Electronic Supplementary Information

Structure-Property Correlation of Crosslinked Domain Hydrogels Exhibiting Thermoresponsive Mechanical Toughening and Hybridization with Photoluminescent Carbon Dots

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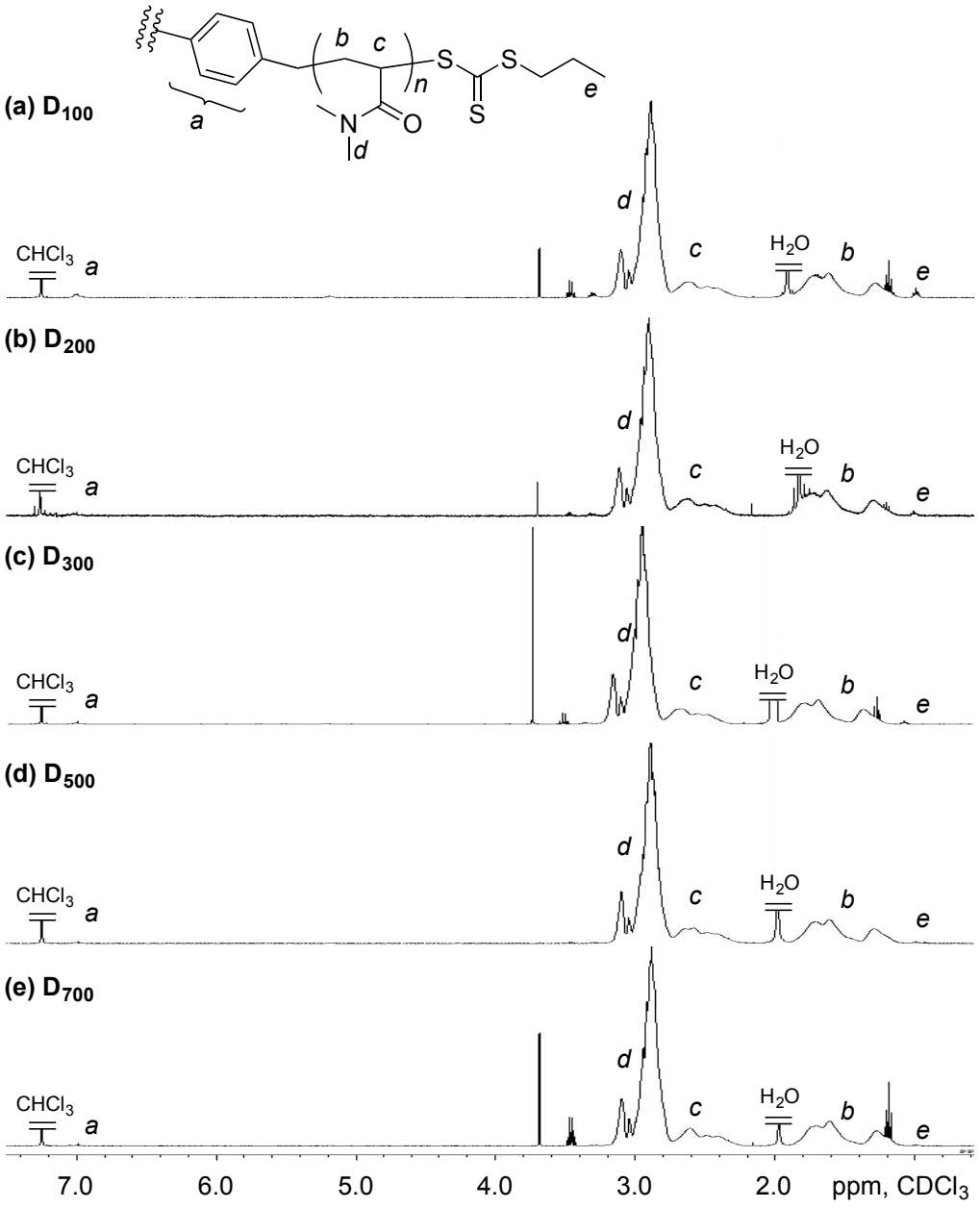

Fig. S1 ^{1}H NMR spectra of PDMAAm macro-CTAs. Reaction condition: see Table 1. DP_n and $M_{n,\,NMR}$ were calculated from the ratio of integral values between *a* and *d*.

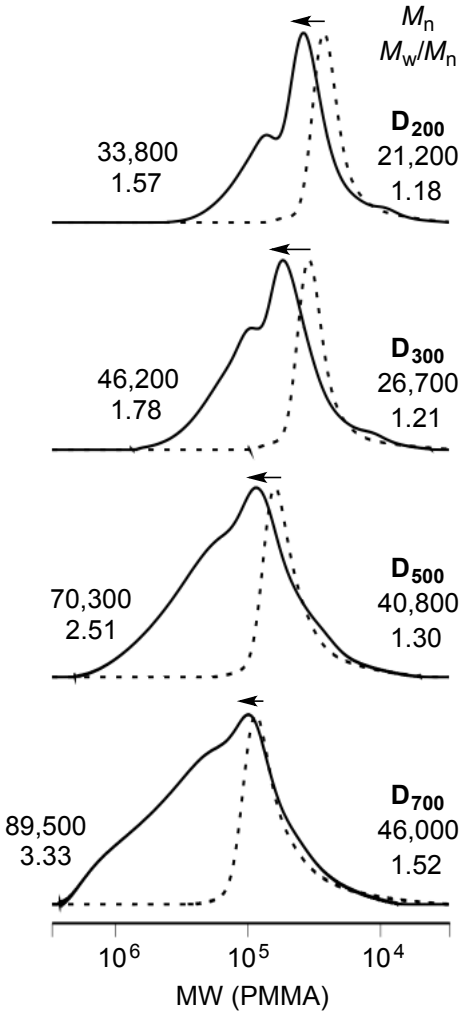

Fig. S2 Verification of propagation of PNIPAAm from PDMAAm macro-CTA by RAFT polymerization in the absence of BIS crosslinker. Reaction condition: [DMAAm unit] = 1500 mM, [NIPAAm] = 500 mM, [APS] = 5.0 mM in H_2O at 60 ˚C for 90 min.

Table S1. Results of uniaxial tensile tests of the gels with CD structure in heating and cooling states prepared from various PDMAAm macro-CTAs with different molecular weights.

Sample	Weight Ratio $W_{cooling}/W_{heating}$	Heating State		Cooling State	
		Elastic Modulus (kPa)	Breaking Strain (%)	Elastic Modulus (kPa)	Breaking Strain (%)
$G_{D200N25}$	1.02	2.36 ± 0.68	139 ± 7.76	2.81 ± 0.56	58.0 ± 16.4
$G_{D300N25}$	0.95	3.01 ± 0.57	119 ± 33.9	2.01 ± 0.12	94.8 ± 22.2
$G_{D500N25}$	1.01	4.06 ± 0.47	118 ± 28.0	4.09 ± 0.36	74.0 ± 35.6
$G_{D700N25}$	0.98	1.90 ± 0.23	97.6 ± 26.1	1.81 ± 0.30	86.7 ± 25.2

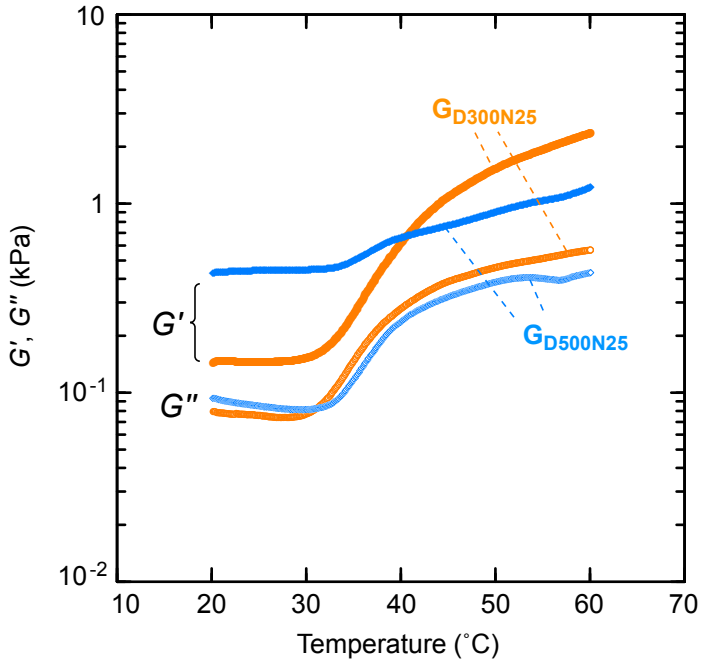

Fig. S3 Temperature dependence of the storage modulus (G') and the loss modulus (G'') of **$G_{D300N25}$** and **$G_{D500N25}$** (heating rate: 1.0 ˚C/min).

Table S2. Structural parameters of the gels with CD structure obtained from SAXS analysis[a].

Gel Code	q_{max} (nm^{-1})	D (nm)[b]	R_{CD} (nm)[c]	C_{CD} (mM)[d]	N_{PDMAAm}[e]
G$_{D300N25}$	0.27	23	5.1	0.76	12
G$_{D300N50}$	0.20	32	9.3	0.24	25
G$_{D300N75}$	0.12	54	20	0.035	87

[a] The gels were prepared from PDMAAm macro-CTA ($DP_{n,\,NMR}$ = 330, $M_w/M_{n,\,SEC}$ = 1.22) synthesized with the condition identical to that of **D$_{300}$**. The calculation method of each parameter is described in our previous study.[1] [b] The distance between CDs obtained from SAXS profile (= $2\pi/q_{max}$). [c] The average radius of CD, which is calculated from D and the end-to-end distance of PDMAAm with DP_n = 330, L_D (= 13.2 nm; this value corresponds to the value of polyacrylamide with same DP_n in water[2]): $R_{CD} = (D - L_D)/2$. [d] The concentration of CD in the network, which is calculated from the volume of a single CD and volume fraction of CDs in the network on the assumption that each CD is spherical and the volume fraction corresponds to the molar ratio of monomeric units. [e] The average number of PDMAAm chains connected to one CD, which is calculated from C_{CD} and the feed concentration of PDMAAm macro-CTA at the gel preparation.

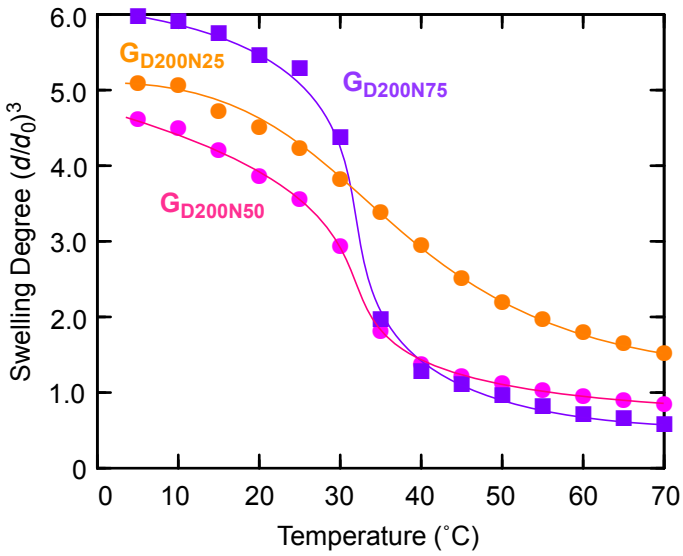

Fig. S4 Swelling behavior in water of the gels having CD structure with various composition prepared from **D$_{200}$**. Preparation condition of **G$_{D200N25}$**: see Entry 4 in Table 2. Preparation condition of **G$_{D200N50}$** and **G$_{D200N75}$**: [DMAAm unit] + [NIPAAm] = 2000 mM, [BIS] = 20 mM, [APS] = 5.0 mM in H_2O at 60 ˚C for 90 min.

Table S3. Results of uniaxial tensile tests of the gels with various compositions in heating and cooling states prepared from $\mathbf{D_{300}}$ and $\mathbf{D_{200}}$.

Sample	Weight Ratio $W_{cooling}/W_{heating}$	Heating State		Cooling State	
		Elastic Modulus (kPa)	Breaking Strain (%)	Elastic Modulus (kPa)	Breaking Strain (%)
$\mathbf{G_{D300N50}}$	0.95	6.74 ± 0.52	53.7 ± 15.1	6.85 ± 0.79	29.9 ± 11.6
$\mathbf{G_{D300N75}}$	0.92	8.58 ± 2.04	93.1 ± 32.3	6.72 ± 0.94	64.5 ± 31.3
$\mathbf{G_{D200N50}}$	0.99	4.79 ± 0.56	70.9 ± 19.6	5.10 ± 0.47	57.5 ± 21.1
$\mathbf{G_{D200N75}}$	0.99	16.1 ± 3.51	102 ± 47.3	8.89 ± 1.35	40.4 ± 23.2

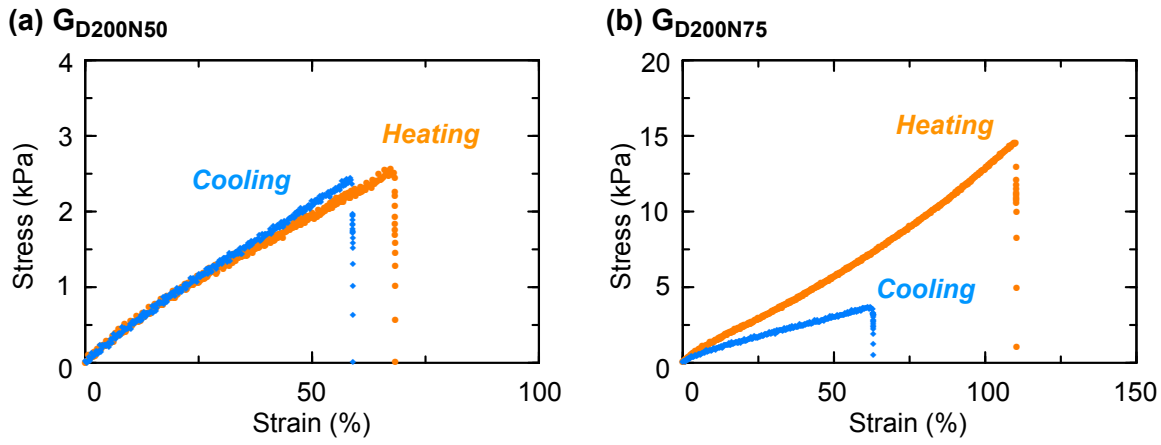

Fig. S5 Uniaxial tensile tests of $\mathbf{G_{D200N50}}$ and $\mathbf{G_{D200N75}}$ in heating and cooling states.

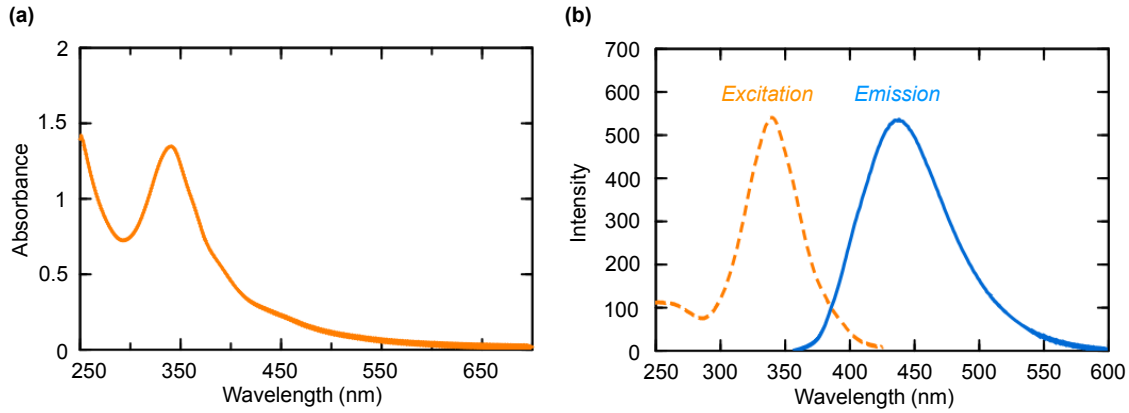

Fig. S6 (a) Absorption and (b) photoluminescence spectra of C-dots dispersion in water (0.10 g/L).

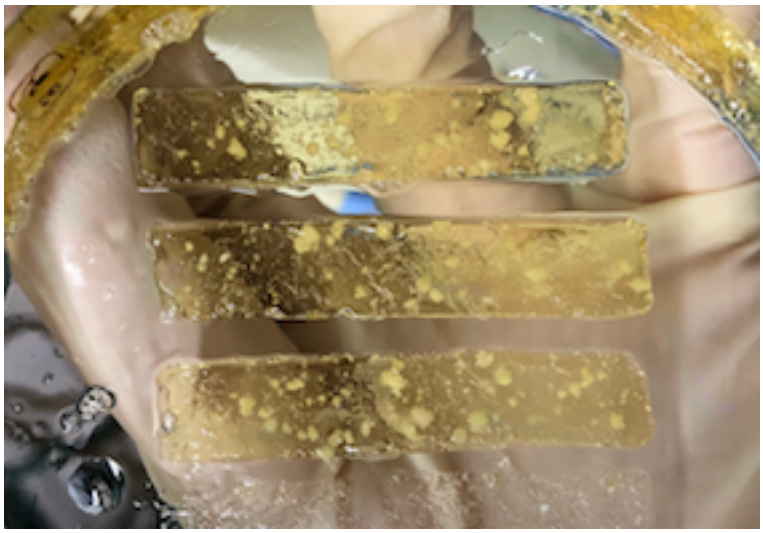

Fig. S7 Appearance of a gel containing 0.50 g/L of C-dots. Preparation condition: [DMAAm unit of $\mathbf{D_{300}}$] = 1000 mM, [NIPAAm] = 1000 mM, [BIS] = 20 mM in C-dots dispersion in water (0.50 g/L) at 60 ˚C for 18 h.

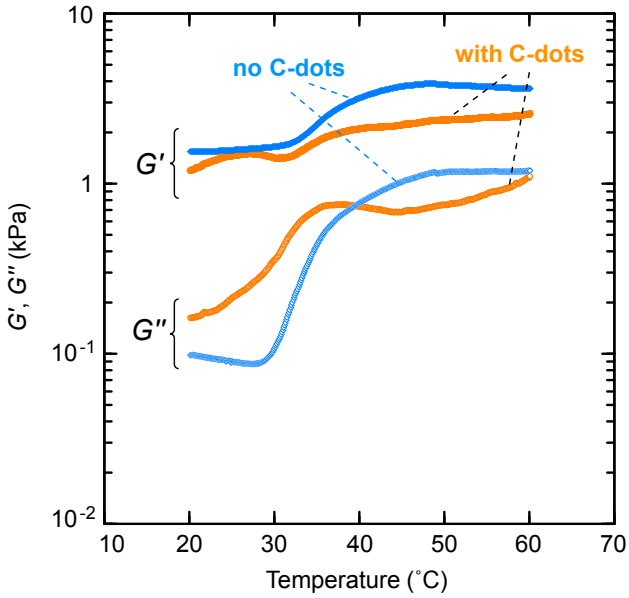

Fig. S8 Temperature dependence of G' and G'' of the CD gel containing C-dots and the gel without C-dots ($\mathbf{G_{D300N50}}$) (heating rate: 1.0 ˚C/min).

Table S4. Results of uniaxial tensile tests of the gel containing C-dots and the corresponding gel in the absence of C-dots ($\mathbf{G_{D300N50}}$).

Sample	Heating State		Cooling State	
	Elastic Modulus (kPa)	Breaking Strain (%)	Elastic Modulus (kPa)	Breaking Strain (%)
C-dots Gel	9.73 ± 0.59	58.8 ± 19.7	7.73 ± 0.43	42.9 ± 3.5
$\mathbf{G_{D300N50}}$	6.74 ± 0.52	53.7 ± 15.1	6.85 ± 0.79	29.9 ± 11.6

References

1. M. Morimura, S. Ida, M. Oyama, H. Takeshita and S. Kanaoka, *Macromolecules*, 2021, **54**, 1732-1741.
2. G. S. Misra and S. N. Bhattacharya, *Eur. Polym. J.*, 1979, **15**, 125-128.