PEG.<sup>40</sup> We do not have measurements of the correlation length with PEG added, but there are some indications that when the polymer is wetted by one component of the mixture, the presence of the polymer increases the correlation length.<sup>13,41,42</sup> We can estimate other relevant sizes: The length of the helix for a  $M_w$  of 1.73



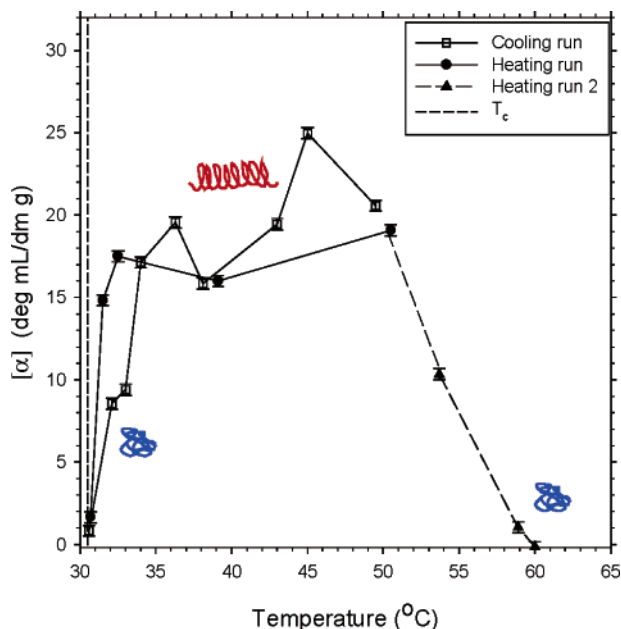


**Figure 2.** Kinematic viscosity of a mixture of isobutyric acid + water at a composition near the liquid–liquid critical composition, with and without the addition of poly(ethylene glycol) as a function of (a and b) temperature,  $T$ , and (c)  $\log(T - T_c)$ , where  $T_c$  is the critical temperature. The  $T_c$  values differ, with and without PEG (see section 2.1). The error bars represent one standard deviation and are usually smaller than the symbols. The vertical lines in a and b indicate the values of  $T_c$ , with and without PEG. The correlation length of critical fluctuations for the system without PEG (see text) is shown in c.

**TABLE 1: Kinematic Viscosity,  $\nu$ , with Standard Deviations (SD), as a Function of Temperature for a Sample of Isobutyric Acid + Water to Which Poly(ethylene glycol) Has Been Added (See Text)**

run no.	$T/^\circ\text{C}$	$\nu/\text{mS}$	SD $\nu/\text{mS} \times 10^3$
1	40.000	1.725	2.9
1	45.000	1.525	5.8
1	50.000	1.342	4.6
1	55.000	1.183	1.9
1	60.000	1.070	2.4
1	65.000	0.963	2.5
1	70.000	0.858	1.0
2	35.268	1.951	1.6
2	33.268	2.105	2.1
2	32.668	2.158	2.9
2	32.468	2.176	2.7
2	32.268	2.201	1.8
2	32.068	2.218	1.6
2	31.868	2.254	2.6
2	31.858	2.255	2.8
2	31.848	2.251	2.4
2	31.838	2.242	2.4
2	31.818	2.249	5.9
3	59.500	1.069	1.4
3	52.000	1.263	2.0
3	54.000	1.202	1.2
3	56.000	1.154	1.4
3	58.000	1.107	1.6
3	62.000	1.012	6.5
3	64.000	0.971	9.7
3	59.000	1.078	1.6
3	60.000	1.060	1.7
3	61.000	1.033	1.2
3	61.500	1.027	1.1
4	31.528	2.293	3.4
4	31.328	2.330	3.9
4	31.128	2.352	2.7
4	30.928	2.415	2.8
4	30.728	2.502	3.5
4	30.708	2.521	4.0
4	30.688	2.528	1.2
4	30.668	2.554	5.3
4	30.648	2.571	4.4
4	30.628	2.596	2.3
4	30.608	2.621	1.5
4	30.588	2.625	2.9
4	30.568	2.606	3.0
4	30.548	2.575	2.5
4	30.538	2.556	2.4
5	35.528	1.948	2.4
5	33.528	2.075	3.9
5	31.528	2.318	4.0
5	31.028	2.408	2.6
5	30.678	2.609	4.4
5	30.658	2.632	3.7
5	30.638	2.639	3.9
5	30.598	2.600	2.3
5	30.558	2.545	3.1
5	30.543	2.592	44.5

$\times 10^3$  g/mol has been found to be about 40 Å;<sup>20</sup> if the helix length is linearly proportional to the molecular weight, then for the samples studied here ( $M_w = 1.01 \times 10^3$  g/mol), the average helix length will be about 23 Å. The radius of gyration of the PEG coil in pure water can be estimated<sup>43</sup> to be about 12 Å, giving a coil diameter of about 24 Å (but we expect it to be smaller in the isobutyric acid + water mixture). In Figure 2c,  $\nu$  of the isobutyric acid + water + PEG solution begins to deviate from  $\nu$  of the isobutyric acid + water solution without PEG at about  $(T - T_c) = 10$  °C, where the correlation length is about 31 Å.<sup>40</sup> Thus the size of the correlation length at the temperature at which  $\nu(T - T_c)$  begins to decrease (31 Å) is roughly the size of the polymer helix (length = 23 Å) or coil



**Figure 3.** Specific optical rotation,  $[\alpha]$ , as a function of temperature,  $T$ , of PEG in a critical mixture of isobutyric acid + water in the presence of (S)-(+)-1,2-propanediol as a chiral dopant. Error bars represent the precision in  $\alpha$  only and are given as one standard deviation.

(diameter = 24 Å), and the polymer molecule could already be contained within a fluctuation region of the solution. The peak in  $\nu$  for the PEG mixture occurs at a correlation length in the mixture without PEG of about 800–900 Å.

**3.3. Polarimetry on Isobutyric Acid + Water + PEG + Chiral Dopant.** Figure 3 shows the net optical rotation,  $\alpha$ , as a function of temperature for PEG in a critical mixture of isobutyric acid + water, doped with (S)-(+)-1,2-propanediol. At temperatures between 32 and 50 °C, the optical rotation is positive, indicating the presence of helices, and is roughly constant with temperature. At temperatures near  $T_c$ , the optical rotation vanishes, indicating the unfolding of the helix to a coil, consistent with the viscosity measurements discussed above. Over temperatures between 50 and 60 °C, the optical rotation again decreases to zero, indicating a high-temperature helix-to-coil transition, as seen in our earlier work by small-angle neutron scattering,<sup>20</sup> which was not seen in the viscosity data discussed above, even on close inspection.

#### 4. Conclusions

To, Chan, and Choi have also investigated PEG in isobutyric acid + water, using a high molecular weight polymer of unknown polydispersity, at a polymer composition above the overlap composition.<sup>28</sup> They found evidence of regions of three liquid phases. They found no evidence of polymer conformational change in a solvent of critical composition as a function of temperature using light scattering. We have used a low molecular weight polymer of narrow polydispersity, at a concentration below the overlap concentration. We do not observe a third phase in this case.

We do see evidence of conformational change by capillary viscometry. The evidence is a decrease in the kinematic viscosity near the critical point. We know that PEG of molecular weight less than  $1.7 \times 10^3$  g/mol in isobutyric acid + water at the critical composition takes a helical conformation.<sup>20</sup> We interpret the decrease seen in the kinematic viscosity near the critical point to be due to the conversion of those polymer helices to polymer coils. Polarimetry measurements using a chiral dopant

confirm that the helix reverts to a coil near the critical point, and show another helix-to-coil transition at higher temperatures. We have previously observed that PEG of some molecular weights in this mixture can be a helix at intermediate temperatures and a coil at high temperatures.<sup>20</sup> Now, for PEG of molecular weight of about  $10^3$  g/mol, we observe a coil at temperatures near  $T_c$ , helices at intermediate temperatures, and coils again at higher temperatures.

The high temperature helix–coil transition shows no signal in the kinematic viscosity measurements. We surmise that the kinematic viscosity effect is very small and is subsumed in the overall decrease of viscosity with temperature. Indeed, the intrinsic viscosity is more directly related to the molecular volume of the polymer than is the kinematic viscosity.<sup>44</sup> A determination of intrinsic viscosity as a function of temperature,<sup>45</sup> or a measurement of the hydrodynamic radius as a function of temperature by light scattering, might detect both the low-temperature coil–helix transition and the high-temperature helix–coil transition.

The unfolding of the helix near the critical point may be related to the predicted re-swelling of polymer globules near a liquid–liquid critical point<sup>9,10</sup> in that it occurs when the critical correlation length is large enough for the polymer molecules to fit within a correlation volume. It is also possible that the unfolding of the helix near  $T_c$  is related to “critical Casimir forces,” which are fluctuation-induced attractions between the segments of the polymer.<sup>9,10,46,47</sup> The formation of the helix itself is not related to critical Casimir forces, since it occurs in pure isobutyric acid. It is not obvious how increased attractions would cause the helix to unfold.

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