Cyclopolymerization of Bisacrylamide Derived from α-Pinene through Larger Chiral Ring Formation

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Cyclopolymerization of bifunctional monomers requires predominant intramolecular ring-closing reaction than intermolecular propagation that typically causes cross-linking reaction. The ring-closing reaction generally produces thermodynamically stable five- or six-membered rings as the repeating units along the backbone. For example, *N*-methyldiacrylamide,[1] *N*-*tert*-butyl-*N*-allyacrylamide,[2] α-(allyoxylmethyl)acrylate,[3] diallyammonium salts,[4] and 1,6-heptadiynes[5] can polymerize through formation of five- or six-membered ring without yielding cross-linked products. However, it is difficult to construct cyclopolymerization system accompanying larger ring formation because of large ring distortion and remote distance for ring-closing that allows intermolecular side reactions. To synthesize polymers with larger rings selectively, the appropriate design of monomers and dilute conditions are necessary. For instance, Kakuchi et al. have demonstrated that a diisocyanate monomer having a crown ether cavity successfully cyclopolymerizes though the resulting cyclic repeating units require to form a 28-membered ring.[6] However, the high dilution resulted in the low yields, and cross-linking reaction cannot be suppressed completely. We thought that constrained conformation will be effective to attain selective ring-closing, hence, focused on a bisacrylamide (**1**) prepared by the reaction of α-pinene and acrylonitrile in the presence of cerium(IV) ammonium nitrate.[7] The compulsive conformation arranges the two acrylamide groups in **1** in an easy distance for ring-closing to produce the polyacrylamide having larger rings in its backbone, potentially applicable as chiral stationary phase and chiral catalyst based on the superior chiral properties of chiral cyclic amides.[8] Herein, we describe the radical cyclopolymerization of **1** (Scheme 1).

The radical polymerization of **1** was conducted using 2,2′-azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), or *tert*-butyl peroxide (TBPO) ([**1**]/[I] = 50) as initiators in DMF for 24 h by the sealed tube technique (runs 1−10 in Table 1). Although the polymerization at 60 °C gave no polymer (runs 1 and 2), the corresponding polymers were obtained at 80 and 120 °C in high yields. Polymerization at 0.12 M gave the polymers soluble in various common solvents (methanol, chloroform, etc.), which may suggest the formation of polymers with predominant cyclization units (runs 3, 6, and 8). However, the molecular weights were relatively low. To obtain the polymers with higher molecular weight, the polymerization of **1** was conducted at 0.30 M DMF. Although the cross-linked polymer was obtained by the polymerization using BPO (run 7), the soluble polymers with higher molecular weights ($M_n > 10^4$) were obtained in quantitative yields using AIBN and TBPO (runs 4 and 9). However, the molecular weight distributions (M_w/M_n) of the obtained soluble polymers were very wide due to the bimodal elution peaks in the SEC profiles. Furthermore, the polymerization at 0.5 M gave cross-linked products (runs 5 and 10). These results suggested that the polymerizations at higher concentrations (>0.30 M) were accompanied by cross-linking or branching due to the lower selectivity.

Table 1. Cyclopolymerization of 1 in DMF[a]

run	initiator	RAFT	temp (°C)	concn (M)	yield[b] (%)	M_n[c] (M_w/M_n)[c]
1	AIBN		60	0.12	*d*	*d*
2	AIBN		60	1.0	*d*	*d*
3	AIBN		80	0.12	92	3800 (3.02)
4	AIBN		80	0.30	98	10500 (6.59)
5	AIBN		80	0.50	96	*e*
6	BPO		80	0.12	97	4000 (3.33)
7	BPO		80	0.30	98	*e*
8	TBPO		120	0.12	85	2000 (3.13)
9	TBPO		120	0.30	97	11400 (6.99)
10	TBPO		120	0.50	99	*e*
11[f]	AIBN	BDB	80	0.12	31	3600 (1.43)
12[f]	AIBN	BDB	80	0.30	45	5200 (1.78)
13[f]	AIBN	BPD	80	0.12	89	4600 (2.01)
14[f]	AIBN	BPD	80	0.30	95	6000 (3.39)

[a] Conditions: monomer **1** (0.700 mmol, 193.5 mg), initiator; $[\mathbf{1}]_0/[I]_0 = 50$, $[I]_0 = 0.014$ M, reaction time; 24 h. [b] Insoluble part in ether. [c] Estimated by SEC based on polystyrene standards. Eluent: DMF (50 mM LiBr solution). [d] No reaction. [e] Formation of cross-linked polymer. [f] $[\mathbf{1}]_0/[CTA]_0 = 50$, $[CTA]_0 = 0.014$ M, $[AIBN]_0 = 0.010$ M.

To attain selective cyclopolymerization, we attempted polymerization with slower propagation that would allow to take a thermodynamically favorable process. We employed the reversible addition−fragmentation transfer (RAFT) polymerization technique using benzyl dithiobenzoate (BDB) and benzyl 1-pyrrolecarbothioate (BPD) as reversible chain transfer agents (CTAs).[9] The RAFT polymerization was carried out at 80 °C in the presence of BDB and BPD in DMF for 24 h (runs 11−14). In the cases using BDB, the yields of the polymers were lower, whereas the narrower molecular distribution suggested the improved selectivity of the propagation. In contrast, the higher yields were attained by employing BPD, and we assumed that the narrower molecular weight distribution originated from the selective ring-closing (discussed later). The different yields are attributable to the lower chain transfer constant ($C_{tr} = 9$) of BPD than that ($C_{tr} = 18$) of BDB,[9b] resulting in the appropriate rate of propagation. The structure of the obtained polymer was analyzed by ^{1}H NMR spectroscopy (Figure 1). The vinyl protons of **1**, which were observed at 5.54−5.65 and 6.10−6.23 ppm in the spectrum of **1**, were not observed in the spectrum of poly**1**, indicating the complete conversion of the vinyl groups. Although the upfield shift of the methine proton **f** is ascribable to the magnetic shielding by surrounding ring structure, we could not determine the structure enough. Therefore, we analyzed poly**1** by MALDI−TOF mass spectroscopy (Figure 2). The MALDI−TOF mass spectrum of the obtained polymer (run 13) clearly shows that the polymer has only one initiating group and terminating groups. These data indicate that the radical polymerization of **1** proceeded through the selective ring-closing without cross-linking and branching reactions. The obtained polymer may involve 10- and 11-

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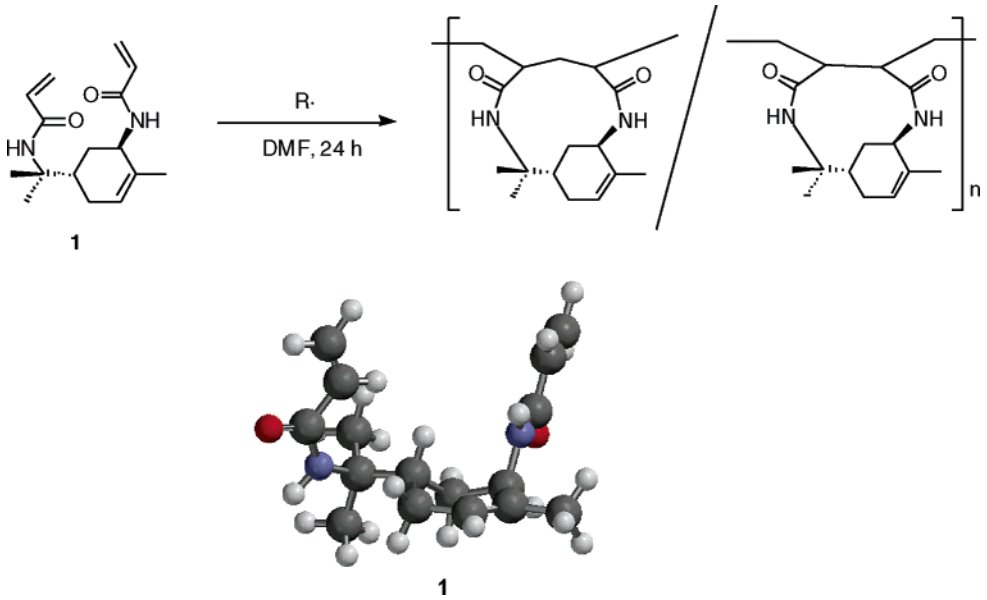
Scheme 1. Cyclopolymerization of 1 and the Optimized Geometry of 1 (Hartree−Fock Method, 3-21G Basis Set)



membered rings as well as the different head-to-tail structure. However, we suppose that the formation of the 11-membered ring predominated over that of the 10-membered ring, considering the stability of the propagation end and the steric hindrance due to the methine proton (**f**).

To characterize the chiroptical properties of poly**1**, we evaluated the CD spectra (Figure 3) of **1** and poly**1** (run 11). Although the small Cotton effect of **1** attributed to the vinyl groups (C=C) of the acrylamide groups was observed at 220 and 230 nm, no Cotton effect was observed in the same region of the spectra of poly**1**. In

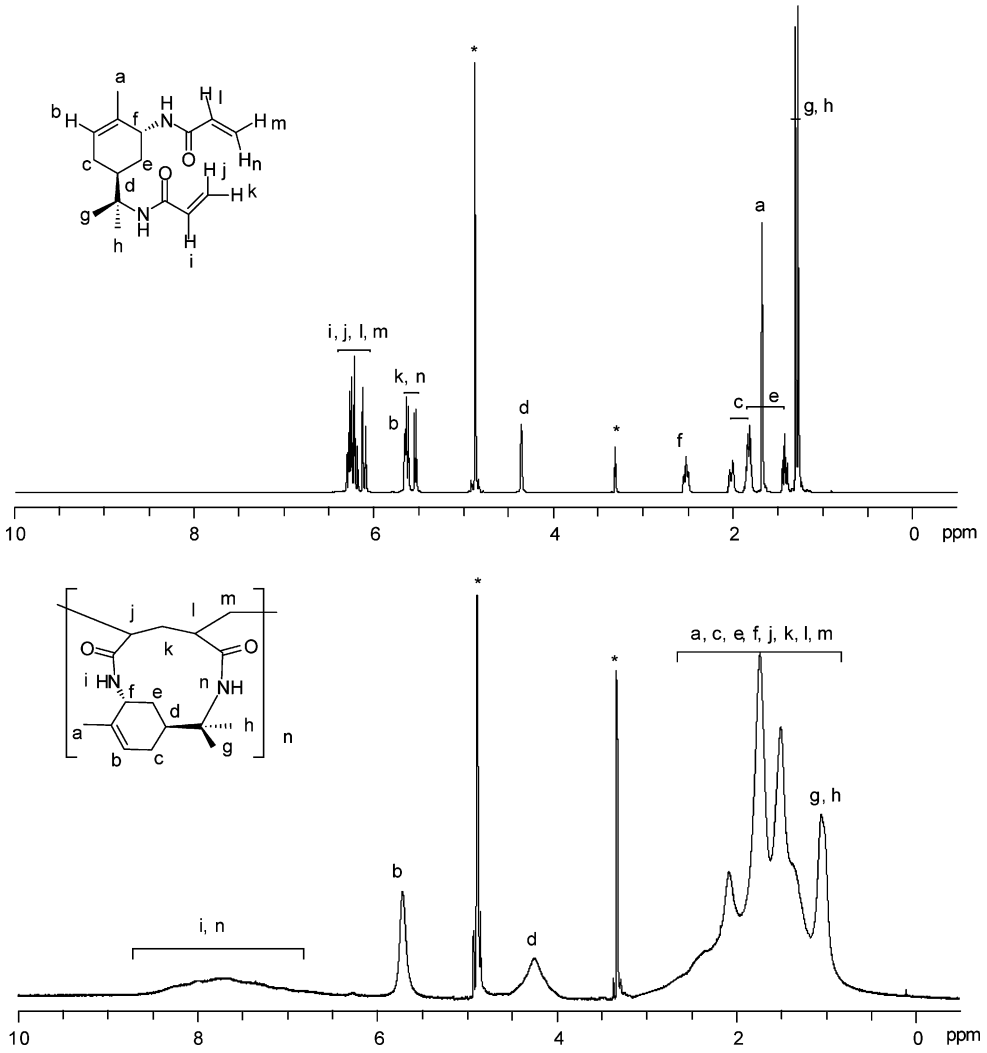


Figure 1. ^{1}H NMR spectra of **1** (a) and poly**1** (b) (run 3 in Table 1) in CD_3OD (asterisks indicate residual protons in CD_3OD).

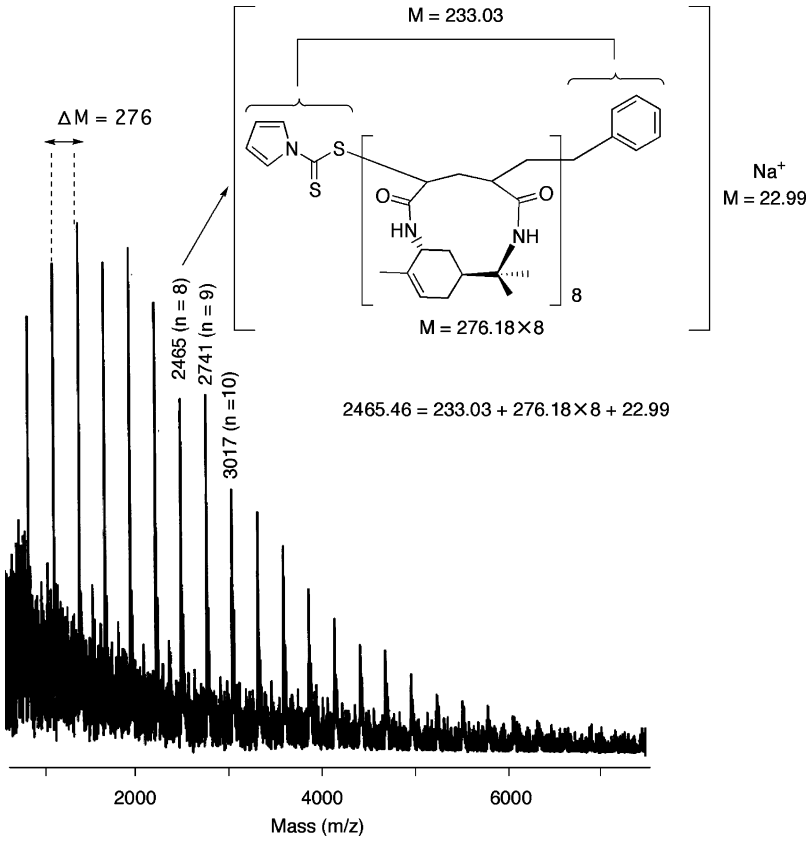


Figure 2. MALDI−TOF mass spectra of poly**1** (run 11).

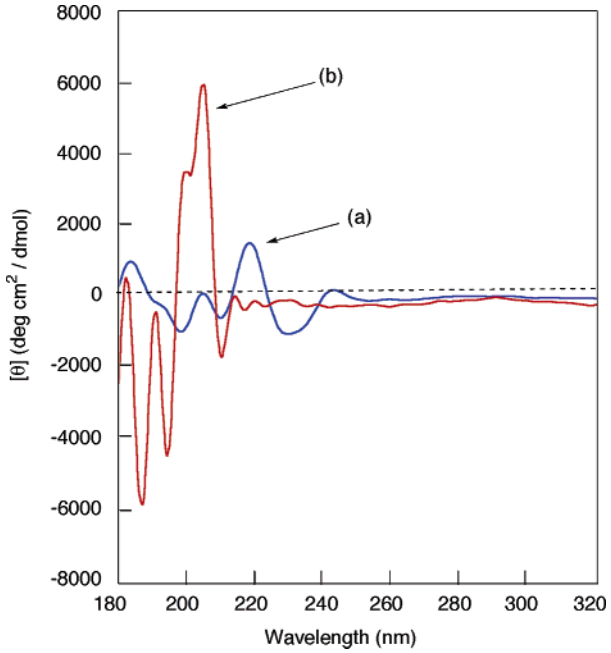


Figure 3. CD spectra of **1** (a) and poly**1** (b) (run 7 in Table 1) in CH_3OH (c = 0.1 g/dL).

contrast, the clear Cotton effects attributable to the amide groups were observed in the lower wavelength region, supporting that the poly**1** has a regulated asymmetric ring structure.

In summary, we have described the first synthesis of polyacryamide containing 10- or 11-membered rings as repeating cyclic units by cyclopolymerization of an optically active bisacrylamide derived from α-pinene. The unique chiral cavity in poly**1** will offer potential utility, including applications as chiral stationary phase and chiral gels.

Supporting Information Available: Typical experimental procedures and the synthetic methods of **1**. This material is available free of change via the Internet at http://pubs.acs.org.

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