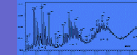




Charge-Induced break-up of multiply charged Poly(dimethylsiloxane) and poly(ethylene glycol) chains

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Overview

•Polymers are difficult to characterize based on mobility alone due to the many configurations that arise (i.e stretched to globular). Mass analysis of electrospray ions produces also exceedingly complex spectra due to the presence of very many masses and charges that turn the spectrum into a continuum.

•Tandem use of a Differential Mobility Analyzer (DMA) and a mass spectrometer (MS) simplifies the analysis of compact polymers ions, but not for the more common linear configurations (mass/charge & mobility are linear with each other). The question of when and how a polymer ion can be spherical is thus related to the viability of inferring polymer mass distributions by DMA-MS.

•Studies of single mass-selected polymers of PDMS & PEG electrosprayed into tandem DMA-MS reveal the presence of near spherical shaped nanodrops of 2 to 9 nm above a critical mass $m^*(z)$, where z is the charge. For $m < m^*$, polymers unfold & stretch abruptly to allow a higher size to charge ratio.

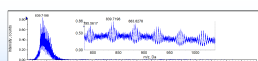
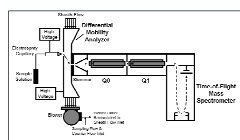
Introduction

•In a preceding paper, Ude et al.¹ carried studied the electrical mobility Z of mass-selected PEG chains as a function of their mass and charge. They were able to investigate globular and stretched regions up to $m/z=3000$ and $z=5$.

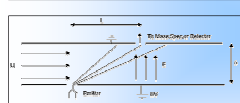
•For each given charge z , they found a characteristic critical mass m^* below which a change away from globular shape occurs. They saw that m^*/z^2 was fixed, as in the Rayleigh criterion¹¹, where it is proportional to the ratio γ/ρ =(surface tension)/density, of the polymer. Although interesting, the criterion fails to give correct value of bulk value of γ/ρ by a constant of 2/3. They hypothesize that this anomaly is due to the fact that PEG is solid.

•Here, a flat DMA^{III} coupled with a QSTAR MS with m/z of up to 40,000 and resolving power of 10000 are used. We study ion shape over this much wider mass range for samples of PDMS and PEG. We see a wider range of structures and provide an explanation for their peculiarities and transitions from fully stretched to spherical.

Methods



Mass Spectra (PEG 14kDa)



Mobility Spectra (PEG 14kDa)

•Charged polymer drops are produced from a 10-100 μ M PDMS (or PEG) solution in 50/50 toluene/methanol or water/methanol with addition of 10-30mM of ammonium acetate or dimethylammonium formate.

•The sample is raised to -2kV floating over the DMA, pushed through a capillary needle and electrosprayed into a flat DMA through its inlet.

$$\frac{L}{U} = t_L = t_d = \frac{\delta}{ZE} = \frac{\delta^2}{ZV_{DMA}} \quad Z = \frac{\delta^2 U}{LV_{DMA}}$$

Results

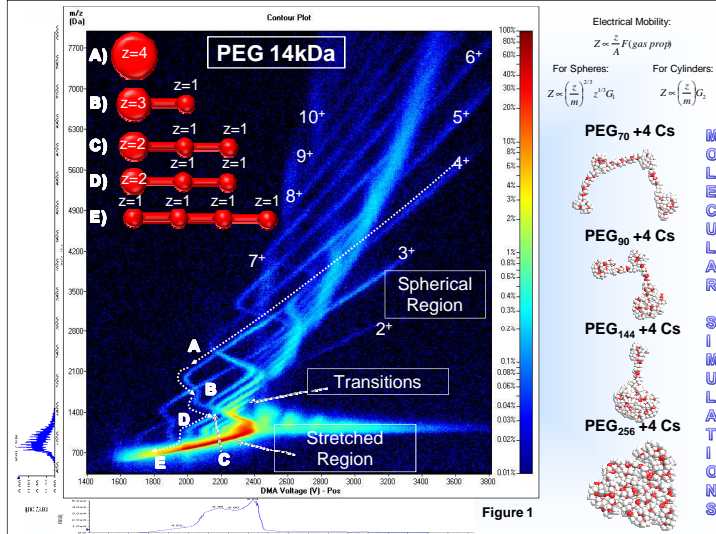


Figure 1

Electrical Mobility:
 $Z = \frac{z}{A} F(\mu_{gas} \text{proj})$
For Spheres:
 $Z = \left(\frac{z}{m}\right)^{0.5} \frac{1}{G_1}$
For Cylinders:
 $Z = \left(\frac{z}{m}\right) \frac{1}{G_2}$

MOLECULAR SIMULATIONS
PEG₇₀ +4 Cs
PEG₉₀ +4 Cs
PEG₁₄₄ +4 Cs
PEG₂₅₆ +4 Cs

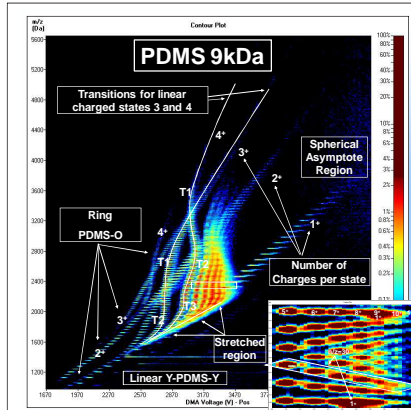


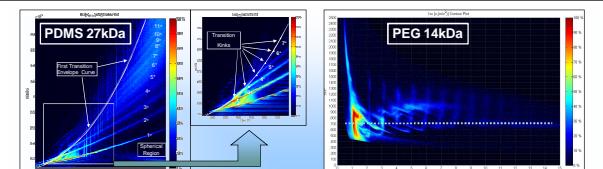
Figure 2

•Figures 1 & 2. Contour Plot of DMA voltage (V_{DMA}) vs. m/z vs. Intensity. Through mobility and mass over charge, one can study the different transitions and shapes from stretched to spherical as well as different charged states and polymer configurations (i.e. ending groups vs. ring structures).

•Charged clusters remain spherical as long as the stress caused by the repulsion of the charges does not overcome the surface tension that holds the liquid/solid together. When this equilibrium fails, some of the charge tends to be expelled from the parent droplet, as in the Rayleigh limit¹. This effect corresponds here to the unfolding of part of the polymer with charge attached to it.

Number of monomers per charge:
$$n/z = \frac{m/z - m_{endgroup}}{m_{monomer}} = f(m/z, z)$$

Conclusions

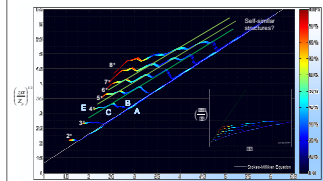


•For a given z , there is a critical mass $m^*(z)$ below which the polymer loses sphericity and rather undergoes a transition in which some of the charges are left out while the rest group together (First Transition, T1). $m^*(z)$ is given by simple manipulation of Rayleigh's charge fission equation yielding:

$$q_R = ze = 8\pi\sqrt{\gamma\rho_0 R^3} \Rightarrow \frac{m^*}{z^2} = \frac{\rho_{pol} \epsilon^2}{48\pi^2 \gamma \epsilon_0} = \text{const}$$

Charged state	m/z (Da)	m^*/z^2 (Da)	γ_{pol} (dyn/cm)	γ_{cal} (dyn/cm)
2+	2363/1146	1181/573	9.50/22.52	19.39/45.97
3+	3457/1839	1152/613	9.74/21.05	19.89/42.97
4+	4550/2596	1137/646	9.87/19.89	20.14/40.59
5+	5680/3450	1136/690	9.89/18.71	20.17/38.17
6+	6873/4206	1145/701	9.80/18.41	20.00/37.57
7+	8017/4970	1145/710	9.80/18.18	20.01/37.10
Mean		1145.7	9.77/19.67	19.93/40.15

¹¹ is the calculated surface tension supposing that the division occurs at 70% of Rayleigh's limit charge. Bulk density values used are -970kg/m³ for PDMS and -1150kg/m³ for PEG. The bulk surface tension is 19-21 dyn/cm for PDMS and 40 dyn/cm for PEG.



•Mobility Z and m/z have been determined separately and they both depend on z . Using computational software (see poster 662), one can disentangle the snarl to separate m and z .

•Figure shows the unscrambled data for PEG. The plot variables are specifically chosen by the fact that for a sphere of a given diameter d , both $(z/z)^{1/2}$ and $m^{1/3}$ are linear with d . The spherical region agrees excellently with the line labeled Stokes-Millikan (S-M) equation.

•Spheroidal self-similar configurations appear for other transitions and differ from S-M by a constant that corresponds to a stretched segment that leaves the sphere.

•Mobility of fully stretched follow linear m/z law.

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