Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Effects of Network Junctions and Defects on Crystallization of Model Poly(ethylene glycol) Networks

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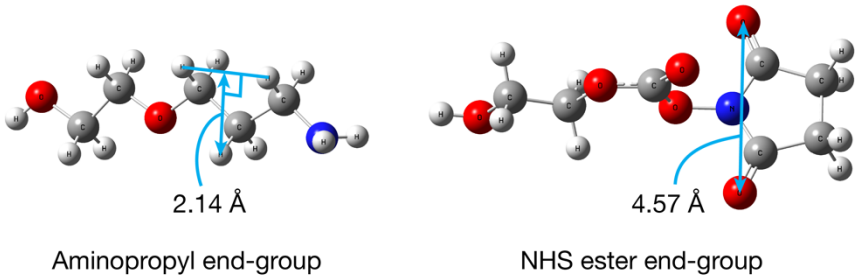

Fig. S1 Estimation of bulkiness of the end-groups. Model compounds with aminopropyl or NHS ester end-groups attached to ethylene glycol were constructed and the structure was optimized at HF/3-21G level of theory using the Gaussian 16 software. The molecular width was calculated based on the atomic coordinates as shown in the figure.

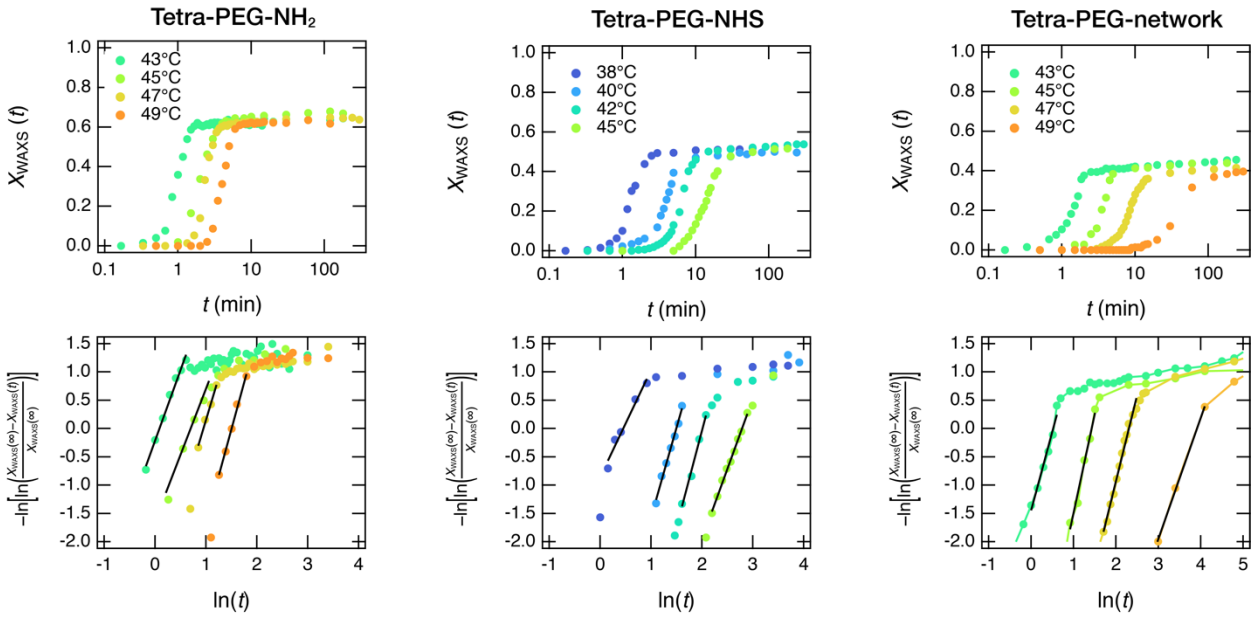

Fig. S2 The time variation of crystallization degrees X_{waxs} (t) and Avrami plot in the isothermal crystallization process at various cyclization temperatures. The solid black lines indicate the fitting results of the Avrami equation.

Table S1 The Avrami exponent n, half time of crystallization $t_{1/2}$, and correlation coefficient R^2 at various cyclization temperatures T_c.

	T_c (ºC)	n	$t_{1/2}$ (min)	R^2
Linear-PEG NH2	45	2.2	1.3	0.9998
Tetra-PEG NH2	43	1.9	0.9	0.9905
	45	2.3	2.1	0.9796
	47	3.0	2.3	0.9923
	49	3.2	4.0	0.9963
Tetra-PEG NHS	38	1.9	1.4	0.9695
	40	3.2	4.4	0.9959
	42	3.4	6.5	0.9921
	45	2.2	14.0	0.9940
Tetra-PEG Network	43	2.0	1.6	0.9741
	45	2.6	4.3	0.9804
	47	3.0	8.7	0.9865
	49	2.2	42.1	0.9994

Table S2 The Avrami exponent n, half time of crystallization $t_{1/2}$, and correlation coefficient at various cyclization temperatures T_c of PEG network samples.

M_{pre}	C_0 (wt%)	n	$t_{1/2}$ (min)	R^2
10k	1.0	3.0	92.6	0.9805
	2.5	2.3	67.9	0.9948
	5.0	3.1	71.0	0.9988
	10	2.5	62.7	0.9991
	20	3.2	83.0	0.9944
20k	1.0	1.7	2.4	0.9987
	2.5	2.3	1.0	0.9984
	5.0	2.5	1.3	0.9973
	10	2.1	1.8	0.9991
	20	1.9	1.6	0.9860
40k	1.0	3.1	2.9	0.9927
	2.5	1.8	3.0	0.9971
	5.0	1.9	2.2	0.9960
	10	2.0	4.1	0.9988
	20	2.8	3.7	0.9971

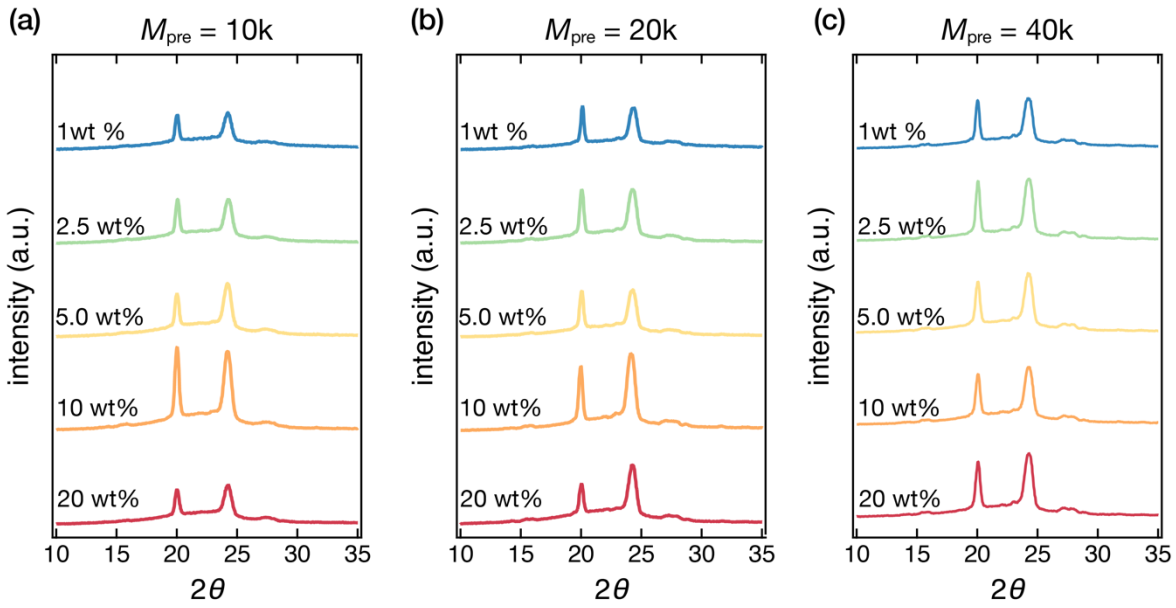

Fig. S3 1D-WAXS profiles of tetra-PEG networks after the isothermal crystallization completed at 45 ºC. (a) M_{pre} = 10k, (b) M_{pre} = 20k, (c) M_{pre} = 40k.

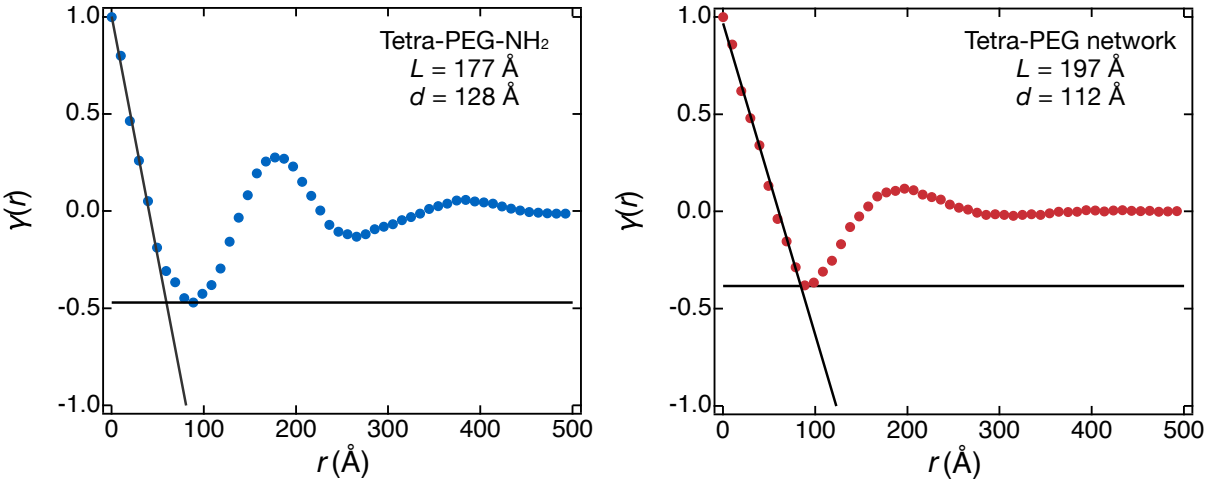

Fig. S4 Normalized 1D correlation functions $\gamma(r)$ of tetra-PEG-NH_2 (M = 20 kg/mol) and tetra-PEG network (M_{pre} = 20 kg/mol, c_0 = 20 wt%) calculated by the Fourier transform of 1D Lorentz-correlated SAXS profiles. SAXS profiles used for Fourier transform in the low q range ($q < 0.01$ Å^{-1}) were extrapolated by the Guinier law, and the high q range ($q > 0.2$ Å^{-1}) was extrapolated by the Porod law. The long period L and the crystal lamellar thickness d were evaluated based on the approximation of Strobl.