# Polymers with Necklace Configuration? Comments on Paper by Dobrynin et al.

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In a recent paper, Dobrynin et al.[1] concluded that a polyelectrolyte can assume in a poor solvent a “necklace configuration” in which globular clusters are linked by flexible chain segments. In the introductory paragraph they write “water, a poor solvent for many polymers ... causes chains without charged groups to collapse into spherical globules”. This implies that the analysis with which the paper is concerned is meant to apply to polyelectrolytes such as poly(styrenesulfonic acid), where the ionic functions are attached to a hydrophobic backbone.

The model used for the calculations consists of a freely jointed uniformly charged chain, but nowhere do the authors refer to the mutual **attraction** of ion pairs, which leads to a collapse of polyions at a critical charge density when the dielectric constant of the medium is sufficiently reduced below that of water. This effect has been demonstrated for poly(acrylic acid) and poly(methacrylic acid) in methanol where the solution viscosity first increases but then precipitously drops during the titration.[2,3] The collapse of polyelectrolyte gels under certain conditions when their charge density is increased has also been ascribed by Khokhlov and his collaborators[4] to ion-pair interactions. Similar effects are amply documented in studies of ionomer solutions.[5]

In view of this deficiency in the analysis of Dobrynin et al., it remains an open question whether a **uniform** polymer chain can assume a necklace configuration. On the other hand, two systems are known where the adsorption or covalent attachment of aromatic moieties at wide spacings to a hydrophilic polymer leads in water solution to a local clustering of the chain around the hydrophobe. Such an effect was first described by Molyneux and Frank[6] for poly($N$-vinylpyrrolidone), where it was shown that ten monomer residues are enclosing a variety of adsorbed aromatic additives. More recently, a similar effect was studied for poly(methacrylic acid) (PMA), where cluster formation around adsorbed or covalently bound aromatic labels was demonstrated in aqueous solutions at low pH by changes in the fluorescent properties and the rotational diffusion of the label.[7,8] Such clustering of PMA around the atropisomeric binaphthyl has also been shown to lead to a change in the chemical behavior of the label.[9]

## References and Notes

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(4) Starodubtsev, S. G.; et al. *Macromolecules* **1995**, *28*, 3930.
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(7) Ghiggino, K. P.; Tan, K. L. In *Polymer Photophysics*; Phillips, D., Ed.; Chapman and Hall: London, 1985; Chapter 7.
(8) Bednar, B.; et al. *Macromolecules* **1991**, *24*, 2054.
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## CORRECTIONS

**Zsolt Fodor, Young Cheol Bae, and Rudolf Faust***: Temperature Effects on the Living Cationic Polymerization of Isobutylene: Determination of Spontaneous Chain Transfer Constants in the Presence of Terminative Chain Transfer. Volume 31, Number 14, July 14, 1998, p 4439.

Line 11 of the right column of p 4445 should read $[\mathrm{PIBCl}]_0 = 2 \times 10^{-3}$ M instead of $[\mathrm{PIBCl}]_0 = 2 \times 10^{3}$ M.

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