Supplementary material (ESI)

I. Dissipative Particle Dynamics method

The dissipative particle dynamics (DPD) simulations technique is a version of coarse-grained molecular dynamics adapted to polymers and mapped onto the classical lattice Flory-Huggins theory (see Refs. 30–33 in the main text). In this method, polymer chains are represented in terms of the bead-and-spring model, with particles interacting with a conservative force (repulsion), a dissipative force (friction), and a random force (heat generator). A soft repulsive potential enhances the stability of the numerical scheme for integrating the equations of motion and makes it possible to access large time and spatial scales when complex polymeric structures are studied.

In this work, simulations were performed using the DPD-VV integration scheme (see Besold et al, *Phys. Rev. E*, 2000, 62, R7611), that implements the modified velocity-Verlet algorithm (see Allen and Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, 1987) for solving Newton's equations of motion for interacting particles

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i, \ m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i.$$
(1)

Here \mathbf{r}_i , \mathbf{v}_i , and m_i denote the radius vector, velocity, and mass of the *i*-th particle. The force \mathbf{F}_i acting on it is a sum of pairwise additive contributions of conservative, dissipative and random forces,

$$\mathbf{F}_i = \sum_{i \neq j} (\mathbf{F}_{ij}^{\mathrm{C}} + \mathbf{F}_{ij}^{\mathrm{D}} + \mathbf{F}_{ij}^{\mathrm{R}}),$$
(2)

where the summation is performed over all other particles within a certain cutoff radius r_c . We assume that all quantities in Eqs. (1) and (2) are dimensionless, and for simplicity we set all m_i and r_c to unity.

The conservative force \mathbf{F}_{ij}^C includes a soft core repulsion force \mathbf{f}_{ij}^{nb} between non-bonded particles and a bond elasticity force \mathbf{f}_{ij}^b in bead-spring polymer chains

$$\mathbf{F}_{ij}^{\mathrm{C}} = \mathbf{f}_{ij}^{nb} + \mathbf{f}_{ij}^{b},\tag{3}$$

$$\mathbf{f}_{ij}^{nb} = \begin{cases} a_{ij}(1-r_{ij})\bar{\mathbf{r}}_{ij} & r_{ij} < 1\\ 0 & r_{ij} \ge 1, \end{cases}$$
(4)

$$\mathbf{f}_{ij}^b = -K_{ij}(r_{ij} - l_{ij})\mathbf{\bar{r}}_{ij},\tag{5}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\mathbf{\bar{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$, a_{ij} is a maximum repulsion between particles *i* and *j* is attained at $\mathbf{r}_i = \mathbf{r}_j$; K_{ij} is a bond spring constant, l_{ij} is the equilibrium bond spring length (K_{ij} and l_{ij} are non-zeros only for the bonded pairs of particles). The dissipative force \mathbf{F}_{ij}^D (friction) and the random force \mathbf{F}_{ij}^R are defined as follows:

$$\mathbf{F}_{ij}^{\mathrm{D}} = -\frac{\sigma^2}{2k_B T} \left[\omega(r_{ij}) \right]^2 (\mathbf{v}_{ij} \cdot \bar{\mathbf{r}}_{ij}) \bar{\mathbf{r}}_{ij}, \tag{6}$$

$$\mathbf{F}_{ij}^{R} = \boldsymbol{\sigma}\boldsymbol{\omega}(r_{ij}) \frac{\boldsymbol{\zeta}}{\sqrt{\delta t}} \mathbf{\bar{r}}_{ij}, \ \boldsymbol{\omega}(r) = \begin{cases} (1-r) & r < 1\\ 0 & r \ge 1, \end{cases},$$
(7)

where σ is the amplitude of noise, k_B is the Boltzmann constant, T is the system temperature, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, ζ is a normally distributed random variable with zero mean and unit variance chosen independently for each pair of particles, and δt is the time step. For simplicity, we assume that $k_B T = 1$ and introduce a dimensionless time unit as

$$\tau = r_c \sqrt{\frac{m}{k_B T}} = 1. \tag{8}$$

The Groot-Warren thermostat is defined by Eqs. (6) and (7). The random and the dissipative forces serve as a heat source and a heat sink, respectively, preserving the momentum for each pair of the interacting particles. Following Ref. 30 in the main text, we chose the noise parameter σ and the reduced particle density ρ_0 both equal to 3 as that provides an optimal balance

between fast thermal relaxation and stability of the equilibrium state. In the same paper it was shown that for $\rho_0 = 3$ the repulsion parameter for dissimilar particles is related to the Flory-Huggins interaction parameter χ :

$$a_{ij} = \chi/0.306 + 25, \, i \neq j. \tag{9}$$

The time step for integrating Eq. (1)was set to $\delta t = 0.004$, which is 10 times smaller than the commonly used value. This was done to enhance the stability of the numerical scheme at the elevated values of repulsion and bond stretch strengthes used in our work. The periodic boundary conditions were used in all three directions.

II. Controlling phantom behavior of the subnetworks

The soft nature of the potential of the conservative interaction between particles is one of the distinctive features of the DPD method that helps the system to reach the state of equilibrium faster. At the same time, the soft potential has a limited amplitude of repulsive force, and thus the particles can overlap significantly. In the case of polymer systems, it leads to the possibility for the chains to penetrate through each other, which is usually called "phantom behavior". For interpenetrating networks, the phantom behavior of the chains annihilates the effect of topological entanglements between the subnetworks, which would result in physically incorrect properties. Therefore, the interaction parameters were chosen in a way that allows the researchers to avoid the phantom behavior.

We performed test simulations on a medium-sized IPN microgel ($n_{sub} = 20$, $N \approx 4 \cdot 10^4$, equilibration for 10^7 DPD steps) and checked the results for the presence of topology violations. To this end, we analyzed the instantaneous structures every 10^6 DPD steps. First, the full set of the mesh cycles in the structure was determined for both subnetworks. Then, for each pair of cycles from this set, the Gauss linking number (GLN) defining the topological entanglements was calculated. The GLN defines how many times one cycle passes through another one, as well as the topological direction of those passages. Finally, we compared GLNs for all the pairs of cycles during the equibrilation with the ones obtained for the initial structure. If there were GLNs that did not match the initial value a topology violation occurred, and the system behavior was considered as "phantom".

We increased the values of the repulsion parameters a_{ij} and bond spring constants K_{ij} , and decreased the equilibrium bond spring lengths l_{ij} and repeated the test simulations described above until no topology violations were observed. The resulting interaction parameters were: $a_{ij} = 100$ for the solvent-solvent and polymer-polymer interactions, $a_{ij} = 120$ for the solvent-polymer for the collapsing subnetwork, and $a_{ij} = 80$ for the solvent-polymer for the swelling subnetwork, $l_{ij} = 0.3$, and $K_{ij} = 100$. These values led to non-phantom behavior of the test system and thus were used in our study.

III. Microgel equilibration



Fig. S-1 Time evolution of radius of gyration during the system equilibration for various solvent selectivity. Microgel size $N \approx 3 \cdot 10^4$, subchain length $n_{sub} = 16$.

As mentioned in the main text, the prepared conformations of IPN microgel were equilibrated for for $(5-20) \cdot 10^6$ DPD steps, depending on the size of the system. Fig. S-1 shows the evolution of the radii of gyration (R_g) for the system with $n_{sub} = 16$, $N \approx 3 \cdot 10^4$ in a selective solvent. The selective solvent is set by the repulsion parameter a_{ij} , which is set as following: $a_{ij} = 100$ for the solvent-solvent and polymer-polymer interactions, $a_{ij} = 100 + \Delta a$ for the solvent-polymer for the collapsing subnetwork, and $a_{ij} = 100 - \Delta a$ for the solvent-polymer for the swelling subnetwork. Two cases are shown in Fig. S-1: $\Delta a = 10$ and $\Delta a = 20$. All measurements are done in the productive trajectory part, after the equilibration process is completed.

IV. Microgel collapse in non-selective solvent



Fig. S-2 Microgel collapse in a non-selective solvent. Dependence of radius of gyration on solvent quality.

Fig. S-2, a shows the dependence of the radii of gyration (R_g) on the solvent quality of the system with $n_{sub} = 16$, $N \approx 3 \cdot 10^4$. The solvent is non-selective solvent, and the solvent quality is set by the repulsion parameter a_{ij} , which is set as follows: $a_{ij} = 100$ for the solvent-solvent and polymer-polymer interactions, $a_{ij} = 100 + \Delta a$ for the solvent-polymer for both subnetworks. Fig. S-3 shows that the structure factors for various Δa : $\Delta a = -20$ correspond to very good solvent (Fig. S-3, a), $\Delta a = 0$ corresponds to the theta-conditions (Fig. S-3, b), and $\Delta a = 20$ corresponds to very poor solvent (Fig. S-3, c). The peak at $q \approx 0.15 - 0.2$ in cases of swollen microgels ia an artifact of the ideal diamond-like network model.



Fig. S-3 Microgel collapse in a non-selective solvent, structure factors for various solvent qualities: very good solvent, $\Delta a = -20$ (a), theta-solvent, $\Delta a = 0$ (b) and very poor solvent, $\Delta a = 20$ (c).

V. Microgel collapse in selective solvent

Fig. S-4 shows the dependence of the radii of gyration (R_g) on the solvent quality for the system with $n_{sub} = 16$, $N \approx 3 \cdot 10^4$. The solvent is selective solvent. The selective solvent is set by the repulsion parameter a_{ij} , which is set as following: $a_{ij} = 100$ for the solvent-solvent and polymer-polymer interactions, $a_{ij} = 100 + \Delta a$ for the solvent-polymer for the collapsing subnetwork, and $a_{ij} = 100 - \Delta a$ for the solvent-polymer for the swelling subnetwork. Fig. S-5, a–c show radial density profiles, Fig. S-5, d–f show structure factors for various Δa : $\Delta a = 0$ corresponds to the solvent (Fig. S-5, a,d), $\Delta a = 5$ corresponds to low segregation of subnetworks (Fig. S-5, b,e), $\Delta a = 20$ corresponds to high segregation of subnetworks (Fig. S-5, c,f). Notably, the peak at

 $q \approx 0.15 - 0.2$ corresponding to the artifact of the ideal diamond-like network model virtually disappears in high segregation regime.



Fig. S-4 Microgel collapse in a selective solvent. Dependence of radius of gyration on solvent quality.



Fig. S-5 Microgel collapse in a selective solvent. (a–c) Density profiles and (d–f) structure factors for various solvent qualities: $\Delta a = 0$ (a,d), $\Delta a = 5$ (b,e) and $\Delta a = 20$ (c,f).

VI. Dependence of density profiles and structure factors on the microgel's size

Fig. S-6 shows the radial density profiles and structure factors for the systems with $n_{sub} = 20$ and molecular mass N from 10^4 to 10^5 in the selective solvent ($\Delta a = 20$). Fig. S-6, a, d correspond to the core–corona structure; Fig. S-6, b, e correspond to the shell–corona structure, and Figs. S-6, c, e)correspond to the core–shell–corona structure.

1–5



Fig. S-6 Microgel collapse in a selective solvent, subchain length $n_{sub} = 20$, high segregation regime ($\Delta a = 20$). Radial density distributions (a–c) and structure factors (d–f) for various microgels sizes: $N \approx 10^4$ (a, d), $N \approx 4 \cdot 10^4$ (b, e), $N \approx 10^5$ (c, f).