Supporting Information

Reversible Association and Network Formation in 3:1 Ligand-Metal Polymer Solutions

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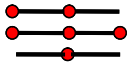
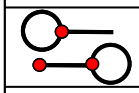
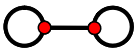
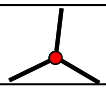
Table 1 (corresponding to Figure 3): Composition dependence of the average number fraction of different species at several metal-to-oligomer ratios (r) for oligomer concentration $c=3.8\times10^{-4}$. The fractions of three most favorable species are depicted in bold and underlined, while the joint contribution of all other species is shown in bold.

species \ r	0.3	0.5	0.67	1.0	2.0
	<u>0.63464</u>	**<u>0.30843</u>**	0.05828	3.461E-4	7.14E-7
	0	1.818E-7	1.114E-4	.01939	**<u>0.86969</u>**
	0.01393	0.02274	0.01449	0.01905	**<u>0.08182</u>**
	0.01308	0.06486	**<u>0.26613</u>**	**<u>0.65011</u>**	**<u>0.0395</u>**
	1.643E-5	4.481E-4	0.0075	**<u>0.05835</u>**	4.867E-4
	**<u>0.19121</u>**	**<u>0.29505</u>**	**<u>0.1934</u>**	**<u>0.02639</u>**	1.943E-4
	0.01339	**<u>0.06889</u>**	**<u>0.13466</u>**	0.00698	0
	**<u>0.05915</u>**	0.02904	0.00218	2.303E-4	1.167E-4
Others	**0.11500**	**0.32763**	**0.40581**	**0.26515**	**0.00899**

Determination of the onset of reversible network formation from molecular weight distribution.

The onset of network formation can be determined from the molecular weight distribution. In Figure S1 the molecular weight distribution at r=0.75 is shown for three different oligomer concentrations on the left. Comparing three different oligomer concentrations, we can see that the weight fraction decreases monotonically with molecular weight for oligomer concentrations below the onset of network formation. Near the critical oligomer concentration (onset of network formation) ($c=7.02\times10^{-4}$)), the weight fraction first decreases and then remains nearly constant for a small range of molecular weights followed by a decrease. Above the critical oligomer concentration (e.g. for $c=7.63\times10^{-4}$), the weight fraction initially decreases followed by a minimum

and maximum and then decreases. The maximum in the weight fraction distribution is a clear indication of the formation of large supramolecular network in the system. Using 20 adjacent data points, we calculate the slope of corresponding molecular weight distribution shown on the right of Figure S1. For all oligomer concentrations, the slope initially increases, reaches its maximum followed by a minimum. For low oligomer concentration, the slope is always less than zero. At the critical oligomer concentration, the maximum of the slope is equal to zero and further increase of oligomer concentration leads to positive slopes indicating the presence of network in the system. Similar behavior was observed for different metal-to-oligomer ratios when the oligomer concentration is fixed with two critical metal-to-oligomer ratios (onset of network formation) being obtained.

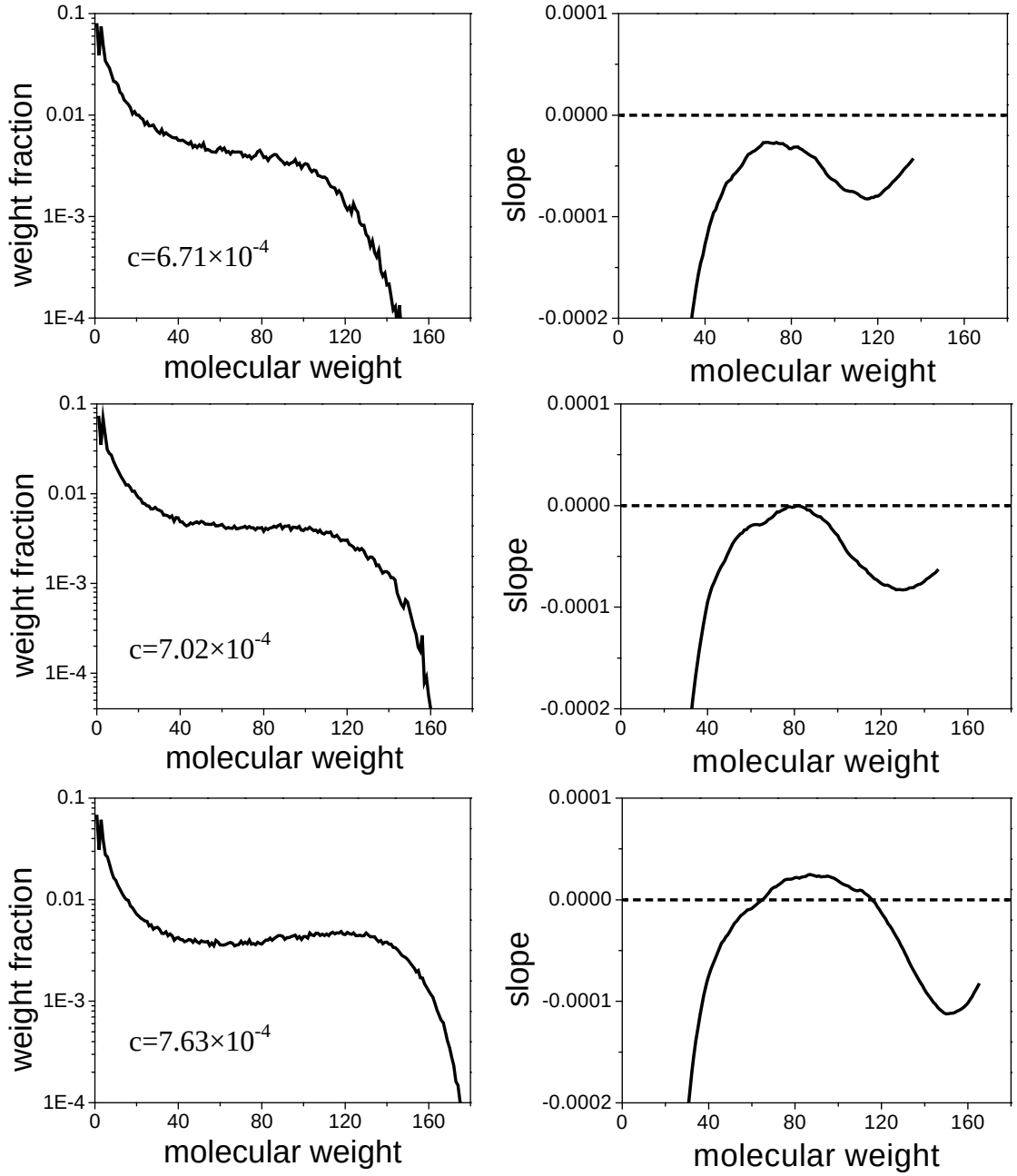


Figure S1: Average molecular weight distribution in terms of weight fraction for r=0.75 for three different oligomer concentrations (in units of oligomer/volume) is shown on the left. The corresponding slope of the molecular weight distribution for each oligomer concentration is shown on the right.

Mesh size calculation.

Mesh size r_m is the average distance between two adjacent effective crosslinks. Mesh size was calculated by averaging over 4×10^6 MCts the end-to-end distance (R_{end}) for the effective strands connecting neighboring effective crosslinks. In Figure S2, the mesh size for different oligomer concentrations (and metal-to-oligomer ratios) is plotted (log-log scale) versus the molecular weight between effective crosslinks (M_e). We found based on our simulation results that mesh size exhibits the following scaling dependence which is similar to the scaling dependence for the end-to-end distance for a linear chain (of molecular weight M) in a polymer melt $R_{end} \sim M^{0.5}$ and somewhat weaker than that for dilute solutions $R_{end} \sim M^{0.63}$ (for our BFM). The difference is likely to originate from higher density in the network core compared to the dilute solution limit or even the average density.

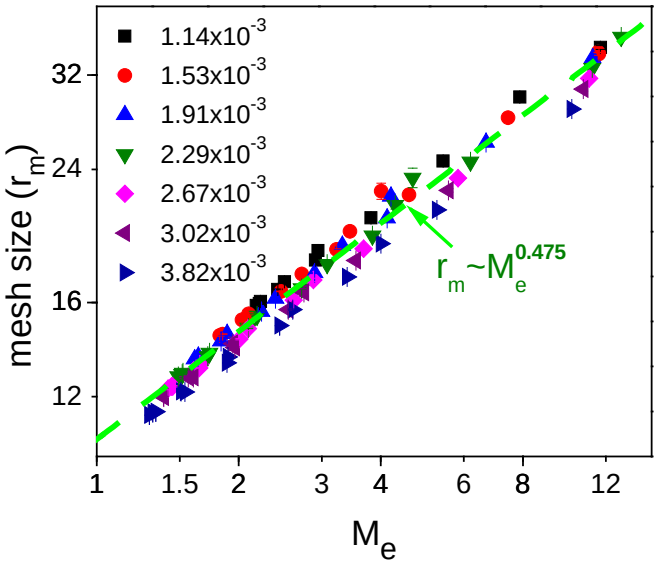


Figure S2. The average mesh size (symbols) versus average molecular weight between effective crosslinks M_e for several oligomer concentrations. The dash line is the fitting of the mesh size data to $r_m \sim M_e^{0.475}$.