

Effects of tacticity and copolymerization on the LCST of PNIPAm.

Tiago E. de Oliveira^{1,2} (PG), Debashish Mukherji¹ (PQ), Kurt Kremer¹ (PQ) and Paulo A. Netz^{2*} (PQ) netz@iq.ufrgs.br

(1) Max-Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz Germany, (2) Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil.

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Abstract

Structure, function and stability of smart polymers are intimately linked to their (macro-)molecular architectures and external stimuli, thus finding uses in a wide variety of technological applications¹. Here, we present the first simulation work to study the effects of stereochemistry and copolymerization on the smart PNIPAm polymer conformations.

Introdução

Poly(N-isopropylacrylamide) (PNIPAm) is a thermoresponsive smart polymer² that collapses from a coil at lower temperatures (T) to a globule upon increase of T, thus presenting a lower critical transition temperature (LCST) of around 305 K. Interestingly enough, this LCST can be tuned to a desirable value by changing its stereochemistry and/or by introducing different monomer along the backbone of a PNIPAm chain. In this context, it has been experimentally observed that - 1) Changing stereochemistry can change T_c ³ 2) A even more interesting effect was observed when the presence of 15-20% of acrylamide (AAm) monomers, along the backbone of an atactic PNIPAm chain, increased the LCST by ~25 K.^{4,5}

Using large scale molecular simulations, we develop a microscopic understanding of the effects of the stereochemistry and copolymerization on the transition temperatures of the PNIPAm-based smart (co)polymers. Our analysis connects the global polymer conformation transition with the microscopic intermolecular polymer-solvent coordination and thus with the hydrogen bond pattern. In the following, we briefly describe our findings.

Resultados e Discussão

In our simulations, we observe a noticeable decrease in polymer size with increasing temperature. For the case of stereochemistry, we find (consistent with the experiments) $T^{\text{isotactic}} < T^{\text{atactic}} < T^{\text{syndiotactic}}$. Furthermore, we find that the polymer conformation goes from a helical conformation along the backbone (for an isotactic chain) to a rather rigid conformation (for syndiotactic chain). We propose that - together with hydrogen bonding network between the amide group of PNIPAm and the water molecules, polymer persistence length play a key role in describing their

conformations. Here syndiotactic chain exhibiting larger l_p than atactic and isotactic chains.

More interesting results are found when studying a P(NIPAm-co-AAm) copolymer. Fig. 1 shows the LCST calculated in our simulations and its comparison with the existing experiments^{4,5}. Here, the strong AAm-water binding (via hydrogen bonding) increases polymer excluded volume and thus is consistent with the increased LCST with increasing AAm fraction.

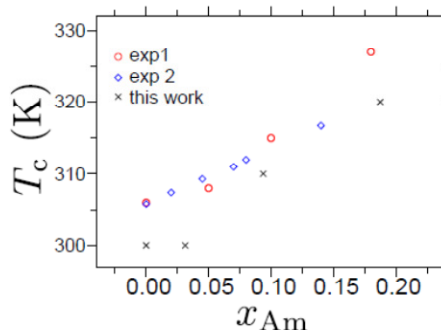


Figura 1. Transition temperature of poly(NIPAm-co-Am) as a function of acrylamide content, showing also two sets of experimental results^{4,5}.

Conclusões

Our findings suggest that the collapse of a PNIPAm chain, upon heating, is due to a rather delicate balance between monomer-water and monomer-monomer interactions and not simply based of pure hydrophobic effects.

Agradecimentos

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