Characterization of Benzene as a Solvent for Poly(2-vinylpyridine)

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ABSTRACT: Static and dynamic light scattering and intrinsic viscosity measurements have been performed on dilute solutions of poly(2-vinylpyridine) in benzene. Several workers have reported a Θ point for this system in the range of 11–16 °C as determined by intrinsic viscosity and virial coefficient measurements. In our laboratory, samples prepared with spectral grade benzene "as received" exhibited an apparent Θ point near 18 °C by virial coefficient and cloud point measurements. Samples which were extensively dried to remove traces of water exhibited good-solvent properties. For these samples second virial coefficients range from 1.1×10^{-4} to 2.0×10^{-4} cm^3 mol g^{-2} over the range 2.5–25 °C, and the Houwink–Mark–Sakurada molecular weight exponent for intrinsic viscosity was 0.58 at 11.40 °C, the lowest of the reported Θ temperatures.

Introduction

A range of reported Θ temperatures for poly(2-vinylpyridine) (P2VP) in benzene motivated efforts to clarify the Θ condition in our laboratory. Measurements at Θ are of importance in polymer physics as one would like to characterize the behavior of unperturbed chains before drawing conclusions from observations of a perturbed state. A number of recent investigations have used poly(2-vinylpyridine) for studies of conformations and dynamics in dilute solution. These have included diffusion, viscosity, copolymer thermodynamics, and surface forces measurements.[1–4] P2VP is in some ways an ideal polymer for these investigations as both neutral and polyelectrolyte behavior can be studied. The anionic preparation of matched ring and linear molecules[5] has also sparked interest in P2VP as an alternative to polystyrene as a model random coil polymer. Unfortunately, there are some disturbing discrepancies in the basic solution characterization work of the neutral species.

Several studies have characterized P2VP in different solvents as a function of molecular weight, temperature, pH, tacticity, and concentration.[1–21] Arichi et al. have done the most extensive characterization of the solution properties of P2VP. Viscometry, osmometry, and light scattering were applied to carefully fractionated atactic P2VP in 20 solvents;[6–9] viscosity–molecular weight relationships were established for 92% ethanol, methanol, dimethylformamide, benzene, and dioxane. Observations of cloud points for four molecular weights in benzene established a Θ temperature of 16.2 °C.

Hyde and Taylor attempted to study P2VP under Θ conditions using a mixed solvent system of 1-propanol and *n*-heptane[14] with the Θ composition obtained from turbidimetric titrations by the method of Schultz and Flory.[22] A Houwink–Mark–Sakurada (HMS) exponent for viscosity of 0.50 was found, which is consistent with the presumption of Θ conditions; however, the radius of gyration scaled as 0.54, indicating a better than Θ solvent. The authors proposed that this is due to the different averages sampled by the two measurements; however, it is also possible that they may have observed the effects of preferential solvation in the mixed solvent system. Such a phenomenon is expected[23] unless the two solvents have the same χ parameter (which would negate the usefulness of the mixed-solvent Θ condition).

Dondos et al.[11] studied P2VP in benzene, a nonprotic, non-hydrogen-bonding solvent. This study measured viscosities for molecular weights ranging from 3.5×10^4 to 23.3×10^4 over a range of temperatures from 15 to 60 °C. The intrinsic viscosities increase with temperature to a maximum near 25 °C and then decrease until about 35 °C where they begin to rise again. The authors attribute this to an order–disorder transition of the polymer backbone. Similar behavior was also seen[12] in the concentration dependence of the reduced viscosity. HMS relationships were established for P2VP in benzene with exponents of 0.53 at 25 °C and 0.62 at 40 °C[12] as well as a Θ condition in benzene at 15 °C.[11]

The most recent study investigating Θ conditions for P2VP in benzene was done by Matsushita et al.,[18] and it is the only study to measure the second virial coefficient by light scattering over a broad temperature range. The initial determination of a Θ point at 11.4 °C was done by interpolation from the molecular weight dependence of the intrinsic viscosity, which was measured at 10, 12, and 15 °C. Elastic light scattering was then performed on two samples for temperatures ranging from 10 to 30 °C; second virial coefficients for both samples were found to be zero near 11.4 °C.

Our study of P2VP was initiated with the goal of investigating matched pairs of linear and macrocyclic polymers near the Θ point. Following the literature we chose benzene as the solvent, and, because the range of the reported values (from 11.4 to 16.2 °C)[8,11,18] did not seem to lie within typical experimental uncertainty, linear samples (Table I) were used to clarify the Θ point. The initial measurements utilized solvent "as received" and, as will be shown, the apparent Θ temperature was 18 °C. However, in the course of this work it became obvious that traces of moisture in the benzene caused irreproducible results. This led us to perform detailed studies with rigorously dry solvent. After drying the samples and the solvent in a drybox, we found the second virial coefficient to be positive at all experimentally accessible temperatures. Analysis of the radius of gyration, hydrodynamic radius, and the intrinsic viscosity (measured at 11.4 °C) confirmed our conclusion that benzene is not a Θ solvent for poly(2-vinylpyridine).

Experimental Section

Sample Preparation. For the initial studies, samples for light scattering were prepared as previously reported[24] using poly(2-vinylpyridine) polymers obtained from Polysciences (described in Table I) and spectral grade benzene (Baker) "as received". The P2VP was prepared by standard anionic polymerization techniques in tetrahydrofuran with *n*-butyllithium as an initiator.

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Table I
Poly(2-vinylpyridine) Molecular Weight Standards

$M_w \times 10^{-5}$ nominal	$M_w \times 10^{-5}$ measd	M_w/M_n	$c^*(3/[\eta]_{\text{measd}})$, mg mL^{-1}	concn range, mg mL^{-1}
0.30	na	1.07	234	5.4–13
1.10	1.17	1.05	102	0.70–5.6
2.40	2.47	1.15	81	0.6–4.2
10.0	9.85	1.1	32.4	0.2–2.5

NMR data[18] on samples prepared with the same solvent and initiator show that polymers prepared under these conditions have an isotactic triad content near 40%. Our P2VP samples were initially dried at 40 °C in a vacuum oven for 8–10 days. All prepared samples were in sealed glass tubes; seal integrity was verified gravimetrically throughout the course of the experiments. Cracks or pinholes in seals were easily detected by this method, and loss of solvent or absorption of moisture could be taken into account.

Discrepancies in the data on these early samples led to preparation of rigorously dry samples that were prepared in a Vacuum Atmospheres drybox with a total oxygen content (as free oxygen or as water) of 1–2 ppm under helium. The benzene was washed with sulfuric acid and predried over $CaCl_2$ before being rigorously dried inside the box by refluxing over sodium and benzophenone. The pot liquid (~200 mL) remained loosely capped inside the box as a measure of the dryness of the He atmosphere; there was no change in the solution's purple color (indicating dryness). The polymer was dried in the vacuum oven as above and then allowed to stand loosely capped in the drybox for 2–3 days before use. Stock solutions were prepared gravimetrically in the box but otherwise in the same fashion as before. The solvent was filtered and used immediately. The stock solutions were equilibrated and diluted into sample tubes equipped with high-vacuum stopcocks. The cells were removed from the box and attached to a vacuum line where they were sealed as before.

Solutions for viscometry were prepared in the drybox in a similar manner to the preparation of light scattering solutions. A specially designed inert-atmosphere viscometer was brought into the drybox where it was charged with the solutions and the diluting solvent. The viscometer was sealed and removed from the box and placed in a constant-temperature bath regulated at 11.40 ± 0.01 °C.

Instrumentation. Static and dynamic light scattering measurements were made as described previously[24] using instrumentation recently upgraded by Brookhaven Instruments to the BI2030AT version and controlled by an IBM PC/AT clone. Laser intensities at 514.5 nm ranged from 200 to 800 mW, and detector aperture settings were optimized for each set of samples to obtain a photocount rate of 10^5–10^6 counts per second for all concentrations at each molecular weight and temperature. Repeated measurement taken over a period of several months indicated no sample degradation over that period.

The weight-average molecular weight, M_w, the second virial coefficient, A_2, and R_G, the root mean squared z-average radius of gyration, were obtained from the static scattering data by the Zimm plot method. The scattering calibration constants used were as follows: refractive index of benzene $n = 1.5011$; refractive index increment[3] $(\partial n/\partial c)_T = 0.1065$ mL mg^{-1}; Rayleigh ratio (for benzene) $R_{vv}(\theta) = 2.30 \times 10^{-3}$ m^{-1} for $\lambda = 514.5$ nm and 25 °C.[25]

Dynamic light scattering data were obtained from the intensity–intensity autocorrelation function of the scattering. Angular dependence of the first cumulant at a minimum of eight angles provided a determination of the diffusion coefficients which were extrapolated to zero concentration. Hydrodynamic radii were calculated from the diffusion coefficients using the Stokes–Einstein relation.

The viscosity measurements were performed with a modified Cannon-Ubbelohde single-bulb viscometer. Figure 1 shows a diagram of the viscometer as modified to maintain an inert atmosphere over the solution. The manifold and solvent addition chamber utilize 2-mm ChemGlass high-vacuum stopcocks with Teflon O-rings. The volume delivered by the measuring column B was calibrated by weighing successive aliquots. Dry inlet gas was passed through a tube of molecular sieves to remove any trace of water. With stopcocks 1, 7, and 9 (S1, S7, and S9) open and all others closed, solvent can be moved from A to B under a low pressure provided by the inlet gas. The pressure is released by closing S1, S7, and S9 and opening S5, S10, S8, and S9 in that order; the aliquot of solvent is delivered to the dilution bulb by opening S6. In order to perform a single measurement one must first push the solution up the capillary by closing all the stopcocks except S1 and S5 and then release the pressure by closing S1 and S5 and opening S3, S4, and S10. Finally, one must allow the solution to flow back down at atmospheric pressure by opening S5. Viscosity measurements were typically repeated three times, and flow times were obtained with a repeatability of ±0.05%.

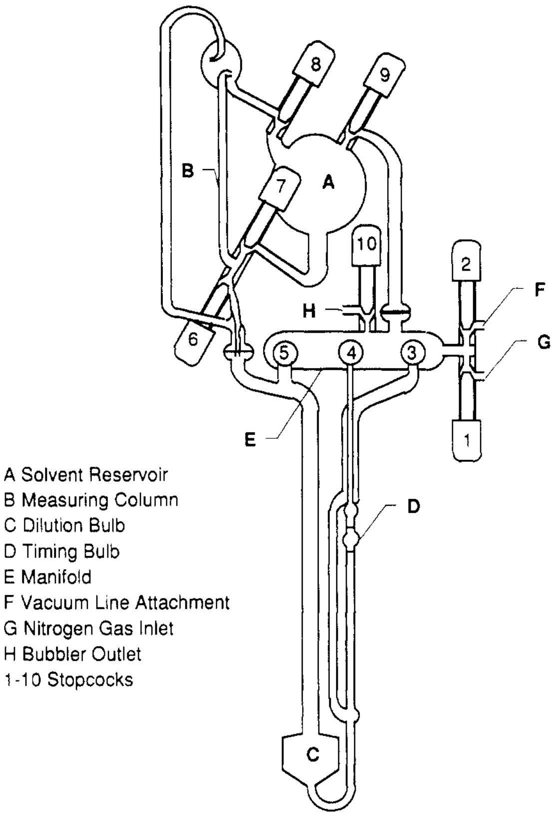

Figure 1. Schematic diagram of controlled-atmosphere viscometer used for dry viscometry measurements.

Results and Discussion

Static light scattering measurements were performed on four molecular weights of poly(2-vinylpyridine) using both dried and undried solvent. As shown in Table I all concentrations used were well below the overlap concentration. The first samples studied were 2.47×10^5 and 9.85×10^5 molecular weight P2VP's dissolved in benzene which was used without further purification. We collected data for these samples over a range of temperatures from 17 to 35 °C. Zimm plots were constructed and from these we obtained values of A_2, R_G, and M_w. We obtained an initial estimate of the Θ temperature by plotting A_2 against temperature. In Figure 2 the filled triangles are values of A_2M_w versus temperature for the 9.85×10^5 molecular weight polymer, and the apparent Θ value is just above 18 °C. Figure 3 is one Zimm plot of data acquired from the 9.85×10^5 molecular weight sample where the solvent has been used "as received" and the second virial coefficient is negative at 17 °C. Since the goniometer is thermostated to ±0.02 °C and as the slope of A_2M_w is quite steep near the Θ temperature, we could not account for this Θ value being 2 °C higher than literature values. This indicated a problem with sample quality or in sample preparation.

During the course of these investigations some samples showed irregular angular dependence in their scattering.

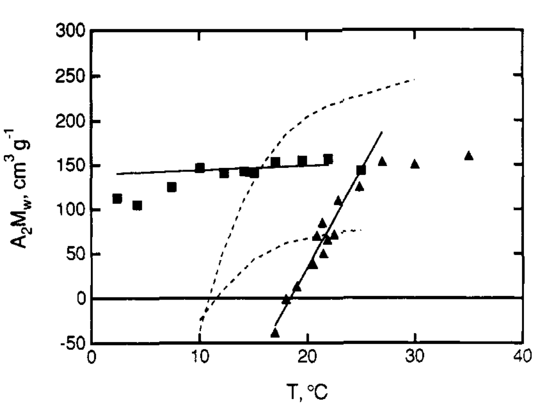

Figure 2. Product of second virial coefficient and molecular weight against temperature for 9.85 × 10^5 molecular weight P2VP in dried solvents (■) and the same polymer in solvent which was used "as received" (▲). Dashed curves represent data from ref 11 for a 1.96 × 10^6 and a 6.7 × 10^5 molecular weight P2VP.

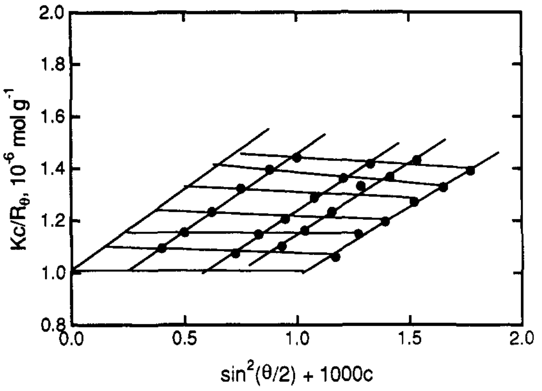

Figure 3. Static light scattering Zimm plot of 9.85 × 10^5 molecular weight P2VP at 18 °C in benzene used "as received".

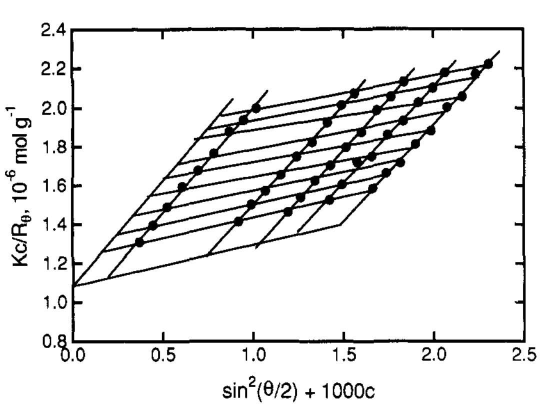

Figure 4. Zimm plot of 9.85 × 10^5 molecular weight P2VP in dried benzene at 4.26 °C.

Zimm plots showed that these samples had smaller slopes than the rest of the samples, and these samples were not used in the final analysis. Careful inspection of the seals of these samples revealed cracks in the glass, and continuous gravimetric analysis showed that these samples lost weight throughout the study. We corrected for the change in concentration, assuming the entire weight loss was due to solvent evaporation; however, the absorption of atmospheric water may have changed the solvent quality to give these results.

Two more sets of samples were made at the two lower molecular weights listed in Table I and gave irreproducible results for the most part. This may be expected as the molecules' radii are less than 3% of the wavelength used for the study. The 1.17 × 10^5 molecular weight sample however gave consistent A_2's and when these were plotted against the temperature, a Θ value of 22 °C was obtained. Because this Θ value was 4 °C higher than for the larger polymer, we were led to question the purity of the solutions. Both the polymer and the solvent used are hygroscopic and benzene is known to form an azeotrope of nearly 9% water by weight,[26] which corresponds to a relatively large mole fraction (0.3) for water. Although spectral grade benzene is labeled as having <0.01% water as measured by Karl Fischer titration, that purity is only specified for an unopened bottle. In using benzene "as received", without drying it, we presume that the solvent composition becomes dependent on the storage conditions of the solvent and even the humidity of the laboratory.

At this point we modified the sample preparation to rigorously dry all components and to ensure sample integrity. All manipulations were performed in a drybox as described earlier and the sealed cells were again weighed during the course of the experiments; samples which lost mass were not included in the analysis. The remaining rigorously dried samples showed no cloud points or unusual changes in scattering behavior down to the freezing point of the solutions. Data were collected on samples prepared in this manner for the three highest molecular weights over the temperature range 4.26–25.0 °C; the 9.85 × 10^5 molecular weight sample was also observed at 2.4 °C. When values of A_2M_w were plotted against temperature, we observed no significant decrease from 25 °C down to 10 °C. A small decrease seen at the lowest temperatures may be due to the residual water which the sodium/benzophenone drying agent was unable to scavenge[27] or perhaps it was simply a result of the increased experimental uncertainty for optical measurements at low temperature. Nonetheless, these data provide definitive proof that carefully prepared samples of P2VP in pure benzene do not constitute a Θ system at any experimentally accessible temperature.

The freezing point of benzene is 5.5 °C and therefore some explanation is required for the data we have obtained at 2.4 and 4.26 °C. The rigorous exclusion of dust from the samples is necessary for light scattering and doing this evidently removes nucleation sites for initiating crystallization. As a result we were able to maintain a temperature of 0.0 °C with both a solvent blank and a 9.85 × 10^5 molecular weight sample for 1 h without freezing either sample. When the temperature was lowered to −1.0 °C, the samples solidified suddenly, changing from a clear liquid to an opaque solid in less than 1 s, as would be expected for the freezing of a supercooled liquid. When the temperature was raised, the samples melted at 5.5 °C. Figure 4 is one example of data acquired on the supercooled samples at 4.26 °C which shows a positive virial coefficient for five concentrations of the 9.85 × 10^5 molecular weight polymer. The supercooling phenomenon may also contribute to the lower A_2M_w values at the low-temperature end of Figure 2.

Figure 2 shows A_2M_w against temperature for the 9.85 × 10^5 molecular weight sample. As stated previously, dry samples exhibit good-solvent behavior over the entire range covered by this study, while wet samples show an apparent Θ point near 18 °C. The dashed curves in Figure 2 represent data obtained by Matsushita et al.[18] for a 1.96 × 10^6 and a 6.7 × 10^5 molecular weight P2VP, both of which show an apparent Θ point at 11.4 °C. The shape of these two curves is qualitatively the same as that for our samples which had been prepared with benzene "as received". There is a steeply sloping region near the Θ point leading up to a plateau region which, for our "wet" samples, is at the same value as that of the rigorously

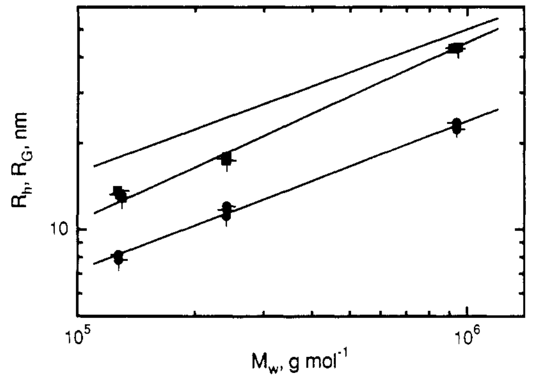

Figure 5. Radius of gyration as a function of molecular weight for dry benzene, interpolations to 10 (■-), 15 (-■), and 20 °C (■). The line indicated is the best fit to a power law dependence where $R_G \propto M_w^{0.62}$. The slope expected for Θ behavior ($R_G \propto M_w^{0.5}$) is drawn above for comparison. Hydrodynamic radius for P2VP in dry benzene at 10 (●-), 15 (-●) and 20 °C (●). The fitted line follows $R_h \propto M_w^{0.52}$.

dried samples. This shape of curve also appears in data presented by Dondos[11] in a plot of the Stockmayer–Fixman B parameter against temperature. The B parameter is also a measure of excluded volume and is directly proportional to A_2.[28] It may be important to note that the "order–disorder" transition observed by Dondos occurs in the region where the excluded volume is increasing the fastest as a function of temperature; it is possible that these observations have a common origin.

Similar effects should be detected in the dimensions of the polymers as temperature changes. Experimentally, the uncertainty associated with static light scattering determinations of R_G is quite large for the smallest molecular weights used in this study; however, the largest gave extremely reproducible results. We used Berry's analysis[29] of the static light scattering data to obtain values of R_G. Samples of the same molecular weight prepared with solvent used "as received" had R_G values that decreased from 42.3 to 34.8 nm as the temperature was lowered from 35 °C down to 17 °C, which is below the apparent Θ point. This coil shrinkage is roughly equivalent to that observed for polystyrene in decalin for temperatures ranging from the Θ temperature (19 °C) to 38 °C.[29] The dry samples of 9.85×10^5 molecular weight polymers showed no significant variation in their radii, which ranged from 42.2 to 44.4 nm, over the entire temperature range studied. In Figure 5, we have interpolated values of R_G and molecular weight for the dry samples at 10, 15, and 20 °C, the range over which others have reported Θ conditions, and our A_2 value is consistently in the good-solvent range of $(1.5 \pm 0.1) \times 10^{-4}$ cm^2 mol g^{-2}. The data are not consistent with a slope of 0.5 expected for Θ behavior.[23] In fact, the least-squares line shown has a slope of 0.62, which is even higher than the 0.588 expected for good solvents.[30] We note that for another good solvent, ethanol, the molecular weight exponent is also 0.62.[14]

Although we are primarily interested in elucidating the thermodynamics of this system, predictions can also be made for hydrodynamic properties. The hydrodynamic radius (R_h) is expected to scale as a power law of the molecular weight with an exponent ν. In Θ solvents, ν is 0.5 while in good solvents the value reaches 0.55.[31] Measurements of R_h and viscosity here yield similar results which differ primarily in degree. Figure 5 shows the scaling of R_h, calculated from dynamic light scattering diffusion measurements, with molecular weight at 10, 15, and 20 °C for the dry P2VP/benzene samples. The molecular weight exponent of 0.52 is independent of temperature and is smaller than the theoretical prediction. This was not as strong an indication of good-solvent conditions as we had expected having found the static exponent (0.62) to be larger than predicted.

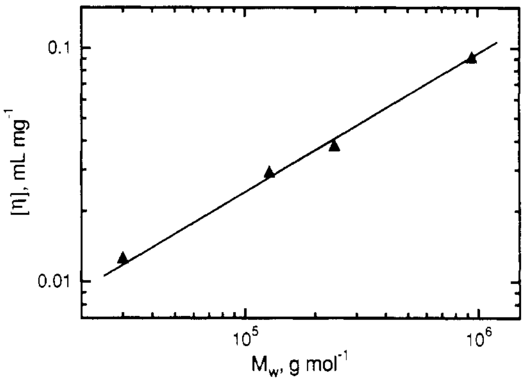

Figure 6. Molecular weight dependence of intrinsic viscosity of P2VP in dry benzene at 11.4 °C (▲), the lowest of the reported Θ temperatures.[18] The line follows $[\eta] \propto M_w^{0.58}$.

Intrinsic viscosity results, shown in Figure 6, were acquired at 11.40 °C, which was the lowest previously reported Θ temperature. The HMS exponent, a, for molecular weight dependence is 0.58, which is consistent with $\nu = 0.52 \pm 0.01$ if, as predicted by theory, $a = 3\nu - 1$. While most of the reported HMS exponents are in the range 0.62–0.73 for P2VP in good solvents,[8,12,14,15,17] values as low as 0.58 have been obtained previously by Arichi et al. for dioxane at 25 °C.[8] To see if dioxane might be a Θ solvent, we prepared a light scattering solution of P2VP in dioxane distilled directly from sodium/benzophenone and did not observe a cloud point before the sample solidified near its freezing point of 11.8 °C.

Previous work on this system and on solutions of polymers in binary solvents has shown different Θ temperatures resulting from the effects of preferential adsorption.[11,12,32,33] One explanation which has been proposed is that the molecular weight dependence of [η] is sensitive to intramolecular interactions, while A_2 is more sensitive to intermolecular interactions.[33] Specific interations (i.e., hydrogen bonds) are distinguished from preferential solvation arising from two χ parameters in a binary solvent. Nevertheless, there may well be a difference between inter- and intramolecular interactions in our P2VP system when water is present due to the long-range contacts mediated by hydrogen bonds. By removing water from the solvent we can suppress these interactions.

Taken together these data indicate that benzene is a good solvent for P2VP with very few remaining inconsistencies in the results. The scaling exponents for the radius of gyration and the hydrodynamic radius are, respectively, above and below their theoretically predicted values for good solvents. We suspect that even with the best purification efforts, some residual water complicates this system. Nonetheless, the intrinsic viscosity measurements are in agreement with the dynamic light scattering results, which indicates that these phenomena manifest common underlying features of this system.

Conclusion

These experiments show that when poly(2-vinylpyridine) is dissolved in carefully dried benzene and precautions are taken to ensure sample dryness, pure benzene is not a Θ solvent for P2VP. When these precautions are taken we find that $A_2 > 0$ for all temperatures between 25 and 2.5 °C. The implication that benzene is a good solvent for P2VP is further supported by dynamic light scattering and intrinsic viscosity measurements. On the other hand, an apparent Θ temperature near 18 °C can be observed in samples prepared without special precautions to rigorously dry the solvent.

It is reasonable that any trace water present in this nonpolar solvent will interact in a very specific way with the basic pyridine ring, and this will, as we have shown, affect the observable behavior. Unusual behavior seen for this polymer in other solvents has previously been attributed to such interactions.[10,11,21] The mechanism by which this polymer–solvent system mimics a Θ system is still unclear. It may be that hydrogen bonds tie together widely separated monomer units or that the existence of dipoles formed by the close association of pyridine rings and water molecules gives an ionomeric effect in the low dielectric solvent leading to intermolecular aggregation. It is, however, necessary that studies relying on the thermodynamic Θ condition for this system will need to be reviewed and perhaps their conclusions reevaluated.

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Registry No. P2VP, 25014-15-7; benzene, 71-43-2.