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Facile Synthesis of Cyclic RAFT Agents and Ring Expansion Radical Polymerization of Vinyl Monomers Having Cyclic Topology

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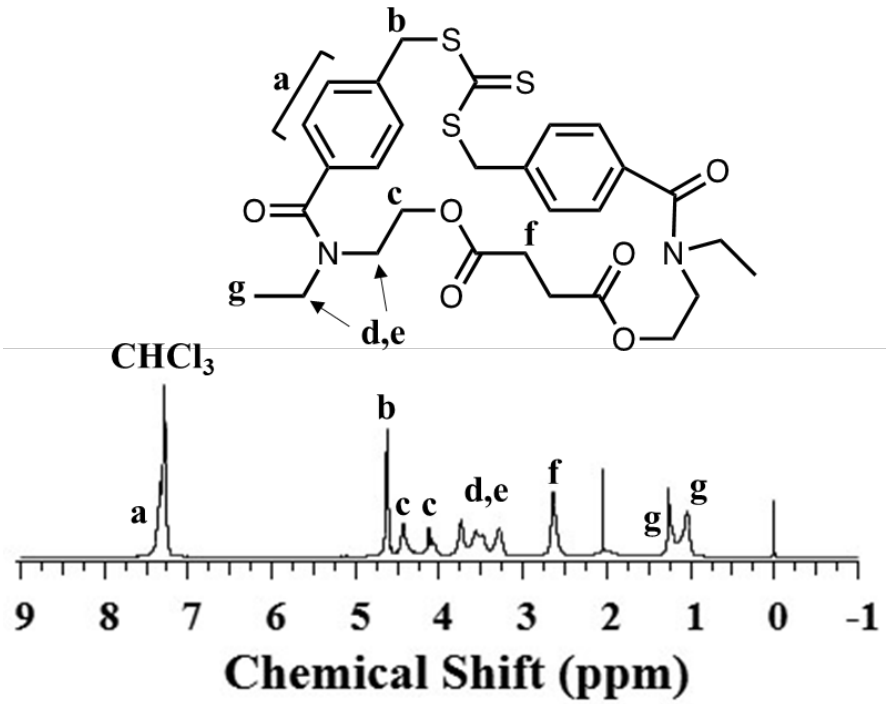

Figure S1. ^{1}H-NMR spectrum of cyclic-TTC prepared in chloroform-*d*.

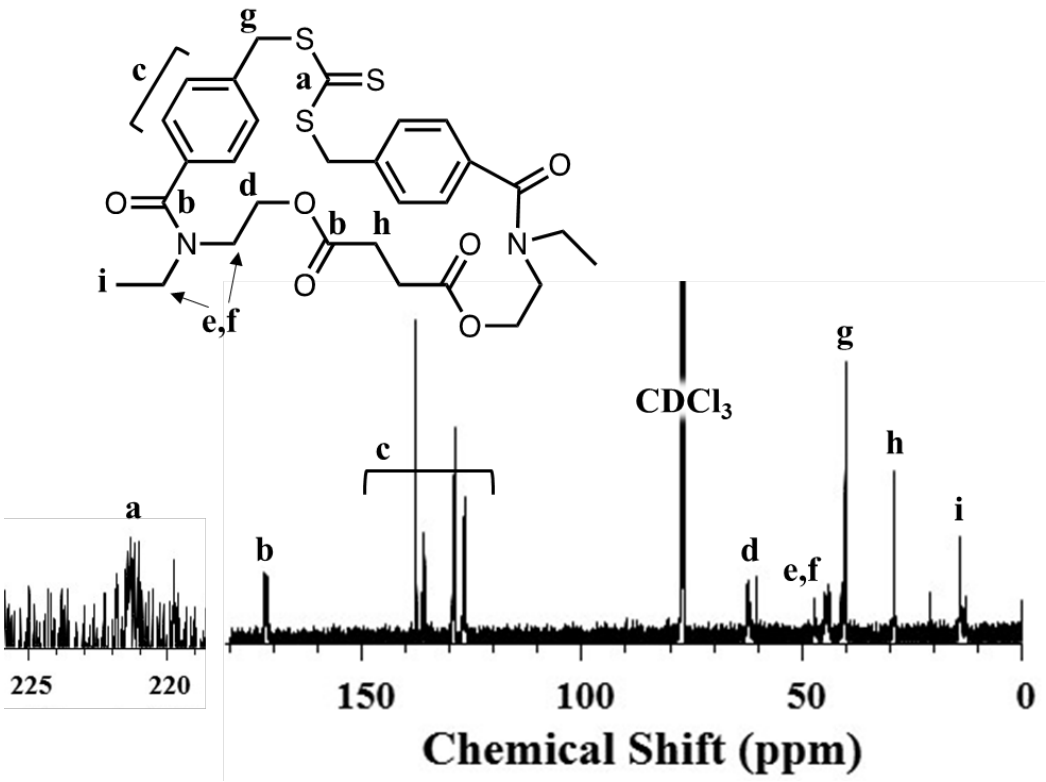

Figure S2. ^{13}C-NMR spectrum of cyclic-TTC prepared in chloroform-*d*.

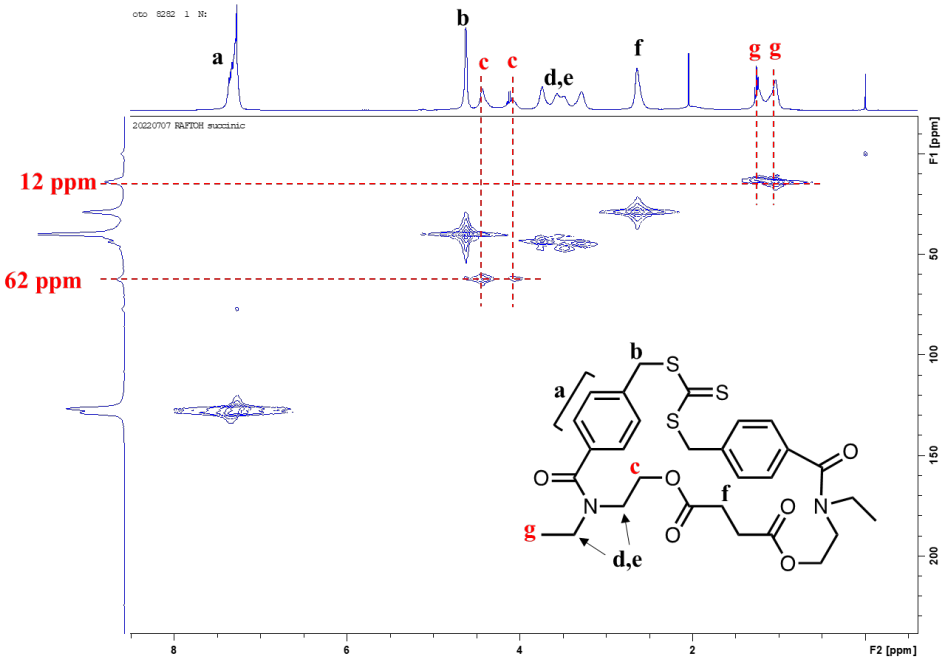

Figure S3. HMQC spectrum of cyclic-TTC prepared in chloroform-*d*.

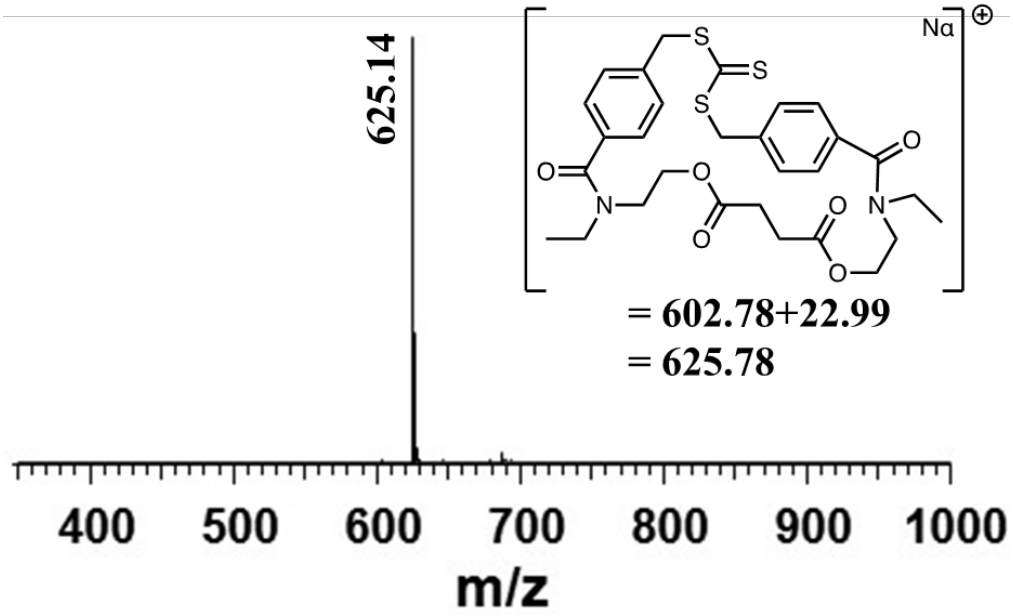

Figure S4. ESI-MS spectrum of cyclic-TTC.

Table S1. **RAFT Polymerization of *n*-BA Monomer via Dihydroxy-TTC.** [a]

run	$[M]_0$/[dihydroxy-TTC]	$[M]_0$(mol/L)	Time (h)	Conv [b] (%)	M_p [c] (kg/mol)	M_w/M_n [c]
1 [d]	100 / 1	2.0	6	53	7.62	1.33
2 [e]	100 / 1	0.67	3	86	9.00	1.56
3 [e]	100 / 1	2.0	3	97	14.7	1.31

[a]Reaction temperature = r. t., in DMF (deoxidized).
[b]Monomer conversion measured by ^{1}H NMR in $CDCl_3$.
[c]Determined by SEC with a standard series of poly(styrene)s.
[d]Polymerization without radical initiator under UV irradiation.
[e]Polymerization using $Ir(ppy)_3$ as a redox catalyst without radical initiator under blue-LED irradiation.

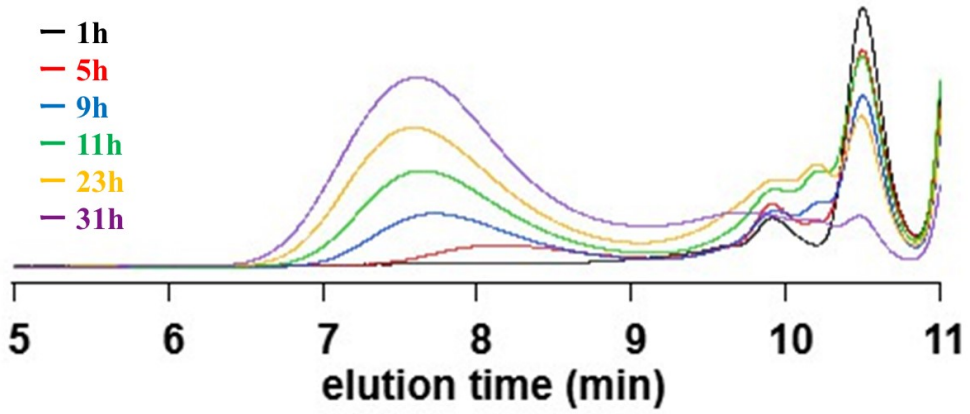

Figure S5. SEC traces of poly(*n*-BA)s (black line = 1 h, red line = 5 h, blue line = 9 h, yellow line = 23 h, violet line = 31 h) (run 3 in Table 2).

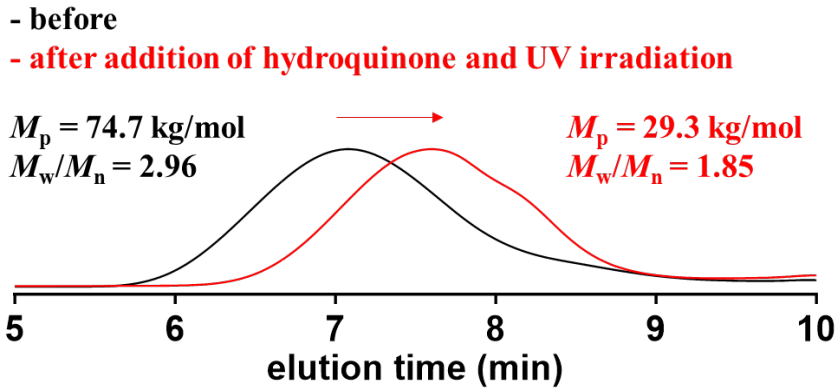

Figure S6. SEC trace of poly(*n*-BA)s (black line = before addition of hydroquinone and UV irradiation, red line = before addition of hydroquinone and UV irradiation).

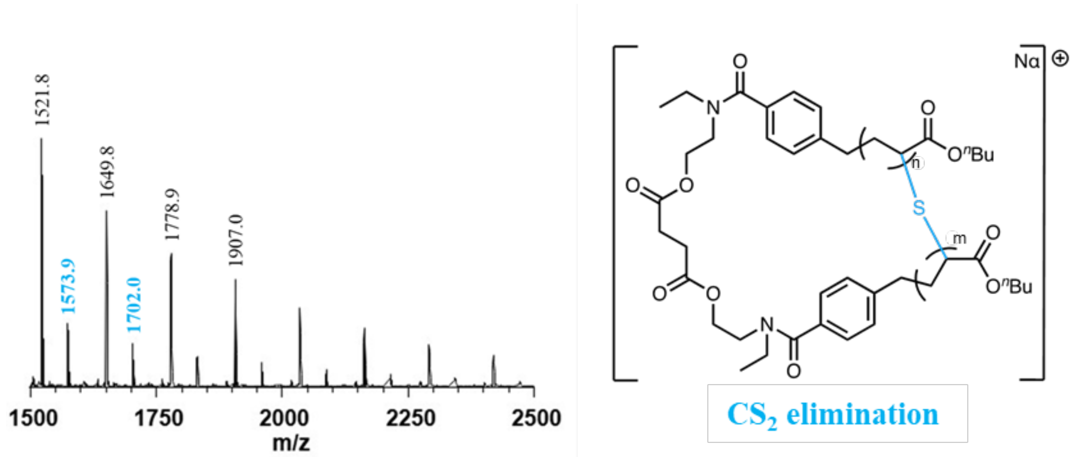

Figure S7. MALDI-TOF mass spectrum of poly(n-BA) synthesized with 2.0 M monomer concentration under UV irradiation (run 3 in Table 2).

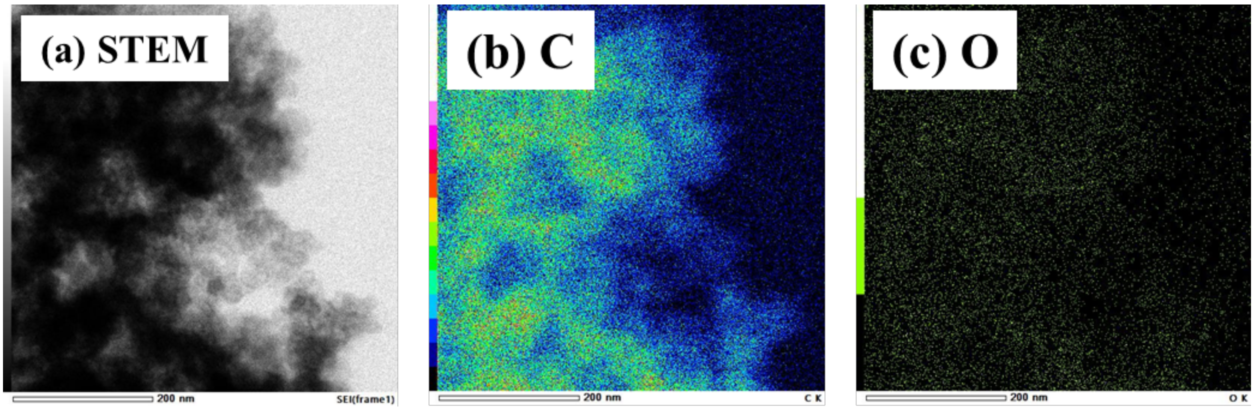

Figure S8. EDS mapping of poly(n-BA) (run 3 in Table 2). (a) STEM image, (b) carbon, (c) oxygen

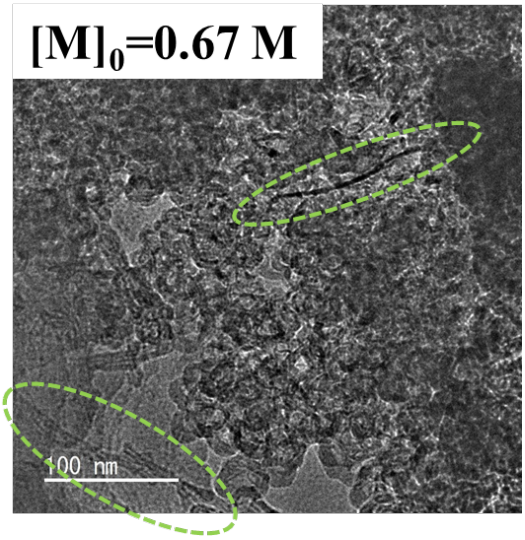

Figure S9. TEM observation of cyclic and linear poly(*n*-BA)s (run 1 in Table 2) prepared from toluene solution at 1.0 μg/mL.

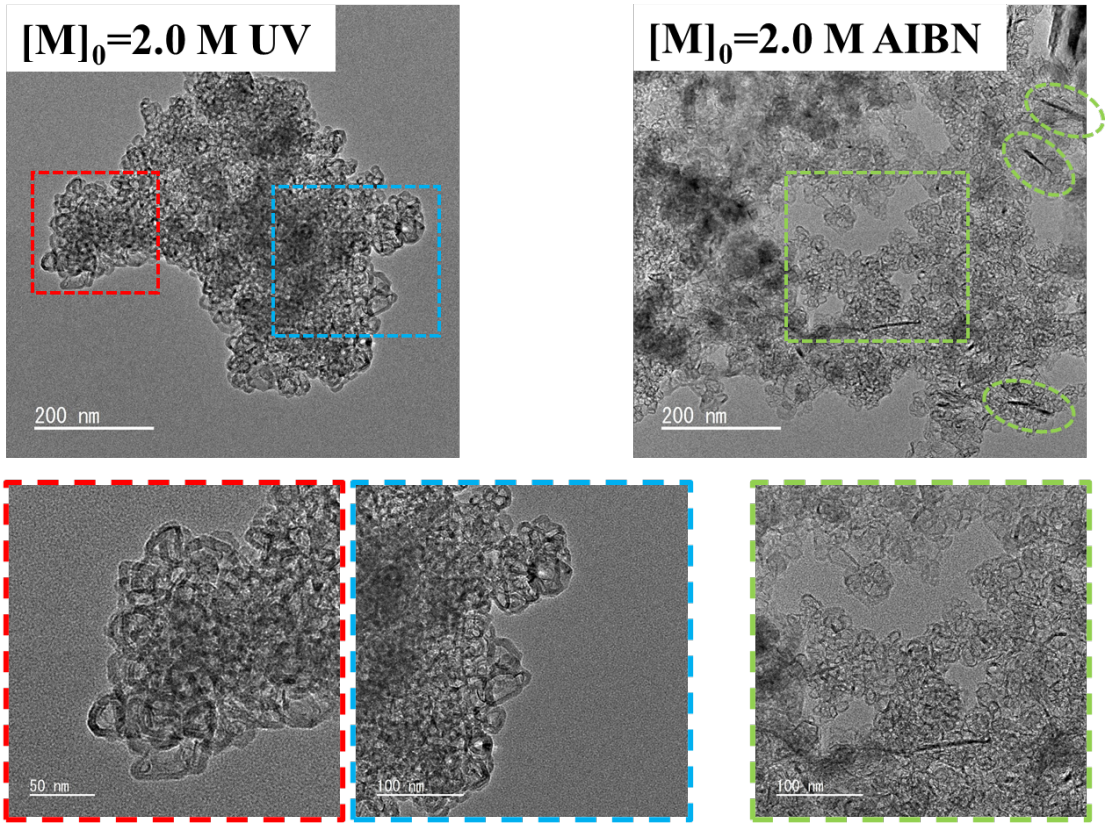

Figure S10. TEM observation of cyclic and linear poly(*n*-BA)s (run 2, 4 in Table 2) prepared from toluene solution at 1.0 μg/mL.

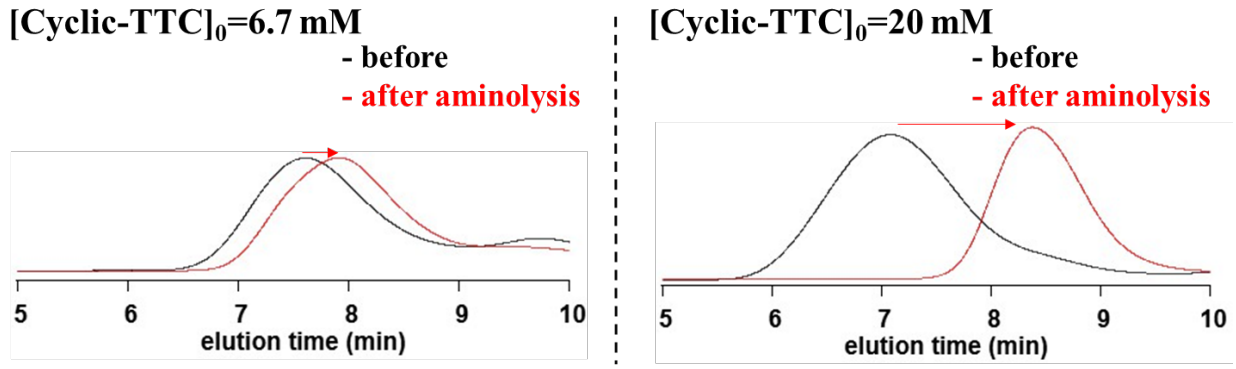

Figure S11. SEC traces of poly(*n*-BA)s synthesized at 6.7 mM cyclic-TTC concentration (black line = before aminolysis, red line = after aminolysis) and 20 mM cyclic-TTC concentration (black line = before aminolysis, red line = after aminolysis).