Fractional Precipitation of Star Poly(ethylene oxide)

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Introduction

The need for monodisperse samples of poly(ethylene oxide) star molecules has instigated a study into possible fractionation methods to obtain such samples from an initially polydisperse preparation of these molecules. The molecules under study were prepared using the core-first method described elsewhere.[1] As determined by GPC−light scattering, these molecules have a polydispersity index ranging from 2 to 15 for the various samples synthesized. Because the arms of the star molecules are synthesized via anionic polymerization of ethylene oxide initiated by divinylbenzene cores, the poly(ethylene oxide) arms of these molecules should all be of the same molecular weight. Therefore it is believed that the polydispersity is a result of the cores growing at different rates resulting in a population of cores having a broad distribution of active carbanion sites from which the arms are subsequently grown.

The method for fractionation currently under investigation is that of classical temperature manipulation. The basis for temperature fractionation lies in the liquid lattice theory of polymer solutions developed by Flory[2] for linear polymer molecules. While multiarmed star molecules cannot be fitted into the logic of Flory's model, we thought it would be of interest to examine experimentally how star-shaped PEO molecules compared to linear PEO. Fractionation of linear PEO using organic Θ solvents does not work if Θ is much below the crystalline melting point (66 °C) and thus one would be forced to seek high temperature Θ solvents. Instead advantage has been taken of PEO's inverse solubility−temperature behavior in aqueous solutions.[3] The lower critical solution temperature (LCST) of linear PEO in water is 95 °C for PEO of infinite molecular weight and increases above the boiling point of water as molecular weight decreases. The LCST is systematically lowered by the addition of salts to water.[4]

We sought to obtain star PEO of more narrow molecular weight distribution by precipitation fractionation in aqueous solutions of sodium carbonate. The precipitation temperature of star PEO in pure water was determined along with its dependence on salt concentration and compared with data found by other investigators on linear PEO. This information was then used as a basis for fractionation of star PEO in aqueous solutions of sodium carbonate (Na_2CO_3).

Experimental Section

Dependence of the Cloud Point of Star PEO on Salt Concentration in Aqueous Solutions. The characteristics of the PEO star molecules which were studied are given in Table 1. One percent (w/v) solutions of star 3510 were prepared. One milliliter was placed in a capped test tube and immersed in an oil bath. The temperature was slowly raised until the solution became cloudy. These experiments were run using ion-free MilliQ water as well as solutions of sodium carbonate, potassium chloride, and sodium phosphate at various concentrations. The results were then compared with those of Bailey and Callard[4] for linear PEO.

Table 1. PEO Star Molecules: Characteristics

code	source	$M_w{}^c$	$M_{arm}{}^d$	$f = M_w/M_{arm}{}^e$
3510	*a*	350 000	5 200	67
73	*b*	173 000	10 000	17

[a] Gift of Dr. Paul Rempp, Centre de Recherches sur les Macromolecules, Strasbourg, France. [b] Purchased from Shearwater Polymers, Inc., Huntsville, AL. [c] Weight-average molecular weight as determined by GPC/LS. [d] Arm molecular weight as reported by Dr. Rempp or Shearwater Polymers Inc. [e] Number of arms.

Fractionation of PEO Star Molecules. Once it was determined that star PEO, like linear PEO, will precipitate in aqueous salt solutions, it was decided to determine the molecular weight dependence of this precipitation. A 1% solution of star 073 in 0.375 M sodium carbonate was placed in a water bath and the temperature raised until the cloud point was reached. The solution was then left undisturbed at this temperature overnight or longer until the two phases were separated. The supernatant was then poured off and placed back into the water bath. The temperature of the bath was raised again until the next cloud point was reached. The procedure was repeated until no appreciable amount of polymer was left in the supernatant phase. The gel phase at each step was redissolved in water and analyzed using gel permeation chromatography (GPC) in series with light scattering (LS). The GPC used was a Waters Model 150C containing two Tosohaas TSK-gel columns in series, G6000PW and G4000PW. The GPC eluate from the columns pass through a Wyatt Dawn Model F laser photometer and then through the refractive index detector contained within the Model 150C system. Voltage measurements taken from the detectors are recorded every second and converted to light intensity and refractive index measurements, respectively. The differential refractive index increment for the PEO stars is assumed to be equal to that of linear PEO, since the weight fraction of PEO is greater than 0.95. All calculations were made through ASTRA, a software package designed for use with the Wyatt Dawn Model F, which is run on a CUI 386 PC.

While these experiments clearly demonstrate that higher molecular weight star PEO polymers do precipitate at lower temperatures than do lower molecular weight star molecules, these successive fractionations did not lead to monodisperse fractions. This result is not surprising considering that according to theory, while the highest molecular weight species is more predominant in the more concentrated phase, all species are present in both phases. Therefore we decided to undertake a rigorous "pyramid" of fractionation based on the work of Thurmond and Zimm.[5] This fractionation method is based on combining supernatants and gels, which have similar molecular weights, taken from the successive fractionation of a sample as described above. Each of these newly created samples then undergo one cloud point separation. Again gels and supernatants of similar molecular weights are combined and the process is repeated. Using such a scheme of combining successive gels and supernatants, we hoped to achieve a polydispersity index closer to unity. For all fractionations the initial polymer concentration was brought to 0.5% PEO concentration and 0.375 M Na_2CO_3 by concentrating the solution using an Amicon stirred ultrafiltration cell with a PM10 membrane and by adding the necessary quantity of a 2.0 M Na_2CO_3 solution.

Results and Discussion

Cloud Point Dependence on Salt Concentration in Aqueous Solutions. The results of these experiments are shown in Figure 1. A 1.0% solution of linear PEO of molecular weight 200 000 or greater precipitates at 95 °C in ion-free water.[4] For the PEO star molecules at zero salt concentration, no cloud point was reached,

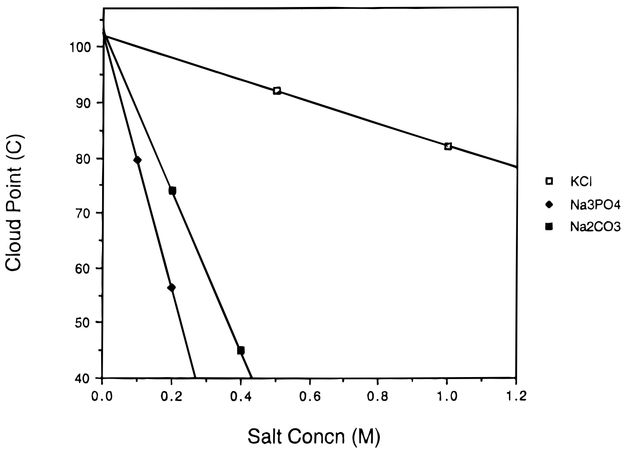

Figure 1. Cloud point of star 3510 as a function of salt concentration. PEO concentration is 1 wt %.

Table 2. Samples Obtained After Combining the Gels and Supernatants from Star 73 and Refractionating

Mw	mass frac	Mw	mass fract	Mw	mass frac
960 000	0.044	393 000	0.028	248 000	0.03
728 000	0.013	381 000	0.014	219 000	0.057
538 000	0.016	349 000	0.041	189 000	0.096
508 000	0.002	286 000	0.004	185 000	0.038
455 000	0.038	278 000	0.039	166 000	0.414
403 000	0.049	270 000	0.076		

even after raising the temperature to 100 °C, so the data were used to extrapolate one. The addition of salts does indeed lower the cloud point temperature, with Na_3SO_4 having the greatest effect and KCl having the least. The same trends were observed by Bailey and Callard using linear PEO.[4]

Fractionation of Star 073. The first cloud point of star 073 occurred at 46 °C and resulted in a gel with a weight-averaged molecular weight equal to 423 000 and a polydispersity index of 2.05. After six more successive fractionations of the supernatant, our last gel precipitated at 54 °C and had a molecular weight of 202 000 and a polydispersity index of 1.31. After this, we found there was not enough polymer left in our initial 100 mg sample to collect any more fractions. As stated earlier, these results clearly show that higher molecular weight star molecules precipitate out of solution at lower temperatures than do lower molecular weight PEO star molecules. The molecular weights, polydispersity indices, and mass fractions of the final samples attained after combining and refractionating the gels and supernatants of the first fractionation are summarized in Table 2. By using this method, we were able to more cleanly separate out the higher molecular weight samples from the solution, with the molecular weight of our highest molecular weight sample being 960 000. However, we were unable to obtain samples with a polydispersity index less than 1.2.

Cloud Point Dependence on Molecular Weight of the Star Polymers. A plot of the cloud point temperature as a function of molecular weight of the star PEO polymers is shown in Figure 2. These data were collected during the second attempt at fractionation described above. Bailey and Callard found that, for linear PEO, at molecular weights greater than 50 000 and concentrations greater than 0.3% the upper consulate temperature becomes independent of both variables.[4] These facts in themselves are at variance with the theory of fractionation as presented for example in ref 2, Chapter 13, since the theory requires that the consulate temperature approach the Θ temperature as molecular weight goes to infinity and that the critical concentration should move to progressively lower values as molecular weight increases. While our results do not show this same insensivitity starting as low as 50 000, we do see the dependence of cloud point on molecular weight diminish greatly once the molecules exceed around 250 000 g/mol. This discrepancy is most likely due to the branching architecture of the star molecules and the fact that while the total molecular weight might be large, the molecule is made up of linear PEO arms whose molecular weights are less than 10 000.

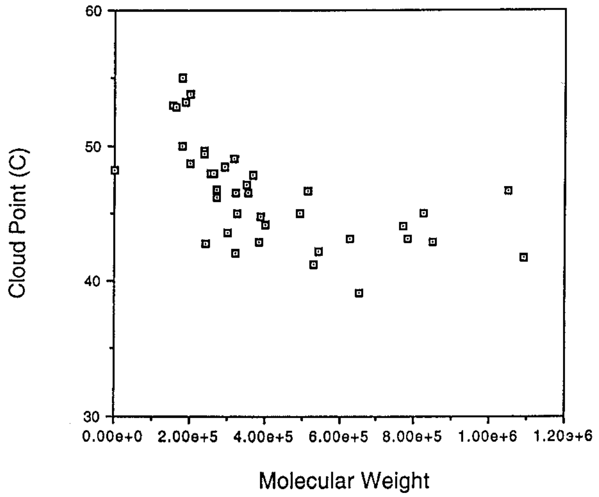

Figure 2. Cloud point of PEO star molecules as a function of molecular weight. PEO concentration is 0.5 wt % in 0.375 M Na_2CO_3.

Instead of comparing the precipitation behavior of PEO star molecules with linear PEO based on molecular weight, more insight might be gained by comparing the two using intrinsic viscosity as a measure of their respective sizes. Using this method, Bailey and Callard showed that in salt-free solutions of linear PEO the cloud point initially decreases as intrinsic viscosity increases but then becomes independent of molecule size when intrinsic viscosity is greater than 1 dL/g.[4] Because star molecules are expected to have lower intrinsic viscosities than linear polymers of equivalent molecular weight, we would expect star PEO macromolecules to precipitate at higher temperatures than would their linear molecular weight counterparts.

References and Notes

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