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Structures and Chiroptical Properties of Block Copolymers based on Acrylamide-Containing L-Proline Moieties

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Table S1. RAFT Polymerization of *N,N*-dimethylacrylamide (DMA) with AIBN in the Presence of Benzyl Dithiobenzoate (BDB) in Chlorobenzene at 60 °C ^{a)}

run	[CTA] /[AIBN]	time h	conv. ^{b)} %	M_n ^{c)} (theory)	M_n ^{d)} (SEC)	M_w/M_n ^{d)} (SEC)
1	2	15	< 5		-	-
2	2	24	80	8200	5500	1.21
3	10	24	67	6900	5200	1.12

^{a)} [DMA]₀/[CTA]₀ = 100, monomer concentration = 1.0 M, where AIBN = 2,2'-azobis(isobutyronitrile), CTA = benzyl dithiobenzoate (BDB). ^{b)} Calculated by ¹H NMR. ^{c)} The theoretical molecular weight ($M_{n,theory}$) = (MW of DMA) × [DMA]/[CTA] × conv. + (MW of CTA). ^{d)} Measured by size-exclusion chromatography (SEC) using polystyrene standards in *N,N*-dimethylformamide (DMF, 10 mM LiBr).

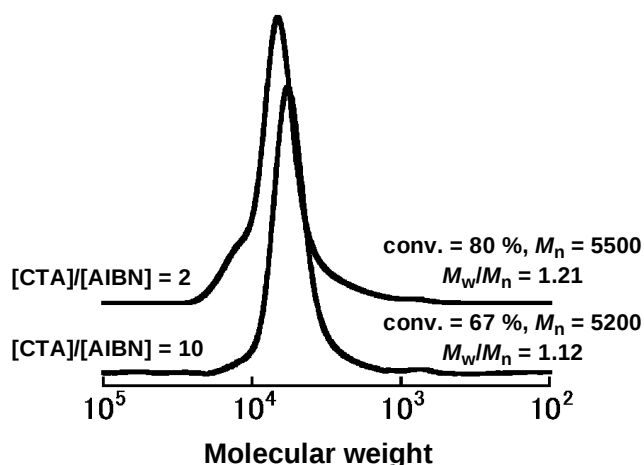


Figure S1. SEC traces of poly(DMA)s obtained by the polymerization of DMA with AIBN in the presence of benzyl dithiobenzoate (BDB) at constant monomer-to-chain transfer agent ratio, [DMA]₀/[CTA]₀ = 100, under different chain transfer agent-to-initiator ratios, [CTA]₀/[AIBN]₀ = 2 and 10, respectively. See Table S1 for detailed polymerization conditions.

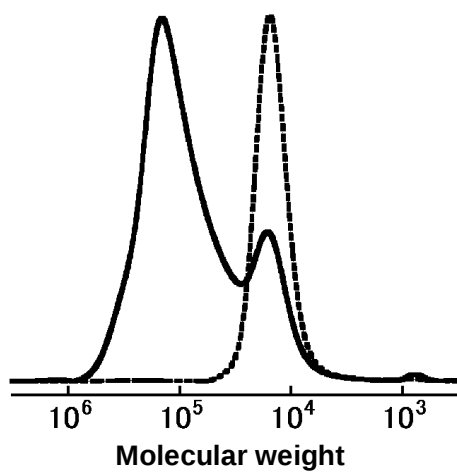


Figure S2. SEC traces of the parent poly(A-Pro-OMe) macro-CTA (dotted trace, $M_{n, \text{GPC}} = 12700$, $M_w/M_n = 1.23$, conv. > 99%) and the block copolymer, poly(A-Pro-OMe)-*b*-poly(DMA), obtained after the polymerization with DMA at 60 °C at the ratio $[\text{DMA}]_0/[\text{macro-CTA}]_0/[\text{AIBN}]_0 = 2000/10/1$ for 24 h (solid trace, $M_{n, \text{GPC}} = 35400$, $M_w/M_n = 3.30$, conv. = 67%).

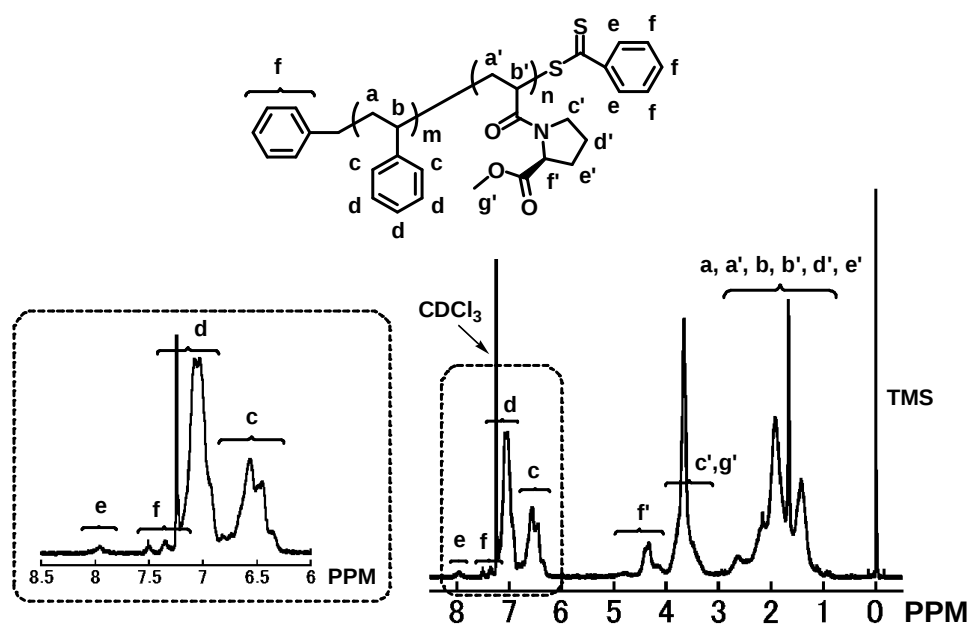


Figure S3. ¹H NMR spectrum (CDCl₃) of the block copolymer, polystyrene-*b*-poly(A-Pro-OMe) ($M_{n, GPC} = 6700$, $M_w/M_n = 1.15$, conversion = 69%, A-Pro-OMe/styrene = 46/54, sample; entry 4 in Table 1).

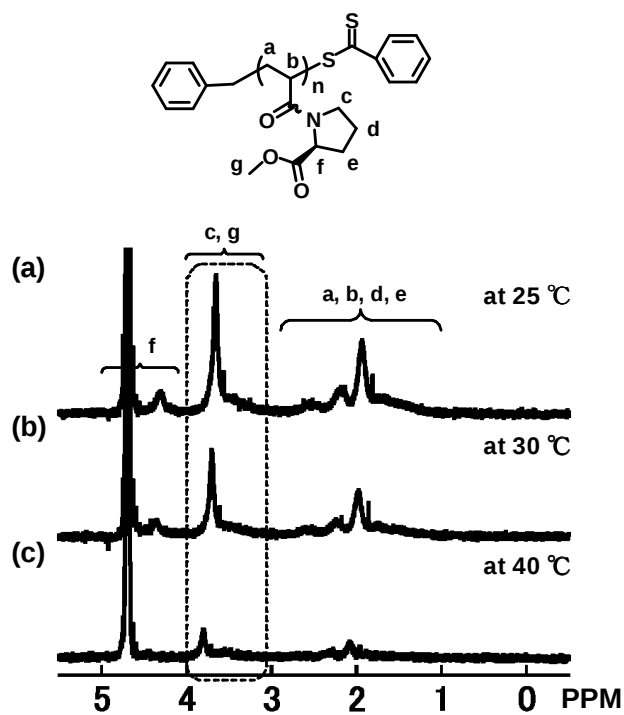


Figure S4. ^1H NMR spectra (D_2O) of poly(A-Pro-OMe) ($M_n = 13300$, $M_w/M_n = 1.14$) measured at different temperatures.

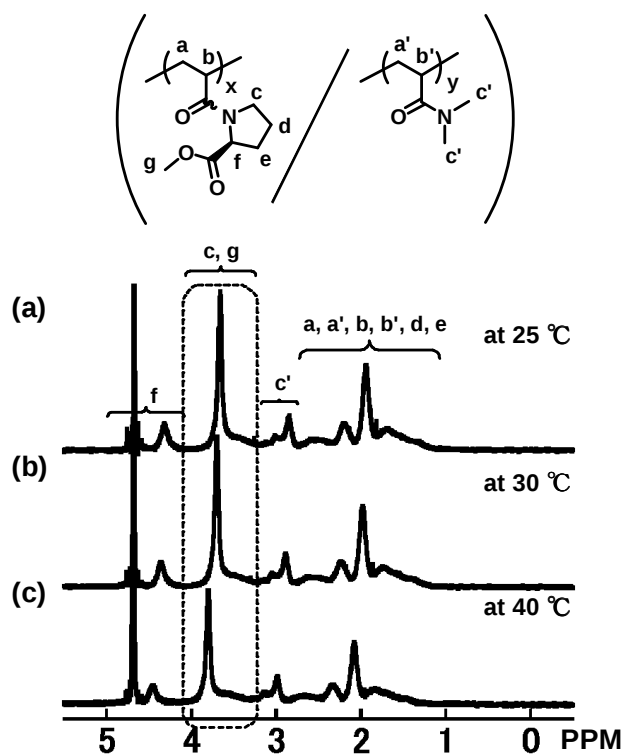


Figure S5. ^1H NMR spectra (D_2O) of a random copolymer, poly(DMA)-*r*-poly(A-Pro-OMe) ($M_n = 15700$, $M_w/M_n = 1.17$, A-Pro-OMe content = 89 mol %), measured at different temperatures.