Question 1

The fundamental equation to use is

$$\frac{Kc}{R_\theta} = \frac{1}{M_\mathrm{w}}\left[1 + \frac{1}{3}q^2 R_\mathrm{g}^2\right] + 2Bc$$

where $q = \frac{4\pi n}{\lambda_0}\sin\left(\frac{\theta}{2}\right)$.
(a) The extrapolation to $\theta = 0$ allows us to determine B and thus the quality of the solvent from the slope of the plot. We see that for solvent B $B > 0$ and for solvent A $B = 0$. Per $B = \left(\frac{1}{2} - \chi\right)\bar{V}_1 \frac{N^2}{M^2}$, we see that solvent B is the better solvent.

(b) As $B = 0$ from the Zimm plot, solvent A is a theta solvent.

(c) Using the extrapolation to $c = 0$, we can find R_g per

$$0.3355 \cdot 10^{-6}\sin^2\left(\frac{\theta}{2}\right) + 1.006 = \frac{1}{M_\mathrm{w}}\left[1 + \frac{1}{3}\frac{16\pi^2 n^2}{\lambda_0^2}\sin^2\left(\frac{\theta}{2}\right)R_\mathrm{g}^2\right]$$

This gives $M_\mathrm{w} = 9.94 \cdot 10^5$ g/mol and $R_\mathrm{g} = 26.8$ nm.

(d) Repeating the same procedure as (d) gives $M_\mathrm{w} = 1.01 \cdot 10^6$ g/mol and $R_\mathrm{g} = 47.3$ nm.

(e) The coil expansion factor is $\frac{R_\mathrm{g}}{R_{\mathrm{g},\theta}} = \frac{47.3}{26.8} = 1.76$.

(f) The characteristic ratio is given by

$$C_\infty = \frac{\langle h^2\rangle_o}{nl^2} = \frac{6R_{\mathrm{g},\theta}^2}{nl^2}$$

We can determine n from $n = 2N = 2\frac{M_\mathrm{w}}{M_0} = 1.93 \cdot 10^4$. As $l = 1.54$ Å, we have

$$C_\infty = \frac{6 \cdot (26.8\ \mathrm{nm})^2}{1.93 \cdot 10^4 \cdot (0.154\ \mathrm{nm})^2} = 9.42$$

(f) We can evaluate the radius of gyration using

$$R_\mathrm{g} = \left(\frac{C_\infty n}{6}\right)^{0.5} l = \left(\frac{9.42 \cdot 1.93 \cdot 10^4}{6}\right)^{0.5} \cdot 0.154\ \mathrm{nm} = 26.8\ \mathrm{nm}$$

By construction, this was calculated based on the solvent a, a theta solvent, as theta solvents have the unperturbed nature that is needed for this calculation.

Question 2

(a) We know we can relate osmotic pressure to molecular weight by

$$\frac{\Pi}{cRT} = \frac{1}{M_{\mathrm{n}}} + Bc$$

As we don't have the necessary data to make an extrapolation to $c = 0$, we will assume that contribution from the Bc term is negligible.

(b) M_{n} is evaluated by

$$M_{\mathrm{n}} = \frac{cRT}{\Pi} = \frac{0.00133\ \frac{\mathrm{g}}{\mathrm{cm}^3} \cdot 303.15\ \mathrm{K} \cdot 82.1 \frac{\mathrm{cm}^3\ \mathrm{atm}}{\mathrm{K\ mol}}}{300\ \mathrm{dyne/cm}^2 \cdot \frac{1\ \mathrm{atm}}{1.013 \cdot 10^6\ \mathrm{dyne/cm}^2}} = 1.12 \cdot 10^5\ \mathrm{g/mol}$$

(c) If the solvent is a good solvent, $B > 0$ and we can assume that the Bc term will have a positive contribution to the osmotic pressure. The value computed in (b) is thus lower than the true molecular weight of the polymer in order to account for the contribution of Bc.

(d) As indicated in the previous parts, the value of the molecular weight obtained is the number-averaged molecular weight M_{n}.

(e) From our formula for osmotic pressure, if c is constant, the source of the increase can come from either the M_{n} term or the B term. Our possible options are the polymer has a lower molecular weight, the solvent quality for that polymer is better than for the first polymer, or some combination of the two along with the possibility of M_{n} being greater of the solvent quality being lower as long as the other terms counterbalance it.

Question 3

(a) We know that the critical composition is given by

$$\phi_{\text{c,PE}} = \frac{N_{\text{PCHE}}^{1/2}}{N_{\text{PE}}^{1/2} + N_{\text{PCHE}}^{1/2}}$$

where the values of N are in the Flory-Huggins lattice. We note that the partial volumes of PCHE and PE are given by, along with the reference

$$\begin{aligned}\bar{V}_{\text{PCHE}} &= \frac{110\text{ g/mol}}{0.92\text{g/cm}^3} = 119.6\text{ cm}^3/\text{mol}\\ \bar{V}_{\text{PE}} &= \frac{28\text{ g/mol}}{0.784\text{ g/cm}^3} = 35.7\text{ cm}^3/\text{mol}\\ \bar{V}_{\text{ref}} &= \frac{56\text{ g/mol}}{0.784\text{ g/cm}^3} = 71.4\text{ cm}^3/\text{mol}\end{aligned}$$

We evaluate the real value of $N_{\text{n,PCHE}}$ to be 23.6. Converting to the Flory-Huggins lattice is done by

$$N_{\text{PCHE}} = N_{\text{n,PCHE}} \cdot \frac{\bar{V}_{\text{PCHE}}}{\bar{V}_{\text{ref}}} = 39.5$$

We then use the above equation for $\phi_{\text{c,PE}}$ to find that $N_{\text{PE}} = 88.9$. Converting this to M_{n} gives

$$M_{\text{n,PE}} = N_{\text{PE}}\frac{\bar{V}_{\text{ref}}}{\bar{V}_{\text{PE}}} \cdot M_0 = 88.9 \cdot 2 \cdot 28\text{ g/mol} = 4.98 \cdot 10^3\text{ g/mol}$$

(b) We evaluate χ_{c} per

$$\chi_{\text{c}} = \frac{1}{2}\left(\frac{1}{N_{\text{PE}}^{1/2}} + \frac{1}{N_{\text{PCHE}}^{1/2}}\right)^2 = 0.035$$

(c) As PCHE is denser than PE, the phase rich with PCHE (phase 1, $\phi_{\text{PE},2} = 0.15$) will be at the bottom of the beaker.

(d) We are given that the total mass of the sample is 20 g and $\phi = 0.3$. We can perform balances on the total mass and volume fraction to yield the linear system

$$\begin{aligned}V_{\text{PE}}\rho_{\text{PE}} + V_{\text{PCHE}}\rho_{\text{PCHE}} &= 20\text{ g}\\ \frac{V_{\text{PE}}}{V_{\text{PE}} + V_{\text{PCHE}}} &= 0.3\end{aligned}$$

Solving this yields

$$\begin{aligned}V_{\text{PE}} &= 6.82\text{ cm}^3\\ V_{\text{PCHE}} &= 15.9\text{ cm}^3\\ m_{\text{PE}} &= \rho_{\text{PE}}V_{\text{PE}} = 5.35\text{ g}\\ m_{\text{PCHE}} &= \rho_{\text{PCHE}}V_{\text{PCHE}} = 14.6\text{ g}\end{aligned}$$

(e) We can perform balances on the overall amounts of PE and PCHE along with balances on each phase. This yields the four equations

$$\begin{aligned} V_{\text{PE},I} + V_{\text{PE},II} &= V_{\text{PE}} \\ V_{\text{PCHE},I} + V_{\text{PCHE},II} &= V_{\text{PCHE}} \\ -0.85V_{\text{PE},I} + 0.15V_{\text{PCHE},I} &= 0 \\ -0.35V_{\text{PE},II} + 0.65V_{\text{PCHE},II} &= 0 \end{aligned}$$

Solving this yields

$$\begin{aligned} V_{\text{PE},I} &= 2.38\ \text{cm}^3 \\ V_{\text{PE},II} &= 4.44\ \text{cm}^3 \\ V_{\text{PCHE},I} &= 13.5\ \text{cm}^3 \\ V_{\text{PCHE},II} &= 2.39\ \text{cm}^3 \end{aligned}$$