Supporting Information for:
An Equilibrium Model for Supramolecular Copolymerizations

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SI-1 Symmetry condition on heterodimer concentrations

In Section 2.3 we have shown that the detailed balance condition implies that the hetero equilibrium constants in the nucleation and elongation part must be related $K_{A-B} = \sigma_A K_{*A-B}$ and $K_{B-A} = \sigma_B K_{*B-A}$. Here we show that if the additional *symmetry condition* $K_{A-B} = K_{B-A}$ holds, the concentration of a copolymer and its reverse are equal.

Let P be an arbitrary copolymer with bottom A, that contains x monomers A, y monomers B, p bonds A$-$A, q bonds B$-$B, r bonds A$-$B and s bonds B$-$A. The concentration of P is then

$$[P] = \sigma_A a^x b^y K_{*A-A}^p K_{*B-B}^q K_{*A-B}^r K_{*B-A}^s \ .$$

Let P^R be the reverse copolymer. Clearly P^R contains the same number of A and B monomers and the same number of A$-$A and B$-$B bonds. However the numbers of A$-$B and B$-$A bonds are now interchanged. The concentration of P^R is thus given by

$$[P^R] = \sigma a^x b^y K_{*A-A}^p K_{*B-B}^q K_{*A-B}^s K_{*B-A}^r \ ,$$

where σ depends on the bottom element of P^R, which is the top element of P. We consider two cases: i) If P has top element A, then $\sigma = \sigma_A$. But in that case P has an A at its bottom and at its top, which implies that $r = s$. Hence the concentrations of P and P^R are equal. ii) If P has top element B, then $\sigma = \sigma_B$. But in that case P has an A at its bottom and an B at its top, which implies that $r = s + 1$. The difference between the concentrations of P and P^R is now

$$[P] - [P^R] = a^x b^y K_{*A-A}^p K_{*B-B}^q \left(\sigma_A K_{*A-B}^{s+1} K_{*B-A}^s - \sigma_B K_{*A-B}^s K_{*B-A}^{s+1} \right)$$
$$= a^x b^y K_{*A-A}^p K_{*B-B}^q K_{*A-B}^s K_{*B-A}^s \left(\sigma_A K_{*A-B} - \sigma_B K_{*B-A} \right) \ ,$$

which vanishes due to the symmetry condition. The case that P has a bottom element B can be treated similarly.

The reverse property also holds. If for each copolymer its concentration equals the concentration of the reverse copolymer, then the symmetry condition must hold. That follows immediately from $[AB] = [BA]$.

SI-2   Initial values recursive relations

Initial values for equivalent monomer and bond concentrations

In Section 2.5 the equivalent concentration of a part X of the copolymers is computed with the iteration process in eq 22:

$$\mathbf{u}_{n+1} = M \cdot \mathbf{u}_n \quad \text{with} \quad M = \begin{pmatrix} M_c & \mathbf{0} \\ M_X & M_c \end{pmatrix} \quad \text{and} \quad \mathbf{u}_n = (c_n^{\mathrm{A}}, c_n^{\mathrm{B}}, f_n^{\mathrm{A}}, f_n^{\mathrm{B}})^{\mathrm{T}} \ .$$

The matrix M_c is given in eq 15 and the matrix M_X depends on the part X. Further c_n^{A} and c_n^{B} are the concentrations of copolymers with length n and top A and B respectively and f_n^{A} and f_n^{B} are the equivalent X concentrations in copolymers with length n and top A and B respectively. In principle the iteration process must be started from $n = 2$. The step from $n = 1$ to $n = 2$ is the nucleation step, but the iteration matrix M is derived for the elongation phase. The initial values for the concentrations are easily found

$$c_2^{\mathrm{A}} = [\mathrm{AA}] + [\mathrm{BA}] = K_{\mathrm{A-A}}a^2 + K_{\mathrm{B-A}}ab \ , \qquad c_2^{\mathrm{B}} = [\mathrm{AB}] + [\mathrm{BB}] = K_{\mathrm{A-B}}ab + K_{\mathrm{B-B}}b^2 \ .$$

The initial values for f_2^{A} and f_2^{B} and the matrix M_X are given in Table S1 for part X a monomer (A or B) or a bond (A$-$A, B$-$A, A$-$B or B$-$B).

In fact the iteration process can also be started from $n = 1$, with $c_1^{\mathrm{A}} = \sigma_{\mathrm{A}}a$, $c_1^{\mathrm{B}} = \sigma_{\mathrm{B}}b$, f_1^{A} and f_1^{B} as given in Table S1. Then $\mathbf{u}_2 = M \cdot \mathbf{u}_1$.

Initial values for block length computations

The computation of the lengths of A blocks was done with an iteration process for the variables $C_n^{\mathrm{A}}(k)$, $C_n^{\mathrm{B}}(k)$ and $O_n^{\mathrm{A}}(k)$. For the computation of B block lengths we use similar variables, with an additional "hat" symbol, and for the computation of the alternating (AB) blocks the variables have an additional "tilde". The initial values for $n = 2$ are as follows:

A blocks:

$$O_2^{\mathrm{A}}(1) = [\mathrm{BA}] = K_{\mathrm{B-A}}ab$$
$$O_2^{\mathrm{A}}(2) = [\mathrm{AA}] = K_{\mathrm{A-A}}a^2$$
$$C_2^{\mathrm{B}}(1) = [\mathrm{AB}] = K_{\mathrm{A-B}}ab$$

B blocks:

$$\widehat{O}_2^{\mathrm{B}}(1) = [\mathrm{AB}] = K_{\mathrm{A-B}}ab$$
$$\widehat{O}_2^{\mathrm{B}}(2) = [\mathrm{BB}] = K_{\mathrm{B-B}}b^2$$
$$\widehat{C}_2^{\mathrm{A}}(1) = [\mathrm{BA}] = K_{\mathrm{B-A}}ab$$

AB (= alternating) blocks:

$$\widetilde{O}_2^{\mathrm{A}}(1) = [\mathrm{AA}] = K_{\mathrm{A-A}}a^2$$
$$\widetilde{O}_2^{\mathrm{A}}(2) = [\mathrm{BA}] = K_{\mathrm{B-A}}ab$$
$$\widetilde{O}_2^{\mathrm{B}}(1) = [\mathrm{BB}] = K_{\mathrm{B-B}}b^2$$
$$\widetilde{O}_2^{\mathrm{B}}(2) = [\mathrm{AB}] = K_{\mathrm{A-B}}ab$$
$$\widetilde{C}_2^{\mathrm{A}}(1) = [\mathrm{AA}] = K_{\mathrm{A-A}}a^2$$
$$\widetilde{C}_2^{\mathrm{B}}(1) = [\mathrm{BB}] = K_{\mathrm{B-B}}b^2$$

Table S1: Initial values and matrix M_X for various X

X	matrix M_X	init values $n = 2$	init values $n = 1$
A	$M_A = \begin{pmatrix} K_{*\text{A--A}}\, a & K_{*\text{B--A}}\, a \\ 0 & 0 \end{pmatrix}$	$f_2^A = [\text{BA}] + 2[\text{AA}] = K_{\text{B--A}}ab + 2K_{\text{A--A}}a^2$ $f_2^B = [\text{AB}] = K_{\text{A--B}}ab$	$f_1^A = \sigma_A a$ $f_1^B = 0$
B	$M_B = \begin{pmatrix} 0 & 0 \\ K_{*\text{A--B}}\, b & K_{*\text{B--B}}\, b \end{pmatrix}$	$f_2^A = [\text{BA}] = K_{\text{B--A}}ab$ $f_2^B = [\text{AB}] + 2[\text{BB}] = K_{\text{A--B}}ab + 2K_{\text{B--B}}b^2$	$f_1^A = 0$ $f_1^B = \sigma_B b$
A$-$A	$M_{\text{A--A}} = \begin{pmatrix} K_{*\text{A--A}}a & 0 \\ 0 & 0 \end{pmatrix}$	$f_2^A = [\text{AA}] = K_{\text{A--A}}a^2$ $f_2^B = 0$	$f_1^A = 0$ $f_1^B = 0$
B$-$A	$M_{\text{B--A}} = \begin{pmatrix} 0 & K_{*\text{B--A}}a \\ 0 & 0 \end{pmatrix}$	$f_2^A = [\text{BA}] = K_{\text{B--A}}ab$ $f_2^B = 0$	$f_1^A = 0$ $f_1^B = 0$
A$-$B	$M_{\text{A--B}} = \begin{pmatrix} 0 & 0 \\ K_{*\text{A--B}}b & 0 \end{pmatrix}$	$f_2^A = 0$ $f_2^B = [\text{AB}] = K_{\text{A--B}}ab$	$f_1^A = 0$ $f_1^B = 0$
B$-$B	$M_{\text{B--B}} = \begin{pmatrix} 0 & 0 \\ 0 & K_{\text{B--B}}b \end{pmatrix}$	$f_2^A = 0$ $f_2^B = [\text{BB}] = K_{\text{B--B}}b^2$	$f_1^A = 0$ $f_1^B = 0$

Not all tables have already elements for $n = 2$. For instance, in a copolymer of length n and top A the maximal length of a closed A block is $n - 2$, so the table C_2^A needs no initialization.

SI-3   More examples of allowed regions

Here some more examples of allowed regions for a system with one copolymer type are given. Consider the homopolymer system with monomer A and reactions given in eq 1 and 2 in the paper. For the concentration c_n^A the recurrent relation $c_{n+1}^A = K_{*\text{A--A}}ac_n^A$ holds. That means that in a chemical system always $K_{*\text{A--A}}a < 1$, otherwise $c_{n+1}^A \geq c_n^A$, which implies that the equivalent A concentration in the system would be infinite. Hence the free monomer concentration a must always lie in the "allowed interval" $0 \leq a < 1/K_{*\text{A--A}}$. In that case the equivalent A concentration in all polymers can be computed with a summation formula, which leads to the standard one component mass-balance equation given in eq S4. Although

the mathematical equation S4 may have solutions with $a \geq 1/K_{*A-A}$, these solutions are not chemically relevant, i.e., they do not correspond with existing polymer systems.

Next consider two homopolymer systems, for a monomer type A and a similar system for a monomer type B. Then the free monomer concentrations a must lie in the interval $0 \leq a < 1/K_{*A-A}$ and the free monomer concentration b must lie in the interval $0 \leq b < 1/K_{*B-B}$. Now consider these two systems together as a copolymerization system, that has accidentally no hetero interaction, i.e., $K_{*A-B} = K_{*B-A} = 0$. Then the free monomer point (a, b) must be in the allowed region, which is in this case the rectangle given by $0 \leq a < 1/K_{*A-A}$ and $0 \leq b < 1/K_{*B-B}$, see the orange lines in Figure S1.

If the copolymerization system does have hetero interaction, i.e., $K_{*A-B} > 0$ and $K_{*B-A} > 0$, the allowed region becomes smaller. The addition of hetero interaction means that, for the same free monomer concentrations a and b, more material occurs in (co)polymers. Hence the allowed a and b values to keep the system finite, will be smaller. Mathematically the allowed region is bounded by the critical curve, i.e., the curve where the largest eigenvalue of iteration matrix M_c (see eq 15) equals 1. The shape of the allowed region is, for fixed K_{*A-A} and K_{*B-B}, determined by the product $K_{*A-B}K_{*B-A}$ of the hetero interaction constants. Larger values of $K_{*A-B}K_{*B-A}$, i.e., smaller values of $D = K_{*A-A}K_{*B-B} - K_{*A-B}K_{*B-A}$, lead to a smaller allowed region. In Figure S1 the allowed region is shown for four values of the dimensionless parameter $d = D/(K_{*A-A}K_{*B-B})$.
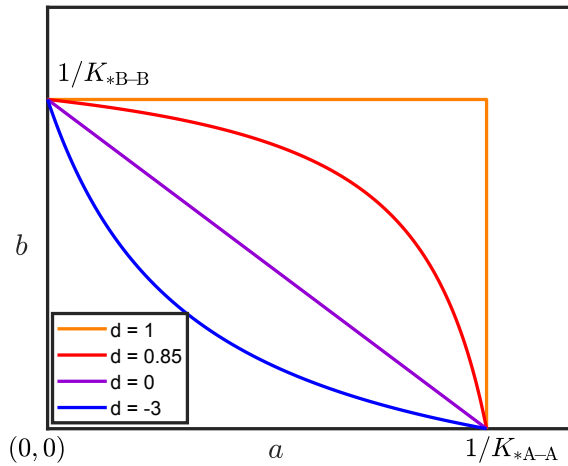

Figure S1: Allowed regions (below/left of the colored lines) for the monomer concentrations a, b, for four values of $d = D/(K_{*A-A}K_{*B-B})$. If $d = 1$ there is no hetero interaction and the allowed region is a rectangle. The case $d = 0.85$ corresponds with the weak hetero interaction as shown in Figure 2a. If $d = 0$ then $K_{*A-B}K_{*B-A} = K_{*A-A}K_{*B-B}$, the critical curve is a straight line (the pink line) and the allowed region ia triangle. Finally $d = -3$ corresponds with the strong hetero interaction as shown in Figure 2b.

SI-4 Computing mass weighted copolymer lengths

The average concentration weighted copolymer length was given in eq 32 as

$$\langle n \rangle = \frac{\sum_{n=2}^{\infty} n(c_n^{\mathrm{A}} + c_n^{\mathrm{B}})}{\sum_{n=2}^{\infty} (c_n^{\mathrm{A}} + c_n^{\mathrm{B}})} = \frac{P_{\mathrm{tot}}}{C_{\mathrm{tot}}}.$$

The average *mass weighted* copolymer length is given by

$$\langle n \rangle_{\mathrm{mw}} = \frac{\sum_{n=2}^{\infty} n^2(c_n^{\mathrm{A}} + c_n^{\mathrm{B}})}{\sum_{n=2}^{\infty} n(c_n^{\mathrm{A}} + c_n^{\mathrm{B}})} = \frac{Q_{\mathrm{tot}}}{P_{\mathrm{tot}}}.$$

The computation of P_{tot} and C_{tot} was described in Section 2.5 of the paper, in particular eqs 26-28. In a similar way Q_{tot} can be computed. Since P_{tot} and C_{tot} are computed while solving the mass-balance equations, the value of $\langle n \rangle$ can be found as side effect of the mass balance solver. Here we describe how C_{tot}, P_{tot} and Q_{tot} can also be found using the iteration process for the concentration of the copolymers alone, as given in eq 14: $\mathbf{c}_{n+1} = M_c \cdot \mathbf{c}_n$, where $\mathbf{c}_n = (c_n^{\mathrm{A}}, c_n^{\mathrm{B}})^{\mathrm{T}}$. Then using the identities

$$\sum_{n=2}^{\infty} \mathbf{c}_n = \sum_{n=2}^{\infty} M_c^{n-1} \mathbf{v}_1 = (I - M_c)^{-1} \cdot M_c \cdot \mathbf{c}_1$$

$$\sum_{n=2}^{\infty} n\mathbf{c}_n = \sum_{n=2}^{\infty} nM_c^{n-1} \mathbf{v}_1 = \left((I - M_c)^{-2} + (I - M_c)^{-1}\right) \cdot M_c \cdot \mathbf{c}_1$$

$$\sum_{n=2}^{\infty} n^2\mathbf{c}_n = \sum_{n=2}^{\infty} n^2 M_c^{n-1} \mathbf{v}_1 = \left(2(I - M_c)^{-3} + (I - M_c)^{-2} + (I - M_c)^{-1}\right) \cdot M_c \cdot \mathbf{c}_1 ,$$

with $\mathbf{c}_1 = (c_1^{\mathrm{A}}, c_1^{\mathrm{B}})^{\mathrm{T}} = (\sigma_{\mathrm{A}} a, \sigma_{\mathrm{B}} b)^{\mathrm{T}}$, the values of C_{tot}, P_{tot} and Q_{tot} can be computed. If the mass weighted copolymer length is known, also the *polydispersity index*, defined as $\langle n \rangle_{\mathrm{mw}} / \langle n \rangle$ can be computed. The Matlab function ComputeBonds, described in Section SI-8 also computes the average mass weighted copolymer length.

SI-5   Derivation analytical expressions special cases

General notions

The expressions for the equivalent monomer and bond concentrations (P_X in eq 26) and the total copolymer concentration (C_{tot} in eq 28) are in terms of vectors and matrices. By computing the individual matrix elements explicit expressions for these notions can be found. These explicit expressions are the starting point for the analysis of the special cases in Section 4 of the paper and will be given here. We use the following abbreviations:

$$
\begin{aligned}
y_1 &= 1 - K_{*\text{B–B}}\, b + K_{*\text{A–B}}\, b \ , \\
y_2 &= 1 - K_{*\text{A–A}}\, a + K_{*\text{B–A}}\, a \ , \\
z_1 &= \sigma_\text{A}\, a(1 - K_{*\text{B–B}}\, b) + \sigma_\text{B}\, K_{*\text{B–A}}\, a\, b \ , \\
z_2 &= \sigma_\text{A}\, K_{*\text{A–B}}\, a\, b + \sigma_\text{B}\, b\, (1 - K_{*\text{A–A}}\, a) \ , \\
w_1 &= \sigma_\text{A}\, K_{*\text{A–A}}\, a^2 + \sigma_\text{B}\, K_{*\text{B–A}}\, a\, b \ , \\
w_2 &= \sigma_\text{A}\, K_{*\text{A–B}}\, a\, b + \sigma_\text{B}\, K_{*\text{B–B}}\, b^2 \ , \\
\delta &= 1 - K_{*\text{A–A}}a - K_{*\text{B–B}}b + D\, a\, b \quad (D = K_{*\text{A–A}}K_{*\text{B–B}} - K_{*\text{A–B}}K_{*\text{B–A}}) \ .
\end{aligned}
\tag{S1}
$$

The equivalent bond concentrations are then given by

$$
\begin{aligned}
P_\text{A–A} &= y_1\, K_{*\text{A–A}}\, a\, z_1/\delta^2 \ , \\
P_\text{B–B} &= y_2\, K_{*\text{B–B}}\, b\, z_2/\delta^2 \ , \\
P_\text{A–B} &= y_2\, K_{*\text{A–B}}\, b\, z_1/\delta^2 \ , \\
P_\text{B–A} &= y_1\, K_{*\text{B–A}}\, a\, z_2/\delta^2 \ .
\end{aligned}
\tag{S2}
$$

A simple computation shows that always

$$
\frac{P_\text{A–B}P_\text{B–A}}{P_\text{A–A}P_\text{B–B}} = \frac{K_{*\text{A–B}}K_{*\text{B–A}}}{K_{*\text{A–A}}K_{*\text{B–B}}} \ ,
$$

which turns out to be a useful relation. Moreover, if the symmetry condition $K_\text{A–B} = K_\text{B–A}$ (i.e., $\sigma_\text{A}K_{*\text{A–B}} = \sigma_\text{B}K_{*\text{B–A}}$) holds, then

$$
P_\text{A–B} = P_\text{B–A} \ .
$$

Introducing C_A and C_B as the total concentration of copolymers with top A and B respectively yields the following identities

$$
\begin{aligned}
C_A &= ((1 - K_{*\text{B–B}}\, b)\, w_1 + K_{*\text{B–A}}\, a\, w_2)/\delta \ , \\
C_B &= (K_{*\text{A–B}}\, b\, w_1 + (1 - K_{*\text{A–A}}\, a)\, w_2)/\delta \ .
\end{aligned}
$$

Since each copolymer has either top A or top B the total copolymer concentration C_{tot} is given by

$$C_{\text{tot}} = C_A + C_B \ .$$

As the equivalent concentration of A monomers in all copolymers (P_A) is the sum of the equivalent concentration of all A's followed by an A, the equivalent concentration of all A's followed by a B, and the concentration of polymers with an A at the top, we can also write the identities:

$$P_A = P_{\text{A–A}} + P_{\text{A–B}} + C_A \ , \tag{S3}$$
$$P_B = P_{\text{B–B}} + P_{\text{B–A}} + C_B \ .$$

The total amount of monomers occurring in copolymers is then given by

$$P_{\text{tot}} = P_A + P_B$$

and the degree of copolymerization is

$$\phi = \frac{P_{\text{tot}}}{a_{\text{tot}} + b_{\text{tot}}} \ .$$

One-component model

In the case that $K_{\text{*A–B}} = 0$ and $K_{\text{*B–A}} = 0$ we obtain:

$$y_1 = 1 - K_{\text{*B–B}}\, b \ ,$$
$$y_2 = 1 - K_{\text{*A–A}}\, a \ ,$$
$$z_1 = \sigma_A\, a\,(1 - K_{\text{*B–B}}\, b) \ ,$$
$$z_2 = \sigma_B\, b\,(1 - K_{\text{*A–A}}\, a) \ ,$$
$$w_1 = \sigma_A\, K_{\text{*A–A}}\, a^2 \ ,$$
$$w_2 = \sigma_B\, K_{\text{*B–B}}\, b^2 \ ,$$
$$\delta = (1 - K_{\text{*A–A}}a)(1 - K_{\text{*B–B}}b) \ .$$

The equivalent bond concentrations are then given by

$$P_{A-A} = \sigma_A K_{*A-A}\, a^2/(1 - K_{*A-A}a)^2 \ ,$$

$$P_{B-B} = \sigma_B K_{*B-B}\, b^2/(1 - K_{*B-B}b)^2 \ ,$$

$$P_{A-B} = 0 \ ,$$

$$P_{B-A} = 0 \ ,$$

$$C_A = \sigma_A K_{*A-A}a^2/(1 - K_{*A-A}a) \ ,$$

$$C_B = \sigma_B K_{*B-B}b^2/(1 - K_{*B-B}b) \ ,$$

$$P_A = \sigma_A K_{*A-A}\, a^2/(1 - K_{*A-A}a)^2 + \sigma_A K_{*A-A}a^2/(1 - K_{*A-A}a) = \sigma_A K_{*A-A}\, a^2 \frac{2 - K_{*A-A}a}{(1 - K_{*A-A}a)^2} \ ,$$

$$P_B = \sigma_B K_{*B-B}\, b^2/(1 - K_{*B-B}b)^2 + \sigma_B K_{*B-B}b^2/(1 - K_{*B-B}b) = \sigma_B K_{*B-B}\, b^2 \frac{2 - K_{*B-B}b}{(1 - K_{*A-A}a)^2} \ .$$

Hence the mass-balance equation for the case of one copolymer type, without hetero interaction, become

$$a + \sigma_A K_{*A-A}\, a^2 \frac{2 - K_{*A-A}a}{(1 - K_{*A-A}a)^2} = a_{\text{tot}} \ , \tag{S4}$$

$$b + \sigma_B K_{*B-B}\, b^2 \frac{2 - K_{*B-B}b}{(1 - K_{*B-B}b)^2} = b_{\text{tot}} \ . \tag{S5}$$

Note that this are indeed the uncoupled one-component mass balance equations for the A and B homopolymers, respectively.

Mixing in a small amount of B monomers
We derive eq 40 of the paper. Since in the "mixing in" case we assume that $K_{*B-B} = 0$, also $P_{B-B} = 0$. Hence in case of a small value of b_{tot} and a high degree of polymerization, $P_B \approx P_{B-A}$, since only Bs at the top of the long copolymers are not taken into account. In eq S2 for P_{B-A} the abbreviation z_2 occurs, that can be rewritten as

$$z_2 = \sigma_A\, K_{*A-B}\, a\, b + \sigma_B\, b\, (1 - K_{*A-A}\, a) \approx \sigma_A\, K_{*A-B}\, a\, b + \sigma_B\, b\, K_{*A-B}\, K_{*B-A} a\, b = K_{*A-B}\, b\, z_1 \ ,$$

where we used that in case of high degree of polymerization $\delta \approx 0$, which in this case means that $1 - K_{*A-A}a \approx K_{*A-B}K_{*B-A}a\, b$. Using this approximation for z_2 in eq S2 gives

$$P_B \approx P_{B-A} \approx y_1\, K_{*B-A}\, a\, z_2/\delta^2 \approx y_1\, K_{*B-A}\, a\, K_{*A-B}\, b\, z_1/\delta^2 = \frac{K_{*A-B}K_{*B-A}b}{K_{*A-A}}P_{A-A} \ .$$

The proof is completed by noting that, for long copolymers and small amounts of b_{tot} the value of $P_{\text{A–A}}$ is almost equal[1] to P_{A}, hence in the considered case

$$P_{\text{B}} \approx \frac{K_{*\text{A–B}}K_{*\text{B–A}}b}{K_{*\text{A–A}}}P_{\text{A}}. \tag{S6}$$

The equilibrium monomer concentrations for small values of b_{tot} can now be approximated as follows. Rewriting eq S6 in terms of a and b gives

$$b_{\text{tot}} - b = \frac{K_{*\text{A–B}}K_{*\text{B–A}}b}{K_{*\text{A–A}}}(a_{\text{tot}} - a) . \tag{S7}$$

Since we consider a highly polymerized case (with $K_{*\text{B–B}} = 0$), also the relation $\delta = 1 - K_{*\text{A–A}}a - K_{*\text{A–B}}K_{*\text{B–A}}ab \approx 0$ holds. Substitution of

$$a = 1/(K_{*\text{A–A}} + K_{*\text{A–B}}K_{*\text{B–A}}b) \tag{S8}$$

in eq S7 leads to a quadratic equation in b. The only positive solution is for small b_{tot} given by

$$b = \frac{K_{*\text{A–A}}^2}{K_{*\text{A–A}}^2 + K_{*\text{A–B}}K_{*\text{B–A}}(K_{*\text{A–A}}a_{\text{tot}} - 1)}b_{\text{tot}} . \tag{S9}$$

The corresponding approximation for the free monomer concentration a can now be obtained from eq S8.

We now study the effect of the addition of B monomers to a pure A system on the degree of polymerization ϕ and the average copolymer length $\langle n \rangle$. We first introduce the dimensionless parameters α, β and γ by setting

$$\alpha = K_{*\text{A–A}}\, a_{\text{tot}} \ ,$$
$$\beta = \frac{K_{*\text{A–B}}}{K_{*\text{A–A}}} \ ,$$
$$\gamma = \frac{b_{\text{tot}}}{a_{\text{tot}}} \ .$$

Keeping all other parameters fixed, we consider all (equivalent) concentrations, the average copolymer length $\langle n \rangle$ and the degree of polymerization ϕ as function of γ. The derivatives of these notions with respect to γ in $\gamma = 0$ indicate what happens if B monomers are added to a pure A homopolymer solution. The derivatives will be written with a prime, like a', b', P'_{tot}, ϕ' and can be computed with the standard calculus rules, starting from eqs S8 and S9.

Some care must be taken in computing δ and δ'. Since eq (S8) was derived from the approx-

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[1] Using the better approximation $P_{\text{A–A}} = P_{\text{A}} - P_{\text{B–A}}$ leads in first order in b_{tot} to the same result.

imation $\delta = 0$, it cannot be used to compute δ. However δ and δ' can still be obtained from eq (S3), with $P^A = a_\text{tot} - a$. After some calculus we finally end up with

$$\phi' = \frac{\frac{\sigma_A}{\sigma_B} \beta^2 (2\alpha - 1) + 1 - \alpha}{\alpha \left(1 + \frac{\sigma_A}{\sigma_B} \beta^2 (\alpha - 1) \right)} \ .$$

Since we assume a high degree of polymerization of the A homopolymers, $\alpha >> 1$. Hence, for small β, i.e. small K_{*A-B}/K_{*A-A}, the value of ϕ' is negative, for large values of β it is positive. The turning point $\widetilde{\beta}$ is given by

$$\widetilde{\beta} = \sqrt{\frac{\sigma_B}{\sigma_A}} \sqrt{\frac{\alpha - 1}{2\alpha - 1}} \ .$$

For the derivative of the average copolymer length in $\gamma = 0$ we find

$$\langle n \rangle' = \frac{\beta \, \alpha}{\sqrt{\sigma_A (\alpha - 1)}} \ \left(\beta \frac{\sigma_A}{\sigma_B} (\tfrac{3}{2}\alpha - 1) - \alpha + 1 \right) \ .$$

Also $\langle n \rangle'$ is negative for small values of β and positive for larger values of β, with turning point

$$\widehat{\beta} = \frac{\sigma_B}{\sigma_A} \frac{\alpha - 1}{\tfrac{3}{2}\alpha - 1} \ .$$

SI-6   Computing elongation temperatures

Consider an A, B mixture with concentrations a_tot and b_tot. Suppose that the dimensionless (elongation) equilibrium constants are described by an enthalpy and entropy term:

$$\hat{K}_{*A-A} = \exp\left(-\frac{\Delta H_{A-A}}{RT} + \frac{\Delta S_{A-A}}{R} \right)$$
$$\hat{K}_{*B-B} = \exp\left(-\frac{\Delta H_{B-B}}{RT} + \frac{\Delta S_{B-B}}{R} \right)$$
$$\hat{K}_{*A-B} = \exp\left(-\frac{\Delta H_{A-B}}{RT} + \frac{\Delta S_{A-B}}{R} \right)$$
$$\hat{K}_{*B-A} = \exp\left(-\frac{\Delta H_{B-A}}{RT} + \frac{\Delta S_{B-A}}{R} \right) \ ,$$

where R is the gas constant and T the absolute temperature. The enthalpy and entropy changes are computed in a reference state, for which we take the hypothetical state with all concentrations equal to $c_0 = 1$ M. The original equilibrium constants like K_{*A-A} are related to their dimensionless version $\hat{K}_{*A-A}$ by $\hat{K}_{*A-A} = K_{*A-A} c_0$, which means that $\hat{K}_{*A-A}$ has the numerical value of K_{*A-A} when this equilibrium constant is written in M units. In the sequel we shall omit the hat symbol and use the same notation for both versions. We assume that all enthalpy changes are negative, which is the usual situation.

The elongation temperature T_e is defined as the temperature such that the point $(a_\text{tot}, b_\text{tot})$ is a critical concentration pair, i.e.

$$\delta(a_\text{tot}, b_\text{tot}) = 1 - K_{*\text{A–A}}\, a_\text{tot} - K_{*\text{B–B}}\, b_\text{tot} + D\, a_\text{tot}\, b_\text{tot} = 0 \;, \tag{S10}$$

where $D = K_{*\text{A–A}} K_{*\text{B–B}} - K_{*\text{A–B}} K_{*\text{B–A}}$. If $b_\text{tot} = 0$, this reduces to the well known condition $K_{*\text{A–A}}\, a_\text{tot} = 1$. This gives the standard formula of the elongation temperature of a one component model:

$$T_{e,A} = \frac{\Delta H_\text{A–A}}{R \ln(a_\text{tot}) + \Delta S_\text{A–A}} \;.$$

Since $\Delta H_\text{A–A} < 0$, also the denominator of this quotient must be negative for $T_{e,A}$ to exist. In the extreme situation that $R \ln(a_\text{tot}) + \Delta S_\text{A–A} > 0$, then even for very large temperatures $K_{*\text{A–A}} a_\text{tot} > 1$, which means that the material is polymerized even for $T \to \infty$. Then an elongation temperature for the A homopolymers does not exist. The same approach can be used for the B homopolymers.

To study the solution of eq S10 in the copolymerization case, write this equation as $f_1(T) = f_2(T)$, with

$$f_1(T) = (1 - K_{*\text{A–A}}\, a_\text{tot})\,(1 - K_{*\text{B–B}}\, b_\text{tot})$$
$$f_2(T) = K_{*\text{A–B}}\, K_{*\text{B–A}}\, a_\text{tot}\, b_\text{tot} \;.$$

Let T_m be the maximum of the homopolymer elongation temperatures $T_{e,A}$ and $T_{e,B}$. Then $f_1(T_m) = 0$ and for $T > T_m$ the function $f_1(T)$ is an increasing function of T, with limit $L_1 = (1 - \exp(\Delta S_\text{A–A}/R)\, a_\text{tot})\,(1 - \exp(\Delta S_\text{B–B}/R)\, b_\text{tot})$ for $T \to \infty$. Moreover $f_2(T)$ is a decreasing function of T, with limit $L_2 = \exp((\Delta S_\text{A–B} + \Delta S_\text{B–A})/R)\, a_\text{tot}\, b_\text{tot}$ for $T \to \infty$. Usually $L_1 > L_2$, which means that there is one unique elongation temperature for copolymerization T_e where $f_1(T_e) = f_2(T_e)$. Clearly $T_e > T_{e,A}$ and $T_e > T_{e,B}$. Unfortunately a simple formula for T_e cannot be found. In the Section SI-8 of this Supplementary Information the Matlab function `ComputeTe` for a numerical computation of T_e is given. If $L_1 \leq L_2$ then the material is copolymerized, even for $T \to \infty$, and an elongation temperature for the copolymers does not exist.

SI-7   Additional data on solvent-dependent copolymerizations

Materials and Methods
All solvents were obtained from Biosolve, Acros or Aldrich and used as received. Molecules used, 6,6,6-Nitrilotris(N-(3,7-dimethyloctyl)nicotinamide) (S-**1**= A), and 4,4,4-nitrilotris(N-((S)-3,7-dimethyloctyl)benzamide) (S-**2**= B), were synthesized as previously reported[S1] and vacuum-oven dried before use.

UV/Vis and circular dichroism (CD) measurements were performed on a Jasco J-815 spectropolarimeter, for which the sensitivity, time constants and scan rates were chosen appropriately. Corresponding temperature-dependent measurements were performed with a Jasco PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-393 K and adjustable temperature slope. In all experiments the linear dichroism was also measured and in all cases no linear dichroism was observed. For spectroscopic measurements spectroscopic grade solvents were employed and sealable quartz cuvette with optic path of 1 cm × 1 cm was used.

Sample preparation

Supramolecular copolymerizations were performed with tri-5-carboxamide tri(pyrid-2-yl)amine tricarboxyamide (S-1) and tri-p-carboxamide triphenylamine (S-2),[S1,S2] see Figure S2.
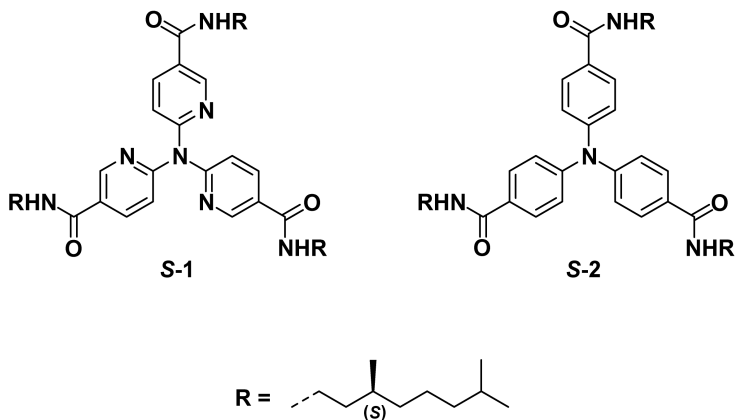
Figure S2: Chemical structures. Tri-5-carboxamide tri(pyrid-2-yl)amines (with (S)-dimethyloctyl chain (S-TPyA, S-1)) tri-p-carboxamide triphenylamines (with (S)-dimethyloctyl chain (S-TPA, S-2))

Supramolecular copolymerization between S-1 and S-2 was performed by slow cooling of monomers: a 1:1 mixture of S-1 and S-2 was heated to 100° C (373 K) and cooled down to 40°C (313 K) (cool rate: 15°C h^{-1}) affording to poly[(S-1)-co-(S-2)]. The copolymerization was monitored by Circular Dichroism (CD) following the evolution of selected wavelengths over temperature and compared with the related homopolymerizations S-1→ poly(S-1) and S-2→ poly(S-2).

The copolymerization was investigated in different solvent conditions: pure methylcyclohexane (MCH), pure decalin, mixture v/v 97:3 decalin:1,2-dichloroethane (DCE). Stock solutions of S-1 and S-2 ($c = 30$ μM) were prepared by weighing the necessary amount of compound for the given concentration and dissolved with a weighted amount of solvent based on its density. The stock solutions were heated up, sonicated till complete dissolution and slowly cooled down to room temperature every time before use unless otherwise specified. Copolymers solutions

were then prepared by mixing 1:1 the stock solution of S-**1** and S-**2**. Homopolymers solution ($c = 15$ μM) were obtained by diluting the stock solution by half. All the spectroscopic measurement were performed with freshly prepared solutions (max. 1 week after the preparation of the stock solution).
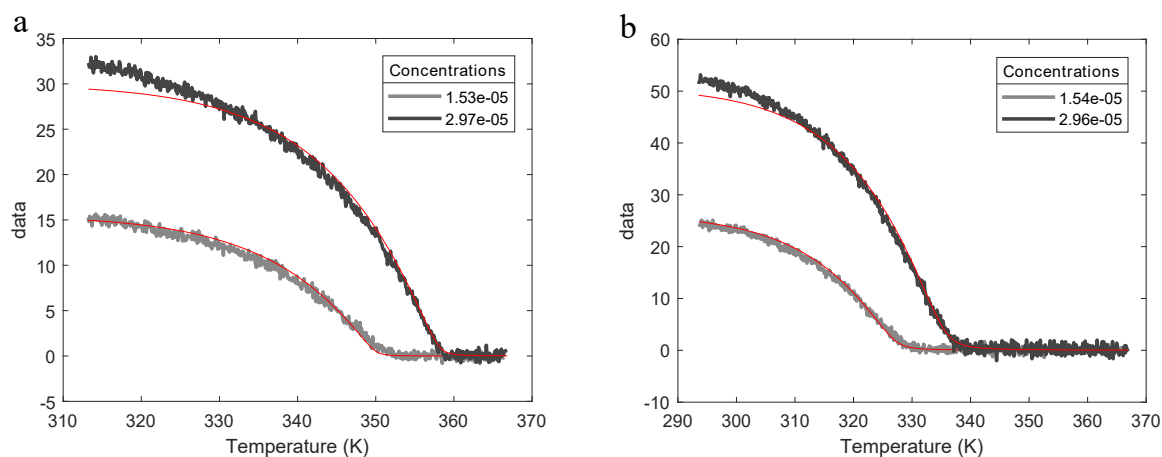

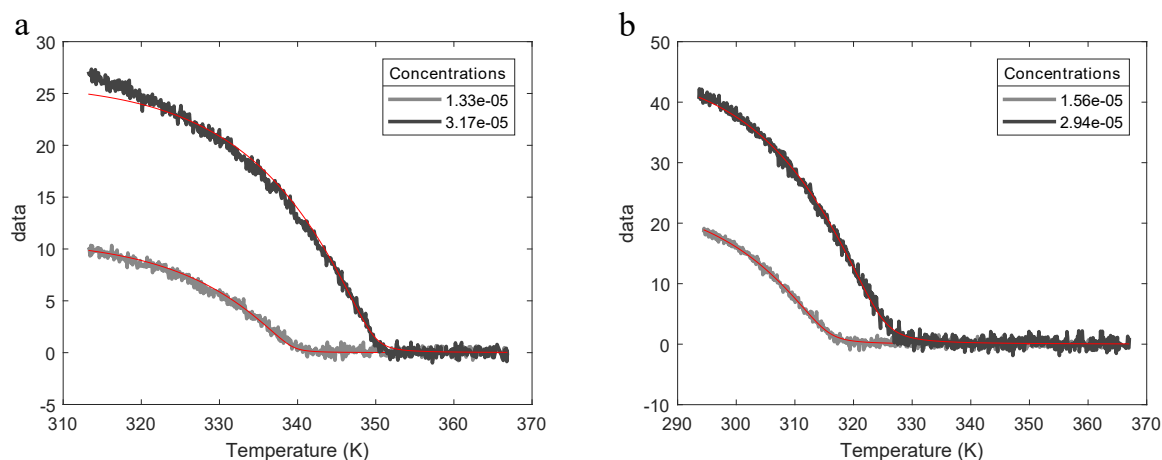Figure S3: Decalin solvent: (a) fit of CD data of S-**1** homopolymers, (b) fit of CD data of S-**2** homopolymers

Figure S4: Decalin/DCE solvent: (a) fit of CD data of S-**1** homopolymers, (b) fit of CD data of S-**2** homopolymers

Additional note on the polymerization

As previously reported, both the homopolymers are subject to pathway complexity. Both S-**1** and S-**2** display the formation of 2 assembled states with opposite handedness.[S1,S3] State I, with positive CD signal, is formed at high temperatures from a molecularly dissolved solution via a nucleation-elongation mechanism. State **II** is formed below room temperature through a sharp transition from the first assembled State **I**. Recent discovery indicates that

the temperature where the transition $\mathbf{I} \rightarrow \mathbf{II}$ occurs is dominated by the concentration of water dissolved in aliphatic solvents. It has been reported that water can interact with the supramolecular polymer chains resulting in State $\mathbf{II}$.[S3]

Although the transition $\mathbf{I} \rightarrow \mathbf{II}$, in standard humidity condition (≈ 25 ppm in MCH) occurs below 25° C (298 K), deviation from classic nucleation-elongation model can be observed starting from 35° C (308 K).[S1] Thus, in order to perform all the copolymerization under thermodynamic control in State $\mathbf{I}$, the cooling curves were performed till 40° C (313 K). The solutions were prepared in ambient conditions and stored in sealable vials or cuvettes to maintain constant humidity through-out all the experiments.

Fitting of the homopolymers

CD data of cooling curves of S-**1** and S-**2** homopolymers in the three solvents are fitted with the one-component model software given in Ref. S4. In each case two cooling curves with different concentrations have been fitted. As mentioned above, only temperatures above 40°C have been used in the fitting process. Moreover, to improve the fit quality around the elongation temperature of the homopolymers the differences between CD data and model results have been given a larger weight factor around the elongation temperature. The fit results per homopolymer and solvent are: i) the enthalpy change ΔH and entropy change ΔS at an elongation step, such that the equilibrium constant at elongation $K = \exp(-\Delta H/RT + \Delta S/R)$, ii) the nucleation penalty NP, such that the cooperativity factor is $\sigma = \exp(NP/RT)$ and finally iii) the normalization factor N (in mdeg/M), which gives the linear relation between model computed material (= equivalent concentration) in copolymers (in M) and experimental CD data (in mdeg). The fit results of the homopolymers are summarized in Table S2, graphs of the CD data and the model results are shown in Figures S3, S4 and S5.
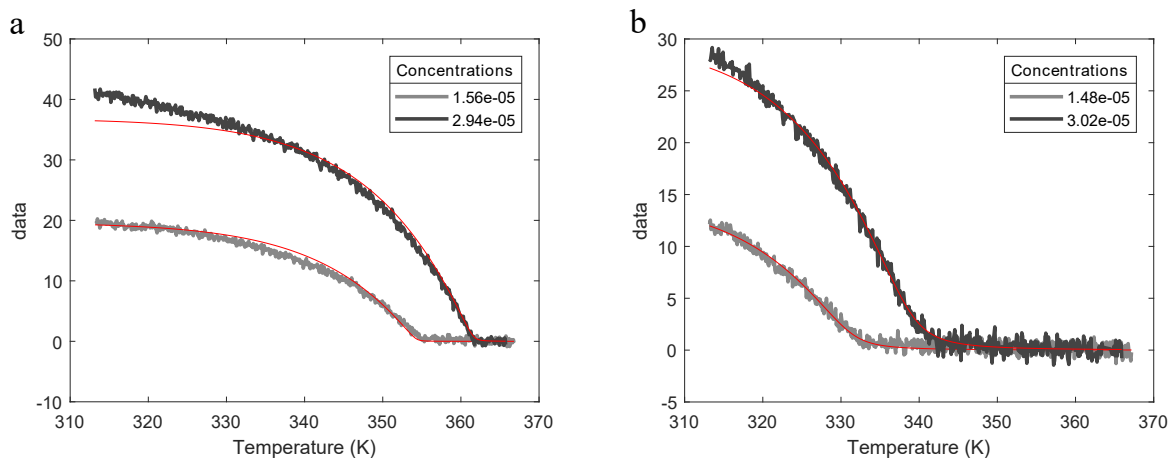

Figure S5: MCH solvent: (a) fit of CD data of S-**1** homopolymers, (b) fit of CD data of S-**2** homopolymers

Table S2: Thermodynamic parameters for triarylamine triamide based homopolymers in three distinct solvents.

monomer/solvent	ΔH [kJ/mol]	ΔS [kJ/mol K]	NP [kJ/mol]	N[mdeg/M]
S-**1**(A) in decalin	-85.4	-0.1520	-25.05	$1.009 * 10^6$
S-**2**(B) in decalin	-71.3	-0.127	-17.6	$1.707 * 10^6$
S-**1**(A) in decalin/DCE	-81.8	-0.148	-20.0	$8.196 * 10^5$
S-**2**(B) in decalin/DCE	-58.2	-0.0931	-15.4	$1.558 * 10^6$
S-**1**(A) in MCH	-92.0	-0.168	-29.5	$1.253 * 10^6$
S-**2**(B) in MCH	-87.5	-0.173	-14.0	$9.842 * 10^5$

Fitting of the copolymers

Once the homopolymer parameters are known, the only remaining parameters for the copolymerization are the thermodynamical parameters for the hetero elongation constants K_{*A-B} and K_{*B-A}. To reduce the number of parameters, we assume the symmetry condition ($\sigma_A K_{*A-B} = \sigma_B K_{*B-A}$), hence only K_{*A-B} remains. We introduce ΔH_{A-B} and ΔS_{A-B} as the corresponding enthalpy and entropy changes, i.e., $K_{*A-B} = \exp(-\Delta H_{A-B}/RT + \Delta S_{A-B}/T)$. To find the values of ΔH_{A-B} and ΔS_{A-B} we fitted a cooling curve of a S-**1**-S-**2** mixture, each with concentration 15 μM, against the results of the copolymerization model. As the normalization factors N given in Table S2 are for each solvent quite different between A and B homopolymers, it is not wise to fit the experimental data against $P_{\text{tot}} = P_A + P_B$, as then the contribution of A and B monomers is equal. Therefore we fitted the experimental CD data against $N_{\text{copol}}(N_A P_A + N_B P_B)$, where N_A and N_B are the normalization factors for S-**1** and S-**2** from Table S2 and N_{copol} is an additional normalization constant. In this way the contribution of S-**1** and S-**2** in the copolymers to the CD signal is in line with their behaviour in the homopolymers. This procedure has been done for all three solvents, resulting in the thermodynamical parameters in Table 2 of the paper. In Figure 7a of the paper the CD data and the model results are shown for decalin solvent. The results for the decalin/DCE and MCH solvents are shown in Figure S6. Besides the experimental CD data (for $T > 40°$ C) and the results of the copolymerization model these Figures also contain a "no interaction" graph, which shows the model results in the case that no mixing of the two monomer types occurs, i.e. $K_{*A-B} = K_{*B-A} = 0$. For all three solvents the copolymerization model gives a good description of the CD data. In the paper the computed equivalent bond concentrations and block lengths for the three solvents are given. Additionally we give in Figure S7 the block lengths in combination with the (concentration averaged) copolymer lengths for the three solvents.
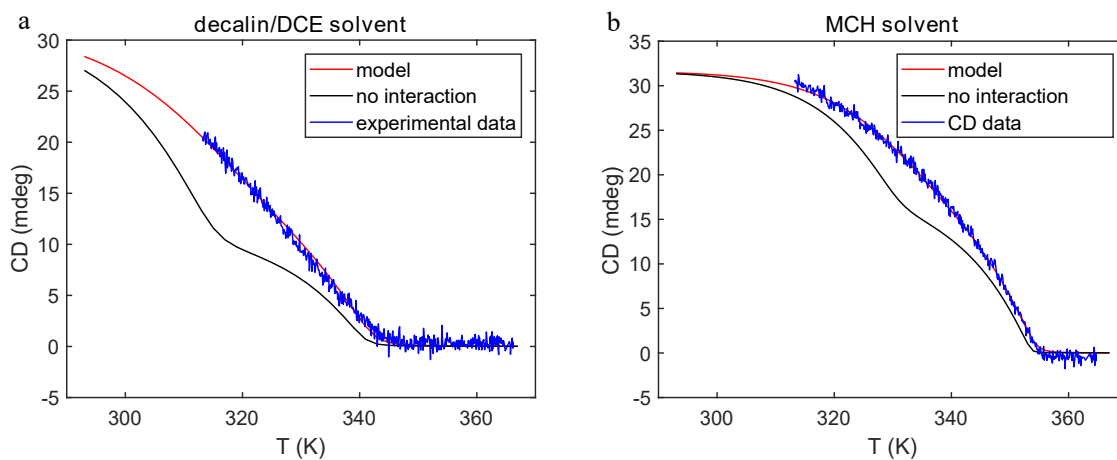
Figure S6: Fit of CD data with results of the copolymerization model and a "no interaction" model result. (a) for decalin/DCE solvent. (b) for MCH solvent.
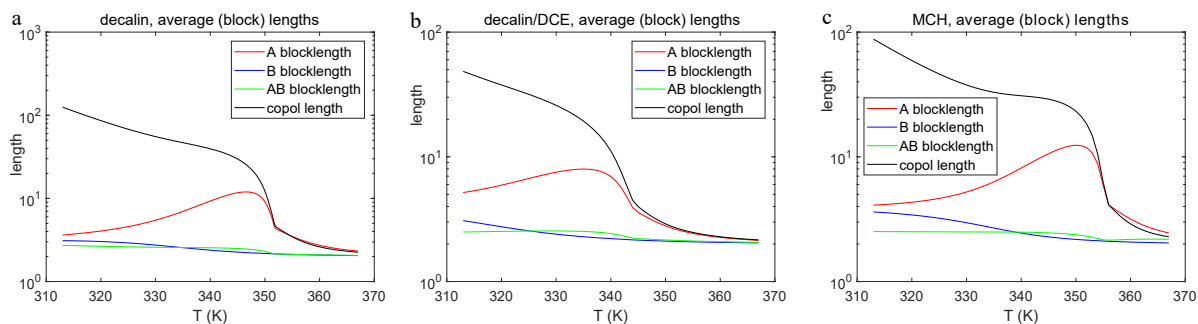

Figure S7: Average block lengths and copolymer lengths. (a) for decalin solvent. (b) for decalin/DCE solvent. (c) for MCH solvent.

SI-8   Description of Matlab scripts

In the attached zip file the following Matlab functions can be found:

SolveMassBal   General solver for mass-balance systems, 2 monomer types, arbitrary polymer types
ComputeBonds   Computes equivalent bond concentration and mass/conc. weighted copolymer lengths
ComputeBlocks Computes block lengths
ComputeTe   Computes elongation temperature of copolymers (requires optimization toolbox)

Description of mass balance solver

SolveMassBal is the general solver for mass-balance equations with two monomer types and an arbitrary number (p) of copolymer types. This Matlab function can be used by:

[c_eq,res_ab,Pout,Lout] = SolveMassBal(c_tot,sigmatable,Ktable);

The parameter c_tot is a 1×2 vector with the total concentrations of the A and B monomers. The parameters sigmatable and Ktable give the ($2p$) cooperativity parameters and the ($4p$) equilibrium constants (for elongation) for all p copolymer types. For the case of one copolymer type ($p = 1$) these variables must be defined as

```
Ktable= [K1AA,  K1BA;
         K1AB,  K1BB];
sigmatable=[ sigma1A;
             sigma1B] ;
```

where K1AA,..., K1BB are the elongation equilibrium constants and sigma1A, sigma1B the cooperativity factors of the copolymers.
For the case of two copolymer types ($p = 2$) these variables must be defined as

```
Ktable= [K1AA,  K1BA,  K2AA,  K2BA;
         K1AB,  K1BB,  K2AB,  K2BB];
sigmatable=[ sigma1A, sigma2A;
             sigma1B, sigma2B];
```

where K1AA,..., K1BB are the elongation equilibrium constants of the first aggregate type and K2AA,..., K2BB are the elongation equilibrium constants of the second aggregate type. Further sigma1A, sigma1B are the cooperativity factors of the first copolymer type and sigma2A, sigma2B are the cooperativity factors of the second copolymer type. For more than two aggregate types more columns must be added to these tables.

The result of the mass-balance solver are: c_eq,res_ab,Pout and Lout. c_eq is a 1×2 column vector with the equilibrium monomer concentration a and b. The $2 \times p$ matrix Pout gives on

the first row the equivalent A concentrations of the p copolymer types and on the second row the equivalent B concentrations, so `Pout(1,i)` contains $P_{A,i}$ and `Pout(2,i)` contains $P_{B,i}$ (for $i = 1, \ldots p$). Furthermore `Lout(i)` gives the average concentration weighted length of the ith copolymer type (for $i = 1, \ldots, p$). Finally, column vector `res_ab` gives the two residues of the numerically solved mass balance equations. This allows to check whether the numerical error is small enough in comparison with the various (equivalent) concentrations.

The mass-balance solver consists of two nested bisection (binary search) methods. The innermost method computes for given b value the $a(b)$ value such that the first mass balance equation is satisfied. The outermost method then computes the b value that the pair $(a(b), b)$ also satisfies the second mass balance equation. The mass-balance solver can also be used for one component systems, with one or more polymer types, by setting $b_{\mathrm{tot}} = 0$.

In the case of a one component systems with one copolymer type, the mass-balance equation can be reduced to a single cubic equation, which can be solved by Cardano's formula. In Ref. S4 we have given Matlab software for one component systems with one copolymer type, that uses this method. This software is faster than the solver described here, but it is restricted to one component one polymer type systems, while the mass-balance solver given here can handle copolymer systems with two monomer types and an arbitrary number of copolymer types.

Matlab functions for bonds, block lengths and elongation temperatures
The equivalent bond concentrations and the average mass weighted and concentration weighted copolymer length for a specific copolymer type can be found by:
`[PAA,PBB,PAB,PBA,Lmw,Lcw] = ComputeBonds(c_eq,sigma,K);`
The parameter `c_eq` must contain the equilibrium concentrations a and b. `sigma` and K must contain the cooperativity parameters and equilibrium constants for elongation of the considered copolymer type, in the same order as in `SolveMassBal` for the case of one copolymer type. The results are the equivalent bond concentrations and the average mass weighted (`Lmw`) and concentrated weighted (`Lcw`) copolymer lengths. Note that this function works for one copolymer type. In case of multiple copolymer types the function may be used repeatedly, with the `sigma` and K of the considered copolymer type.

The average block lengths for a specific copolymer type can be found by:
`[Abl,Bbl,Cbl,nstop] = ComputeBlockLengths(c_eq,sigma,K,eps,verbose);`
The parameters `c_eq`, `sigma` and K are the same as for the function `ComputeBonds`. The computation of block lengths uses an iteration process over the length of the copolymers. The parameter `eps` is the allowed fraction of missing material, if the fraction missing material is below `eps` the iteration process is terminated. In the examples we always used 0.005 for the value of `eps`. The parameter `verbose` determines the amount of output during this process,

i.e., with `verbose=true` intermediate results during the iteration process are shown and with `verbose=false` no additional output is generated. The results are the average A block length `Abl`, the average B block length `Bbl` and the average AB (alternating) block length `Cbl`. Note that also the length of an alternating block is given as the number of monomers in the block. The number of performed iterations (until all material up to a fraction `eps` is considered) is `nstop`.

The elongation temperature of a copolymer type can only be found if the dependence of the equilibrium constants on the temperature is given. Assuming the general relation $K = \exp(-\Delta H/RT + \Delta S/R)$ means that an enthalpy difference ΔH and an entropy difference ΔS must be given for each of the four equilibrium constants (see also Section SI-6). Also the total concentrations `c_tot` of the A and B monomers is needed. Then:
`[Te,Te_A,Te_B] = ComputeTe(c_tot,DeltaHAA,DeltaSAA,DeltaHBB,DeltaSBB,DeltaHAB,`
`DeltaSAB,DeltaHBA,DeltaSBA);`
with the ΔH in kJ/mol and the ΔS in kJ/mol/K results in the elongation temperature `Te` of the copolymers, the elongation temperature `Te_A` of the A homopolymers (based on their own concentration) and the elongation temperature `Te_B` of the B homopolymers (also based on their own concentration). If the elongation temperatures do not exist (see Section SI-6), a negative value is given. Note that the computation of elongation temperatures is only useful for systems with one copolymer type. The computation assumes that all monomers are available for forming the considered copolymer type. For a system with two or more copolymer types that may only hold for the copolymer type with the highest elongation temperature (if the second highest elongation temperature is sufficiently lower). In the case of multiple copolymer types the elongation temperatures of all copolymer types can better be found by computing a cool curve for the whole system.

Examples
The zip file contains the following examples:

`Example_OneComponent`	One monomer type and one polymer type, isodesmic and (anti-)cooperative cases
`Example_NatureComm2011`	Majority Rules case, two monomer types and two copolymer types
`Example_SergSold`	Sergeants and Soldiers case, two monomer types and two copolymer types
`Example_JACS2013`	One monomer type and four polymer types
`Example_JACS2017`	Two monomer types and three copolymer types
`Example_JACS2018`	General copolymerization, two monomer types, one copolymer type

These examples show that almost all mass-balance systems previously published by the authors of this paper can also be solved with the general copolymerization software presented here. Moreover, it also allows to compute equivalent bond concentrations and average block lengths, which gives more insight in the structure of the copolymers. The first example `Example_OneComponent` shows how to treat systems with one component, for the isodesmic, cooperative and anti-cooperative case. The computation of elongation temperatures for copolymers is shown in `Example_JACS2018`. The most extensive example, including the computation of equivalent bond concentrations and block lengths, for two copolymer types, is `Example_SergSold`. This script also generates Figures 4b and 5 presented in the main text.

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(S4) Ten Eikelder, H. M.; Markvoort, A. J.; De Greef, T. F.; Hilbers, P. A. An equilibrium model for chiral amplification in supramolecular polymers. *J. Phys. Chem. B* **2012**, *116*, 5291–5301.