

Supporting Information for “Analysing the molecular weight distribution in supramolecular polymers”

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The formation of supramolecular polymer chains in the UPy-OF-UPy:UPy-OPV blend solutions can be treated analogously to a polycondensation process of a monofunctional reactant R-A (referred to as A) and a bifunctional reactant A-R'-A (referred to as L_1), where A denotes identical functional groups capable of reacting with one another in a reversible addition reaction and R and R' stand for non-reactive chemical restgroups. When A and L_1 are mixed at a certain ratio, in principle three different families of oligomers are expected to form [1]: a chain composed of i bifunctional monomer units can either have 1.) both ends free (L_i), 2.) one end free and while the other is terminated by a monofunctional R-A unit (M_i), or 3.) both ends terminated R-A units (N_i). Let p denote the fraction of all functional groups of identical type which have condensed in the polymerization process. Ercolani showed that in this case the following expressions apply for the relative concentrations of each type of oligomer in the solutions:

$$[L_i] = (\sigma K)^{-1} p^i \quad (1)$$

$$[M_i] = [A] p^i \quad (2)$$

$$[N_i] = K [A]^2 p^i \quad (3)$$

Here, K denotes the equilibrium constants for the dimerisation of A-A and R-A, respectively, and σ is a symmetry number, related to the symmetry of the molecules involved, and was found to be equal to 4 for the bifunctional species in the present case [1]. If K is however very high, so that $K [A]^2 \gg (\sigma K)^{-1} + [A]$, the equations above imply $[N_i] \gg [L_i], [M_i]$. In the present case, this relation obviously holds, as K has been reported to be of the order of $\sim 10^6 - 10^7 \text{ M}^{-1}$ for association of the UPy-groups, while the UPy-OPV concentrations were about $\sim 10^{-4} \text{ M}$. In other words, due to the strength of the quadruple hydrogen bonds, the double terminated chain configurations N_i represent the dominating type of oligomers in the ensemble. As an approximation, both $[L_i]$ and $[M_i]$ can be taken as zero, so that only N_i is of interest in the further discussion.

Following the treatment by Ercolani, the mass balance equation for the bifunctional monomer L_1 gives

$$[L_1]_0 = \sum_{i=1}^{\infty} i [N_i] \quad (4)$$

where $[L_1]_0$ is the initial monomer concentration. By inserting Eqn. 3 and exploiting the relation $\sum_{i=1}^{\infty} i p^i = \frac{p}{(1-p)^2}$ for $0 \leq p < 1$, Eq 4 becomes

$$[L_1]_0 = K [A]^2 \frac{p}{(1-p)^2} \quad (5)$$

In contrast, the mass balance equation for the monofunctional monomer A is given by

$$[A]_0 = 2 \sum_{i=1}^{\infty} [N_i] + 2 [N_0] + [A] \quad (6)$$

with $[A]_0$ being, as in the previous case, the initial concentration of these monomers in the solution. Since each chain N_i (and of course the homodimer N_0) is endcapped by two A units, the corresponding concentrations are weighted twice in the summation. Substituting Eqn. 3 yields

$$[A]_0 = 2K [A]^2 \sum_{i=1}^{\infty} p^i + 2K [A]^2 + [A] \quad (7)$$

Taking into account, that $K [A]^2 \gg [A]$, and exploiting the relation for the geometric series $\sum_{i=1}^{\infty} p^i = \frac{p}{(1-p)}$ for $0 \leq p < 1$, one arrives at

$$K [A]^2 = \frac{[A]_0}{2} (1-p) \quad (8)$$

Upon substitution of this expression into Eqn. 5, the resulting equation can be solved for p , which gives

$$p = 2 \left(2 + \frac{[A]_0}{[L_1]_0} \right)^{-1} \quad (9)$$

Substituting Eqn. 8 into Eqn. 3 yields the following expression for the concentration of chains of configuration N_i in the solution:

$$[N_i] = \frac{[A]_0}{2} (1-p) p^i \quad (10)$$

Finally, by inserting Eqn. 9, N_i can be written as

$$[N_i] = 2^{i-1} \left(\frac{[A]_0}{[L_1]_0} \right)^2 \left(2 + \frac{[A]_0}{[L_1]_0} \right)^{-(i+1)} [L_1]_0 \quad (11)$$

Thus, $[N_i]$ is merely a function of the mixing ratio $x = \frac{[A]_0}{[L_1]_0}$.

This general expression is applied to the system hereafter, with $[A]_0$ replaced by $[OPV]_0$, $[L_1]_0$ by $[OF]_0$ and $[N_i]$ by $[OF_i]$ throughout the main article.

[1] G. Ercolani, Chem. Commun. (2001) p. 1416.

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