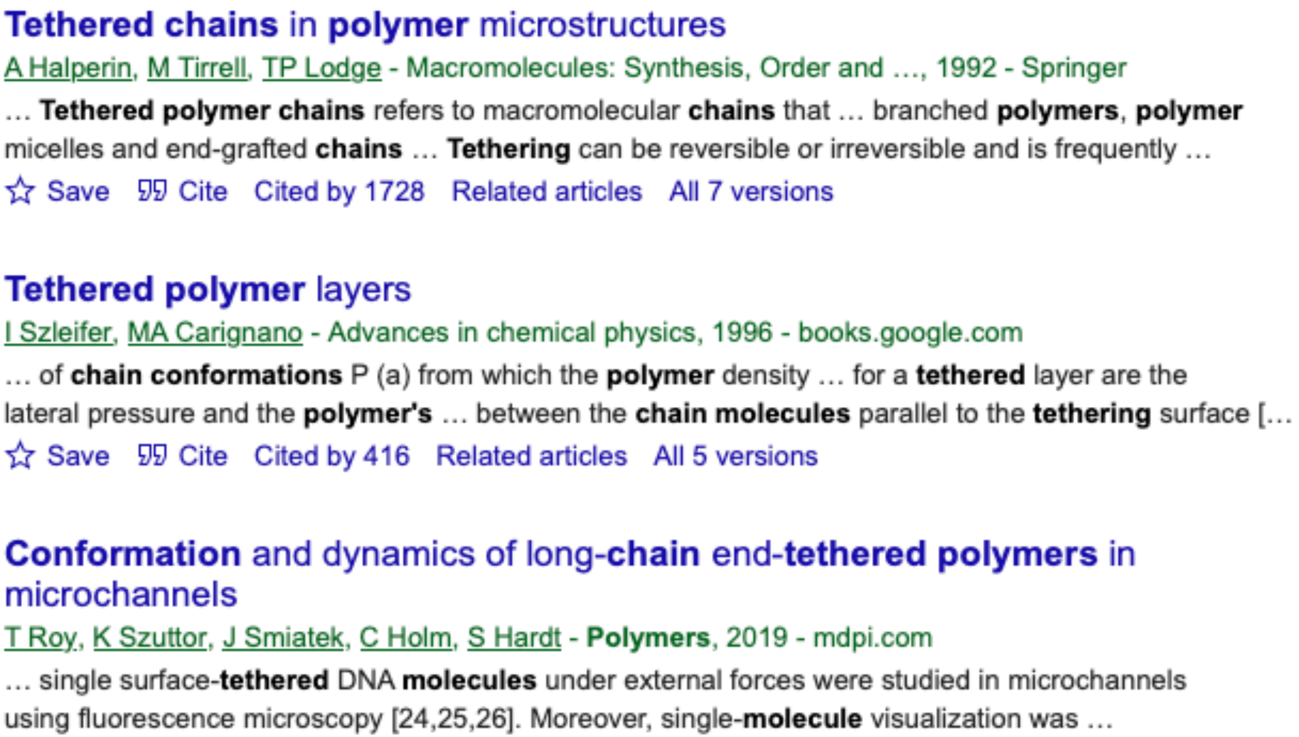
b) I list some of the problems I can see.
i) He is studying the impact of cations on the structure, then he uses surface grafted cations to attach the chains to the surface. Do you think that these cations are any different than the cations he is exploring? In what way are they different in terms of electrostatics?
ii) Bonding of chains to surfaces is a topic that has been studied quite a bit and it is know to distort the structure. I think you could fine 10's of papers on this subject, but this is ignored in this study.
iii) there is not perceptible or obvious difference between any of the micrographs yet we are to believe that the Fiberapp program can somehow distinguish between them and come up with trends that match the expected results exactly. If you read the fiber app paper and look at their YouTube videos on how to use the program it involves extensive image manipulation that is not analytic. The original micrographs do not show fibers at all. So, it isn't clear that if two people worked with the same micrograph they would get the same result. This seems to be a reproducibility problem.
iv) There is not sufficient sample size in one micrograph to make an assessment of persistence. IT would take hundreds of micrographs to get something comparable to a light scattering or neutron scattering measurement on the solution sample.
v) we know that there are chain end effects that are significant. He should be able to observe this but he hasn't mentioned it.
Vi) Figure 4 should have error bars calculated from the data. Otherwise it is not possible to tell if the results are significant.
There are many more problems.
Here are a few papers from google scholar on structural changes when you bond a polymer to a surface.



**Tethered chains** in **polymer** microstructures

A Halperin, M Tirrell, TP Lodge - Macromolecules: Synthesis, Order and …, 1992 - Springer

… **Tethered polymer chains** refers to macromolecular **chains** that … branched **polymers**, **polymer** micelles and end-grafted **chains** … **Tethering** can be reversible or irreversible and is frequently …

**Tethered polymer** layers

I Szleifer, MA Carignano - Advances in chemical physics, 1996 - books.google.com

… of **chain conformations** P (a) from which the **polymer** density … for a **tethered** layer are the lateral pressure and the **polymer's** … between the **chain molecules** parallel to the **tethering** surface [...

**Conformation** and dynamics of long-**chain** end-**tethered polymers** in microchannels

T Roy, K Szuttor, J Smiatek, C Holm, S Hardt - **Polymers**, 2019 - mdpi.com

… single surface-**tethered** DNA **molecules** under external forces were studied in microchannels using fluorescence microscopy [24,25,26]. Moreover, single-**molecule** visualization was …

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**Molecular** motion of isolated single **polymer chains tethered** on a fresh surface of poly (tetrafluoroethylene)

K Yamamoto, S Shimada, K Ohira, M Sakaguchi… - …, 1997 - ACS Publications

… The flexibility of the **tethered polymer chains** having the tail **conformation** can be elucidated by estimating an extent of motionally averaging of anisotropic g values with temperature. …

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Protein adsorption on **tethered polymer** layers: effect of **polymer chain** architecture and composition

I Szleifer - Physica A: Statistical Mechanics and its Applications, 1997 - Elsevier

… The theory has been shown to provide accurate predictions for both thermodynamic and **conformational** properties in **tethered polymer** layers as compared with experimental …

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Relaxation dynamics of nanoparticle-**tethered polymer chains**

SA Kim, R Mangal, LA Archer - Macromolecules, 2015 - ACS Publications

… PI block, it is possible to obtain one of the first quantitative measurements of the fraction of PI **chains** that adopted loop versus bridge **conformations** in a microphase-separated triblock. …

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Transitions of **tethered polymer chains**: A simulation study with the bond fluctuation lattice model

J Luettmer-Strathmann, F Rampf, W Paul… - The Journal of chemical …, 2008 - pubs.aip.org

… of **polymers**. It is of crucial importance in understanding the phase diagrams of **polymer** … in good solvent, where the **conformations** of a **tethered chain change** from "mushroom" to "…

☆ Save 99 Cite Cited by 110 Related articles All 10 versions

[HTML] **Tethered polymer chains**: surface chemistry and their impact on colloidal and surface properties

EPK Currie, W Norde, MAC Stuart - Advances in colloid and interface …, 2003 - Elsevier

… the parameters that determine the **polymer conformation**. … the free energy of a **polymer chain** is assumed to consist of the … and the **conformational** entropy (elasticity) of the **polymer chain**.…

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c) Explain the Odijk-Skolnick-Fixman (OSF) theory and its prediction for the counter ion contribution to chain persistence and the prediction for counter ion condensation. Do Li's results agree with this theory? (Define the Manning number, Bjerrum length, Debye screening length, charge density along chain, electrostatic persistence length.)

The OSF prediction is that the electrostatic persistence length will follow 1/c where c is the counter ion concentration, that is, it follows debye length^2. Li shows this in Figure 6. The plots are log lp vs log of the Debye length and the slope is -2 which is exactly what the OSF theory predicts. Error bars would go a very long way in making this believable. He should have error bars in y and in x. Generally, to see a power-law you would want a decade in both parameters, here he has that in Lpe but not in the Debye length. Insufficient data to be certain he has the power law.

## d) Explain why the polyelectrolyte chain first collapses and then expands as counter ion concentration is increased, Figure 4. What is the Zeta potential and how is it determined, Figures S6 in the supplemental? How does this plot coupled with Figure 4 support your explanation for why collapse and reexpansion occurs?

The Manning theory of counter ion condensation is that counter ions add to the chain in proportion to their concentration until the parameter “u” reaches 1 where kT and the electrostatic potential balance and you have a fixed zeta potential but keep adding counter ions. The impact of these is to stiffen the chain since they add steric restrictions to the chain. The zeta plots shows a textbook example of what you expect from this theory, the zeta potential gets less negative until it reaches a plateau where you see counter ion condensation in the plateau. The plateau is where you expect the persistence length to increase.

## e) In Figure 7, why does $l_{Mg+2}$,> $l_{K+1}$ > $l_{Na+1}$ in chain collapse but $l_{Mg+2}$,< $l_{K+1}$ < $l_{Na+1}$ in chain reexpansion? Why is l always larger than 1?

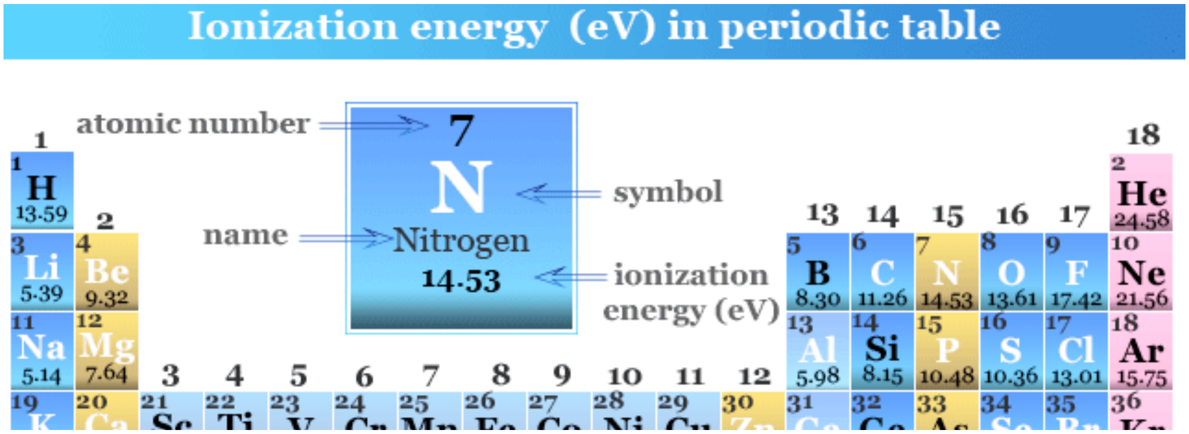
In e I think that there are some problems. The way I understand Li’s explanation is that the first series is due to the “affinity” of the counter ions to the polyelectrolyte. The second series is due to differences in the sizes of the counter ions. But on careful inspection the trends do not follow these explanations. Li doesn’t provide numbers and I guess the referees and editor didn’t bother to look. This is what I got:

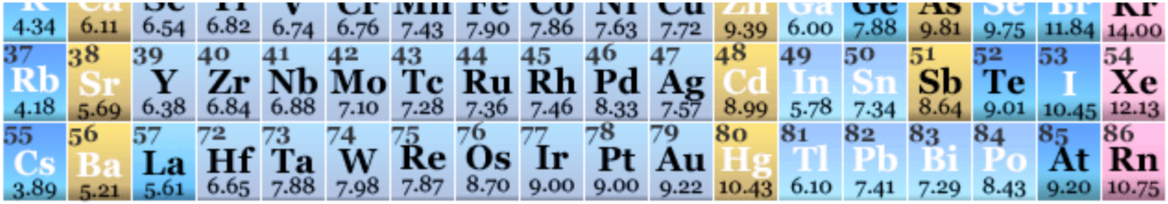
The key words for collapse is “affinity” of the counter ion for the poly anion according to the paper. That is the word that the author uses. It should probably also included the “Debye screening length” and the "OSF theory" which are the theoretical cause. A major problem is that the “affinity" doesn’t impact the Debye screening. “Affinity” also doesn’t impact any of the parameters in the OSF theory. The authors don’t really explain the reason of the lambda order in terms of just Debye screening length. The persistence length shouldn’t depend on “affinity” and “affinity” isn’t even defined in the paper. I suppose “affinity” has to do with the ionization energy of the counter ions, lower ionization energy are more electropositive cations.

Na 5.4eV
K 4.34 eV
Mg 7.64 eV

So order should be K Na Mg by ionization energy or inverse of electro positivity. The Debye screening length depends on the charge so Mg has a boost by a factor of 2 at the same concentration n. So you might expect Mg to have the strongest change, largest lambda and Na and K to be the same except that K is more electropositive than Na, so Mg, K, Na which is what they see. The electropositive part isn’t part of OSF or Debye screening though so it is just a hunch that they don’t explain.

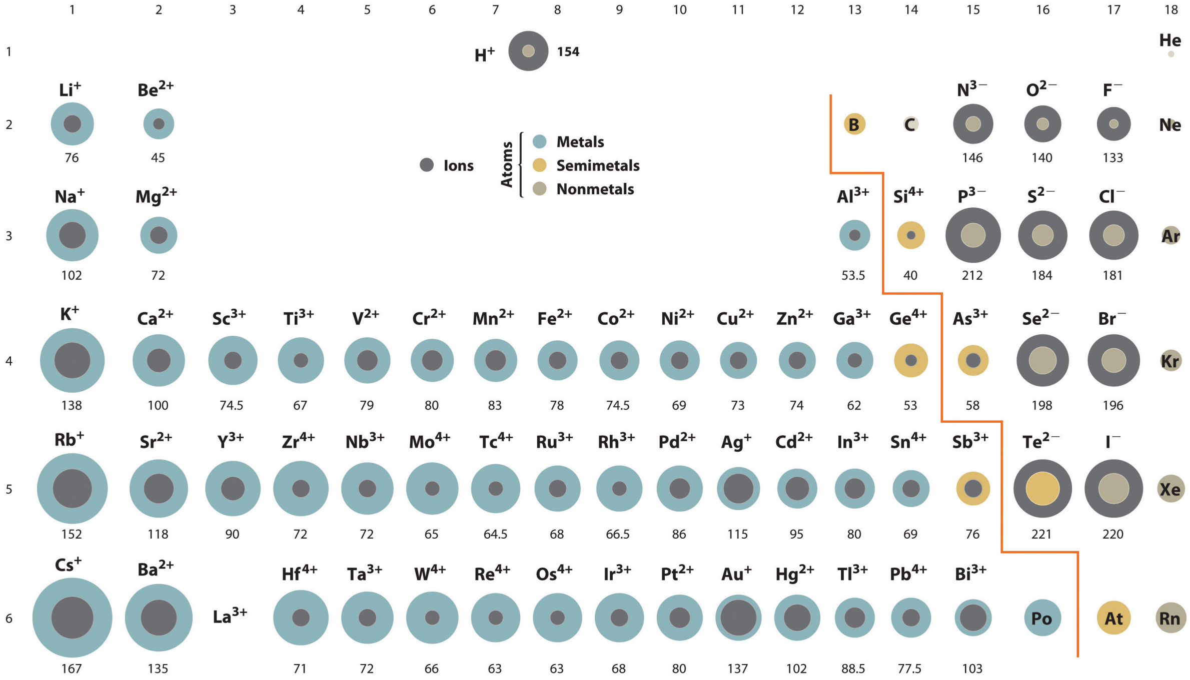
$$r_D = \left( \frac{\varepsilon kT}{4\pi n e^2} \right)^{1/2}$$





| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4.34 | 6.11 | 6.54 | 6.82 | 6.74 | 6.76 | 7.43 | 7.90 | 7.86 | 7.63 | 7.72 | 9.39 | 6.00 | 7.88 | 9.81 | 9.75 | 11.84 | 14.00 |
| 37 Rb 4.18 | 38 Sr 5.69 | 39 Y 6.38 | 40 Zr 6.84 | 41 Nb 6.88 | 42 Mo 7.10 | 43 Tc 7.28 | 44 Ru 7.36 | 45 Rh 7.46 | 46 Pd 8.33 | 47 Ag 7.57 | 48 Cd 8.99 | 49 In 5.78 | 50 Sn 7.34 | 51 Sb 8.64 | 52 Te 9.01 | 53 I 10.45 | 54 Xe 12.13 |
| 55 Cs 3.89 | 56 Ba 5.21 | 57 La 5.61 | 72 Hf 6.65 | 73 Ta 7.88 | 74 W 7.98 | 75 Re 7.87 | 76 Os 8.70 | 77 Ir 9.00 | 78 Pt 9.00 | 79 Au 9.22 | 80 Hg 10.43 | 81 Tl 6.10 | 82 Pb 7.41 | 83 Bi 7.29 | 84 Po 8.43 | 85 At 9.20 | 86 Rn 10.75 |

The key words for expansion are “counter ion condensation” and “steric” effect of the ions. Larger ions have a larger steric impact on the chain rigidity (for instance). Their trend doesn’t follow this logic.



Na 1.02, Mg 0.72, K 1.38 Ångstrom
So K should have the greatest impact, then Na, then Mg
His explanation of the balloon idea doesnt’ work with the order he has given in the paper. So there seems to be a problem with that whole concept. He sees the largest impact with Mg (the smallest counter ion) and the weakest with Na (medium sized counter ion). So the order and the high and low are in the wrong place. Seems to be a mess. This could be the reason that Li doens;t explain what he is talking about and just does a handwaving explanation without even defining terms so that they could be verified.