

Effects of the linear chain structure on the cross-association equilibrium between chainlike molecules in a good solvent



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ABSTRACT

Molecular dynamics (MD) simulations have been performed for solutions of two cross-associating chain molecular species (n -chains and p -chains) one of which (p -component) may contain both associative (“sticky”) and inactive monomer links. The solutions of 63-mer chains show a crowding effect similar to that found in mixtures of short oligomers (J. Phys. Chem B, 2016, 120, 7234): the association equilibrium constant calculated from the stickers’ concentrations increases with the volume fraction of the component with inactive fragments (“spacers”). For p -chains with inactive spacers of more than 3 monomer units, the equilibrium constant at a given concentration of p -component becomes almost independent of the spacer length. A simple mean field approximation for the excluded volume effect works reasonably well for the solutions of cross-associating chains except for mixtures with high concentration of p -component.

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1. Introduction

Weak reversible physical gels are used in various applications because their properties may be controlled by varying molecular structure and concentration of components and applying external stimuli [1–4]. In weak gels reversible association between particles leads to formation of an infinite network of bonds. These bonds are transient: they are created and destroyed many times during the observation period. Such temporary bonding can be caused by attractive interactions when they do not result in forming a strong chemical bond; interactions between ionic or polar groups in polymer chains, hydrogen bonding, etc. can serve as examples.

Experimental data on equilibrium mechanical properties of gels and on gelation kinetics are numerous but little is known about what happens in gels on the molecular level including association equilibrium, kinetics, and local structure. Molecular simulation is a natural tool for providing insight on the microscopic scale and for suggesting plausible molecular mechanisms.

In our previous work on modeling solutions of cross-associating oligomers [5], we presented a brief review of analytical and computer simulation studies of systems containing associative chain molecules. In our own simulations, we observed the crowding

effect (a significant composition dependence of the equilibrium constant for stickers’ association calculated from the stickers’ concentrations) in a system where one of the oligomer species contains non-associative monomers in the chain due to volume exclusion by the inactive fragments. We proposed a simple correction for this effect that proved satisfactory for mixtures of short oligomers (decamers).

The present paper reports simulation results for the association equilibrium in solutions of longer (63-mer) cross-associating chains where one of the two chain species contains non-associative fragments (spacers). Varying the structure of the chain with inactive fragments, we examine the impact of the spacer length on the association equilibrium. We show that the association equilibrium constant is affected by the presence of inactive parts of chains. A simple mean field correction is based on the assumptions that the free volume decrease is proportional to the total number of non-associative monomer units and that the effective monomer unit volume is constant at a given temperature. This mean-field correction works well in homogeneous mixtures at not too high concentrations of the crowder chain.

2. Model and simulation procedure

The model used in our simulations was described in detail in our previous paper [5]. Here, only a brief summary is given. We simulate ternary mixtures where the components are chainlike

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molecules of two sorts (n -component and p -component, or n -chains and p -chains) in a simple Lennard-Jones solvent (denoted AS). Each chain is composed of 63 monomer units. The monomer units are denoted N (n -monomer), P (p -monomer), and O (o -monomer). A monomer unit is a combination of two sites: the backbone atom (AN, AP, AO) and the excentric dummy atom (DN, DP, DO). Association is described through strong attraction between DN and DP atoms (n -stickers and p -stickers), the role of other dummy atoms is to maintain uni-univalent association, repelling free stickers from a pair of stickers engaged in the associative bond. Fig. 1 shows n -chain (ON₆₁O) and all different p -chains considered in this work. For comparison, simulations are also performed for solutions containing N₁₀ and P₁₀ decamers.

Interactions are modeled by truncated Lennard-Jones potentials “switched” to zero [5–7] at certain distance. At long distances, all monomer units and solvent particles are essentially equivalent Lennard-Jones sites; therefore the solvent is nearly athermal. At short range, there is a specific Lennard-Jones attraction between DN and DP dummy atoms (n - and p -stickers) causing association between n - and p -monomers. Non-associating dummy atoms repel (in all combinations except DN–DP), so that association is uni-univalent. The details of the model potentials and parameters are given in Ref. [5].

In contrast to systems simulated in Ref. [5], all “sticky” monomers are non-terminal. These “sticky” monomers are approximately equivalent both energetically and sterically, so that one can expect no significant difference in associativity of these stickers.

The MD simulation has been done using the GROMACS package [7,8] on “Lomonosov” supercomputer in the Supercomputing Center of Lomonosov Moscow State University [9].

The simulation cell with standard cubic periodic boundary conditions contains 40940 solvent particles mixed with 620 chains (n - and p -chains in different proportions). The total number of non-dummy atoms (solvent particles plus AN, AP, AO backbone atoms in

the chains) is $N = 40940 + 63 \cdot 620 = 80000$. Thus $x_n + x_p = 0.488825$ (Fig. 2) where x_n and x_p are the fractions of n - and p -components, respectively. The volume per non-dummy atom or volume per monomer is $v^* = V/N$ where V is the MD cell volume. Nosé-Hoover thermostat [10,11] ($T = 365.4\text{ K} = 0.9\epsilon/k_B$ and $T = 406\text{ K} = \epsilon/k_B$, ϵ is the energy parameter for Lennard-Jones interactions between backbone atoms in the chains) and Martyna – Tuckerman – Tobias – Klein barostat [12,13] ($p = 10$ bar) are used. After 1.5 ns equilibration runs, 2 ns production runs are performed for all the simulated mixtures at the two temperatures (the time lengths of the runs have been chosen, after some trials, so that to obtain consistent statistical averages while remaining within the computational limits). Configurations are saved every 0.5 ps.

3. Results and discussion

Fig. 3 presents the “apparent” (concentration) constants of association equilibrium

$$K_{ass} = \frac{(N_{pairs}/V)}{((N_N - N_{pairs})/V)((N_P - N_{pairs})/V)} = \frac{p_N p_P}{(1 - p_N)(1 - p_P)(N_{pairs}/V)} \quad (1)$$

In this equation, N_{pairs} is the number of associated N–P pairs of monomer units in a volume V , N_N and N_P are the total numbers of N and P monomer units in the volume, and p_N and p_P are the fractions of N and P monomer units that are part of the associated pairs. The number of such pairs in the MD cell is counted for each saved configuration along the trajectory. Two monomer units are considered as forming an associated pair when the distance between n - and p -stickers is less than 0.16 nm [5]. Along with the results for the 63-mer mixtures, Fig. 3 also shows the values of K_{ass} calculated for non-terminal monomer units in mixed solutions of two decamers, N₁₀–P₁₀, at 406 K.

The simulated systems can undergo two kinds of transitions (see e.g. a relatively simple analytical description in Ref. [14] and references therein). The first one is gelation when at large enough concentration of associated N–P pairs, associated molecules form

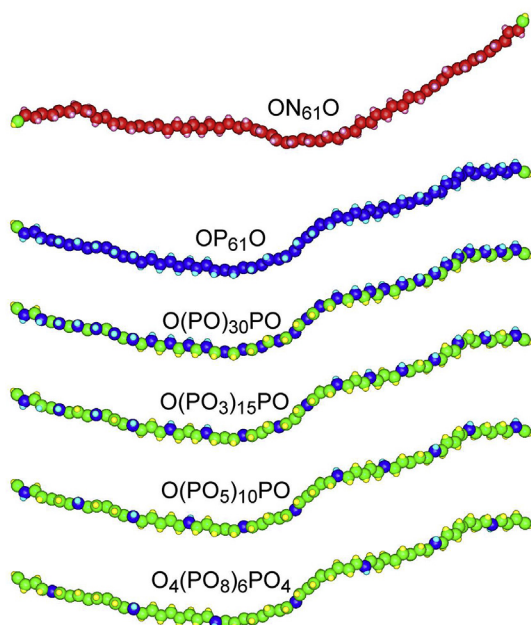


Fig. 1. The structure of n -chains (ON₆₁O) and p -chains (OP₆₁O, O(PO)₃₀PO, O(PO₃)₁₅PO, O(PO₅)₁₀PO, O₄(PO₈)₆PO₄). Each monomer unit (N, P, O) consists of a backbone atom (AN – red, AP – blue, AO – green) and a dummy atom (DN – pink, DP – yellow, DO – cyan). Association is possible between DN atoms (n -stickers) and DP atoms (p -stickers). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

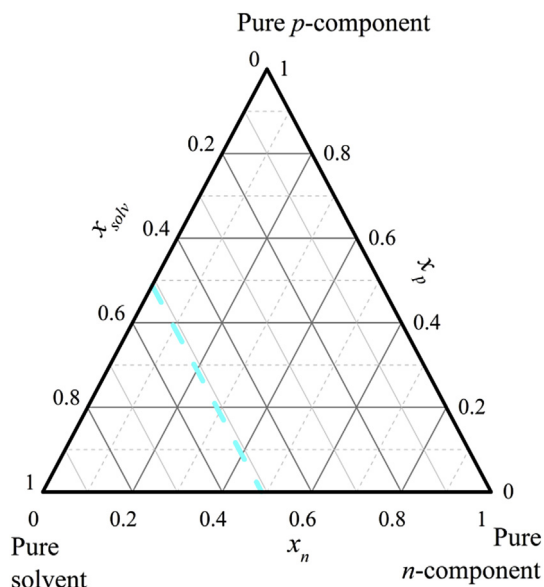


Fig. 2. The composition line $x_n + x_p = 0.488825$ (the solvent volume fraction $x_{soliv} = 1 - x_n - x_p = 0.51175$).

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