Supplemental Material for paper:
Telechelic star polymers as self-assembling units
from the molecular to the macroscopic scale

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COARSE-GRAINING METHOD

The coarse graining used throughout this work, is an extension of the soft effective segment representation (SES) previously developed for both homopolymer linear (grafted and ungrafted) chains [3, 4] and block copolymers [1]. The methodology has been proven extremely efficient in reproducing fundamental physical properties of polymers in the semi-dilute solution. The strategy consists in representing the polymer as a chain of effective segments or blobs. Each blob, representing a group of monomers, interacts with other blobs via effective interactions that have been computed for dimers (at infinite dilution) taking into account many-body contributions [1, 2]. The effective interaction computed at zero density successfully reproduces the physical properties of the system (e.g. pair distribution functions) till the blobs start to overlap, e.g., till the density $\rho_b$ of blobs in solution reaches the overlap density of blobs $\rho_b^*$. The SES strategy consists in representing the polymer chains with a number of blobs high enough to ensure that the condition $\rho_b \leq \rho_b^*$ is satisfied. Hence, the higher the density in solution the finer is the level of the coarse graining required. In the range of densities considered in this paper we found that the minimum number $n_{\text{min}}$ of blobs that is required for obtaining a proper description in the scaling limit of telechelic star polymers, is determined by the local monomer density within the star. Therefore, to tune the level of coarse graining needed to reproduce the physical quantities in the system while guaranteeing that the coarse graining is not affecting the results, we performed an extensive analysis of single star properties, upon increasing the number of blobs per arm, therefore augmenting the detail of the coarse graining that we are using.

We found that for $n > n_{\text{min}}$ all the properties of the single star (radius of gyration of the star, radius of gyration of the arms, radius of gyration of the two components of the arms, intra-aggregation properties), are independent of the level of the coarse graining used to represent the star, thus defining $n_{\text{min}}$ as the minimum number of blobs needed for the results to be independent on the level of coarse graining used. We show in Fig. S1 the estimate of the various radii of gyration calculated with four different level of coarse graining, namely 50, 55, 60 and 65 blobs per arm for stars with $f \in [3, 9]$ and $\alpha = 0.4$. As evident from the figure, the four different coarse graining levels perfectly agree in reproducing the radius of gyration of the whole star, the radius of gyration of each arm of the star, of the self-avoiding head and of the attractive tail of each arm. Therefore, as long as the number of blobs $n$ is bigger than the minimum number of blobs $n_{\text{min}}$ (found to be $n_{\text{min}} = 50$ for the cases at hand), all the properties of stars and system become coarse graining.
Figure S1: Radius of gyration of whole star (black triangles) of each arm (red diamonds) of the self avoiding
head of each arm (blue squares) and of the attractive tail of the arms (green circles) obtained using 50, 55,
60 and 65 blobs per arm for a star with \( f \in [3, 9] \) and \( \alpha = 0.4 \). The various identical symbols correspond
to different number of blobs. The inset shows the comparison between the radius of gyration of the self-
avoiding part of the polymer arms (red \( \alpha = 0.8 \), black \( \alpha = 0.6 \), blue \( \alpha = 0.4 \)) and results obtained with
full monomer simulations for self-avoiding homopolymers of equivalent length (dashed lines). The full
monomers results have been rescaled in terms of the SES representation using the scaling law introduced in
[4].

Moreover, it has already been shown for the case of grafted homopolymer brushes
that the method of coarse graining allows for a controlled back-mapping onto full monomer results
[4]. In this work, we always used a total number of segments or blobs \( n > n_{\text{min}} \), thus satisfying
the constraint for the validity of this approach. Performing simulations for systems slightly below
the \( \Theta \)-temperature for the solvophobic tails, and in the athermal solvent regime for the solvophilic
heads, grants an attractive, effective potential between the \( B \) and a repulsive, Gaussian potential
between the $A$ blobs. The microscopical asymmetry ratio can also be rewritten in terms of the coarse grained model, which reads:

$$\alpha \simeq \frac{n_A \left(r_{gA}\right)^{1/\nu_A}}{n_A \left(r_{gA}\right)^{1/\nu_A} + n_B \left(r_{gB}\right)^{1/\nu_B}},$$

where $r_{gA}$ and $r_{gB}$ are the radii of gyration, and $\nu_A$ and $\nu_B$ are the Flory exponents of the $A$ and $B$ effective segments respectively. Here we chose $r_{gA} = r_{gB} = r_g$. Note that equation (1) assumes that the number of monomers in every segment is large enough to be in the scaling regime of polymers (e.g., large number of monomers per arm).

**THE EULER CHARACTERISTIC**

Systems assembling in low density percolating networks (or gels) are characterized by an inhomogeneous distribution of particles in space; such inhomogeneity makes gels an extremely complex system to characterize, since high order correlations play an important role. For this reason, a structural analysis of network forming systems are not straightforward: common characterizations, essentially based on two particle correlations, do not give a full insight on the assembled status of the system and more complex analysis are required for such phases.

A robust indicator that has been used to describe morphologies on vast scales, ranging from the large-scale structure of the universe [5] to the microscopic scale of molecules and atoms [6, 7] is based on the Euler-characteristic $\chi$. The latter is a topological invariant that was introduced by Leonhard Euler to characterize surfaces of polyhedra by counting their number of corners (vertices), edges and faces. For the topological characterization of the gels, we consider the surface that is formed by a collection of spheres with radius $R$ centered on the position of each solvophobic blob in the TSP. The Euler characteristic $\chi(R)$ that we obtain within our analysis is therefore an indicator for a family of surfaces formally parametrized by $R$. The complexity of the analysed surfaces entails an enhanced sensitivity of this measurement with respect to many-particle correlations and provides insights in both local and global structure of the gel phase. Examples of appropriately normalized $\chi(R)$ at finite densities, only considering the solvophobic blobs, are given in Fig. S2 for systems of telechelic star polymers with $f = 3, 5, 7$ and 10 arms and $\alpha = 0.4, 0.6$ and 0.8.

A change in the value of $\chi(R)$ is brought about by a topological difference in the surface induced by a small increase in the radius $R$ of the covering spheres. The simplest of the events causing
Figure S2: The Euler characteristic $\chi(R)$ for a system of telechelic star polymers with $f = 3, 5, 7$ and 10 arms and asymmetries $\alpha = 0.4, 0.6, 0.8$ at finite densities. The $x$ axis is scaled with the radius $r_g$ of gyration of the blob. Panel (b) is a zoom of panel (a) in the region of the plateaus of the Euler characteristic.

Those changes is found when two unconnected spheres start touching on increasing the value of $R$. In this particular case the topology is modified, because two, initially disjoint, surfaces have merged to a single one. In the same fashion, a plateau in $\chi(R)$ indicates the absence of such events, which implies that at those length-scales “nothing” is happening, or that there is a balance between different types of events in the more clangorous range of distance scales. For a more complete description of the methodology we refer the reader to Refs. [7, 8].

The plateaus of $\chi(R)$ in Fig. S2 in the range $10 \lesssim R/r_g \lesssim 50$ are indicative of the formation of well-separated patches by the telechelic stars. The beginning of each plateau is related to the distances between solvophobic blobs within the same patch, whereas the end and the height of a plateau correspond to the minimal distance between distinct patches and the average number of solvophobic blobs in a patch respectively.
CLUSTER ANALYSIS

The hierarchical self-assembling properties of TSP rely on the ability of the stars to keep their low-density assembled patchy particle structure upon augmenting densities. In the infinite dilution regime, the identification of the patches formed by a single star, together with the characterization of their angular and spatial distribution around the centre of the star, is straightforward. At finite densities on the other hand, particles start aggregating with one another and the more they interact, the more difficult it becomes to distinguish the contribution of each star to the aggregates as well as to characterise the single star self-aggregating properties. The Euler characteristic is capable of identifying the presence of clusters and their sizes, however it does not allow for a proper characterization of the patchy nature of each star.

A simple visual analysis of simulations snapshots shows that the clusters formed by the solvophobic arm ends are nicely defined and isolated (see figure S3), suggesting that a cluster algorithm should be capable of precisely identifying the clusters. Fundamental properties are then measured in details, such as the cluster (patch) size and arrangement around each stars, as well as the counting and classification of the clusters resulting from the merging of distinct patches. The cluster analysis is then performed both at zero density and at finite density to fully characterize the properties both of the single star and of the solution. Clusters are defined by introducing a cut-off radius $R_{\text{cut}}$: particles are classified as neighbours if their distance is below $R_{\text{cut}}$.

Clusters are then built by grouping particles that share at least one neighbour. According to this definition, a patch is a cluster of solvophobic particles. $R_{\text{cut}}$ is a free parameter, that is chosen in a range of values around $R_{\text{cut}} \simeq r_g$, where $r_g$ is the radius of gyration of the blob. The optimal $R_{\text{cut}}$ is such that the number and size of the clusters is not affected by a small variation $\Delta R_{\text{cut}}$ of the cut-off radius. Such a cut-off value exists because the clusters are well separated in solution as it can be seen in the simulations snapshots (see Fig. S3) and by the presence of plateau region in the Euler characteristic (see Fig. S2). Once a list of cluster is obtained for each simulation snapshot, we measure the number of patches that belong to each star, their geometrical arrangement around the center of the star, and the degree of connectivity present in the system. Such quantities are then averaged over the configurations sampled for each density and star parameters (functionality $f$ and arm solvophobicity $\alpha$). Accordingly, we can classify how the patches distribute around the stars and how they are shared among the stars in solution. The averages are then compared to the zero density simulations as showed in Table ST1 and in Table ST2 below, verifying the robustness.
Figure S3: Snapshot of a percolating gel formed by telechelic star polymers with $f = 5$ arms and 60% of attractive monomers per arm. Color coding of the blobs: gray (solvophilic), green (solvophobic), anchor point (red). The snapshot shows the simulation box and some parts of the periodically repeated system.

of the patchiness $p$ across a wide range of concentrations both in the ordered crystalline and in the disordered gel phase.
Table ST1: Properties of the TSP’s in the diamond lattice for two different tetrahedrally coordinated molecules, namely \( f = 15, \alpha = 0.6 \) and \( f = 15, \alpha = 0.4 \) and for a six fold coordinated molecules, namely \( f = 20, \alpha = 0.5 \), over a wide range of densities, indicated at the first column. In the tables, \( p \) represents the average number of patches, \( \omega \) the bond angles between the segments connecting the anchoring point to two different patches, \( L \) the patch extension (the distance from the anchoring point to the center of mass of the patch) and at the last column, \( a \) denotes the bond length in the underlying monomer resolved system.

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<th>( p )</th>
<th>( \omega ) [in degrees]</th>
<th>( L ) [in units of ( a )]</th>
<th>( \rho/\rho^* )</th>
<th>( p )</th>
<th>( \omega ) [in degrees]</th>
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<th>( \omega ) [in degrees]</th>
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Table ST2: Intra particle aggregation properties for star polymers with \( f \in [5, 15] \) and fixed asymmetry \( \alpha = 0.4 \), over a wide range of densities (infinite dilution, \( \rho / \rho^* = 0 \), and in the gel phase, \( \rho / \rho^* > 0 \)).

<table>
<thead>
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<th>( f = 10 )</th>
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<td>( p )</td>
<td>( \rho / \rho^* )</td>
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