Synthesis and Novel Cyclopolymerization of Bis(2-carbomethoxyallyl)methylamine by Group-Transfer Polymerization

There are numerous examples of cyclopolymers[1] done by free-radical, cationic, and anionic techniques; however, exibition of living characteristics for cyclopolymerization has not been investigated yet. Recently, *N*-phenyldimethacrylamide was polymerized to produce a six-membered cyclic recurring unit in the polymer backbone,[2] by group-transfer polymerization (GTP),[3] which has been known as a living polymerization of acrylic or methacrylic monomers. However, in comparison with GTP of typical methacrylic monomers, the reaction was very slow and the yield was low. Furthermore, the molecular weight of the product was obviously very low. Another example of GTP for difunctional monomer is ladder polymer formation, not cyclopolymerization.[4]

In the present paper are described syntheses of a new difunctional methacrylate monomer, bis(2-carbomethoxyallyl)methylamine (DCMA), and a novel example of cyclopolymerization by GTP.

Methyl 2-chloromethylacrylate was prepared according to the literature[5] procedure from methyl 2-hydroxymethylacrylate[6] and thionyl chloride. The monomer, DCMA, was synthesized by the reaction of methylamine and methyl 2-chloromethylacrylate (Scheme I). The reaction conditions were as follows: To the mixture of methylamine (40% aqueous solution, 22 mL) and K_2CO_3 (80 g) in dimethylformamide (100 mL) and tetrahydrofuran (400 mL) was added dropwise methyl 2-chloromethylacrylate (82 g) followed by heating to 80 °C for 3 h. After removal of the solvents, the remaining liquid was washed with water and fractionally distilled under vacuum over CaH_2 to isolate DCMA in pure form; colorless liquid, yield 68%, bp 78 °C (0.1 Torr). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N; 6.16. Found: C, 58.01; H, 7.35; N, 6.53. IR: 1630 cm^{-1} (C=C). ^1H NMR ($CDCl_3$, 60 MHz): 1.9 (s, 3 H, $>NCH_3$), 3.1 (s, 4 H, $>NCH_2-$), 3.7 (s, 6 H, $-OCH_3$), 6.5 (d, J = 27 Hz, 4 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, 20.2 MHz): 42.1 ($>NCH_3$), 51.4 ($-OCH_3$), 57.5 ($>NCH_2-$), 126.0 ($=CH_2$), 137.5 ($>C=$), 167.0 ($-CO_2-$).

Scheme II illustrates the polymerization of DCMA with dimethylketene methyl trimethylsilyl acetal (1)[3] as an initiator. The trimethylsilyl group is transferred to the incoming monomer to form a silyl ketene acetal end group as in the case of the GTP of typical (meth)acrylic monomers. The polymerization (Scheme II) was carried out under positive argon atmosphere at room temperature.

Tetrahydrofuran (THF, dried by the sodium benzophenone method) was used as a solvent, and tris(dimethylamino)sulfonium bifluoride ($THSHF_2$)[3] or tetrabutylammonium bibenzoate (TBAB),[7] as a catalyst. For example, a 50-mL reactor fitted with an argon inlet, a magnetic stirrer, and a thermocouple was charged with THF (10 mL), TBAB (0.07 mL, 0.1 M in THF), and a difunctional initiator **2** (0.55 mmol).[9] Then DCMA (8.9 mmol) was added via syringe over 2 min. After 30 min, a 2-mL aliquot was evaporated and the residue dried to gave 0.32 g of PDCMA ($\bar{M}_n$ = 5900, $\bar{M}_w/\bar{M}_n$ = 1.39). As illustrated in Scheme III, an ABA triblock copolymer was prepared by adding *n*-butyl methacrylate (BMA, 12.7 mmol) to the remaining mixture. The mixture was stirred for an additional 3 h and then treated with methanol (0.5 mL). After evaporation THF and methanol and drying at 40 °C by vacuum pump, 3.49 g of the copolymer was collected. The expected composition of 37 mol % of DCMA and 63 mol % of BMA was confirmed by ^1H NMR analysis. There

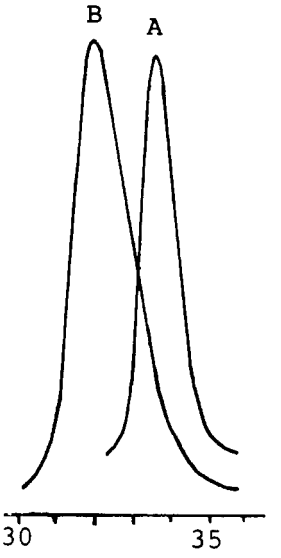


Figure 1. GPC curves for poly(MMA) (A) and for poly(MMA-*b*-DCMA) (B); exp. no. 5 in Table I.

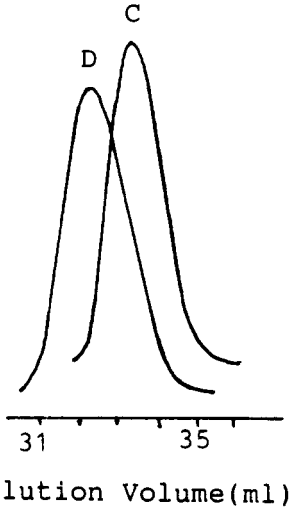
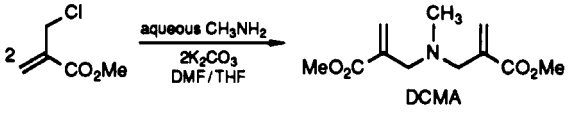
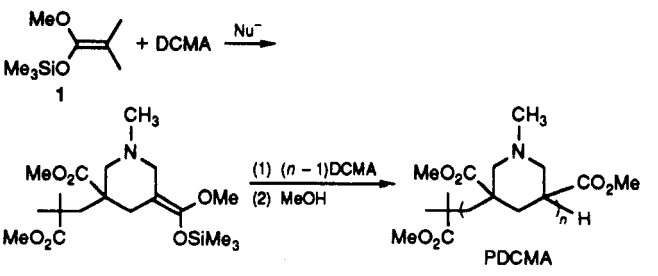


Figure 2. GPC curves for poly(DCMA) (C) and for poly(BMA-*b*-DCMA-*b*-BMA) (D); exp. no. 6 in Table I.

Scheme I



Scheme II



is a possibility of forming a trace of homopolymer, PBMA, or diblock copolymer via termination reactions with, e.g., moisture. To separate homopolymer from copolymer, formic acid, which is a solvent of PDCMA and a nonsolvent of PBMA, was chosen as a solvent. Little decrease

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Table I
Homopolymerization and Copolymerization of DCMA[a]

exp. no.	monomer (mmol)	solvent THF, mL	cat. (mL)	init.[d] (mmol)	$\bar{M}_n \times 10^{-3}$ calcd	$\bar{M}_n \times 10^{-3}$ obsd[e]	$\bar{M}_w/\bar{M}_n$[e]
1	DCMA (6.7)	6	$TASHF_2$[f] (0.08)	1 (0.50)	3.1	4.6	1.34
2	DCMA (6.7)	6	TBAB[g] (0.05)	1 (0.50)	3.1	4.4	1.31
3	DCMA (8.9)	7	TBAB (0.07)	2 (0.55)	3.8	6.2	1.42
4	DCMA (6.7) MMA (14.0)	9	$TASHF_2$ (0.08)	1 (0.50)	5.9	8.9	1.47
5[b]	(1) MMA (14.0)	10	$TASHF_2$ (0.08)	1 (0.50)	2.9	3.8	1.12
	(2) DCMA (6.7)				6.7	10.2	1.45
6[c]	(1) DCMA (8.9)	10	TBAB (0.07)	2 (0.55)	3.8	5.9	1.39
	(2) BMA (12.7)				7.7	12.3	1.52

[a] Yield, all quantitative. Exp. no. 3: Initiator 2 was added to the mixture of DCMA, THF, and cat. Exp. no. 4: A mixture of DCMA and MMA was added dropwise to the solution of THF, init., and cat. [b] See Figure 1. [c] See Figure 2. [d] Initiator 2, 1,6-dimethoxy-2,5-dimethyl-1,6-bis[(trimethylsilyl)oxy]-1,5-hexadiene. [e] Obtained from GPC (Waters 150C) in THF by using polystyrene standards with μ-Styragel columns. [f] 0.1 M in CH_3CN. [g] 0.1 M in THF.

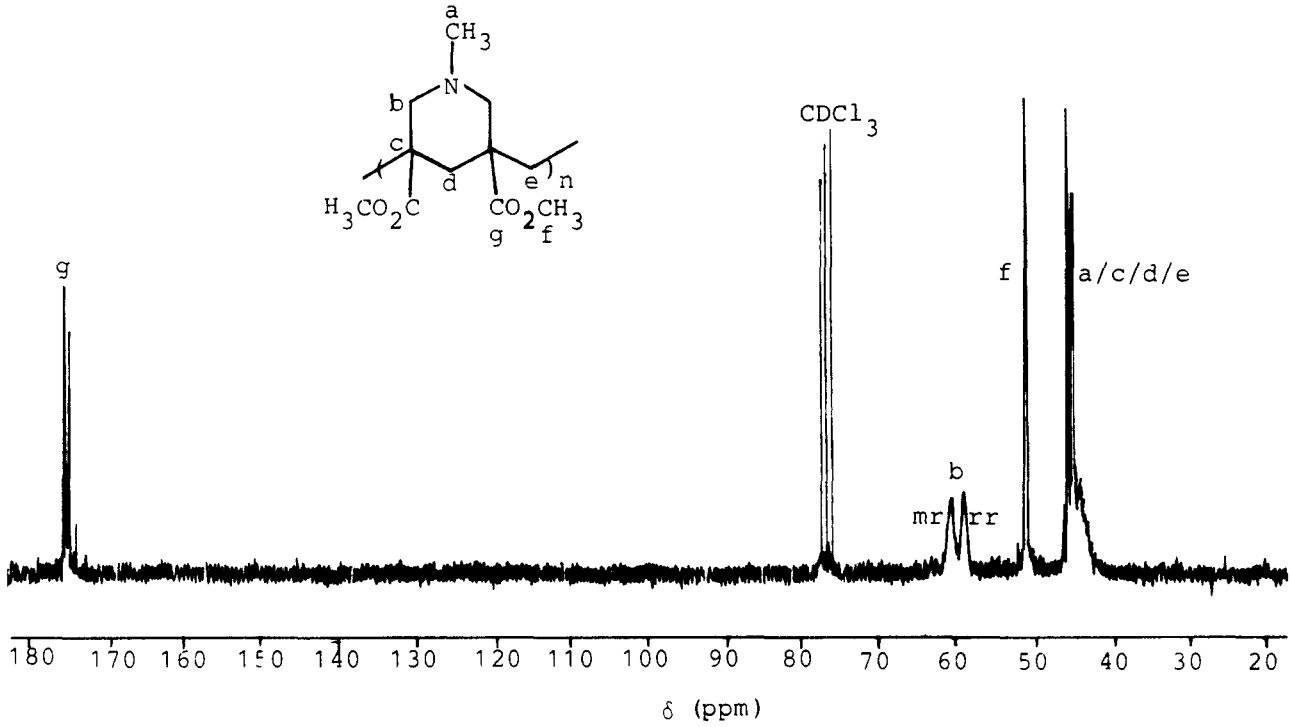
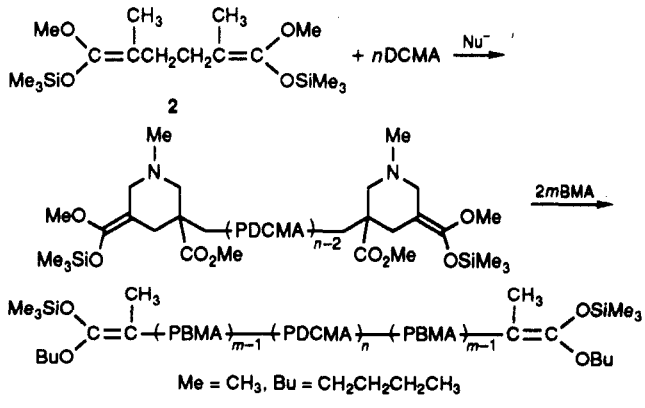


Figure 3. ^{13}C NMR spectrum of PDCMA (exp. no. 1 in Table I) proton-decoupled in $CDCl_3$ (50.5 MHz).

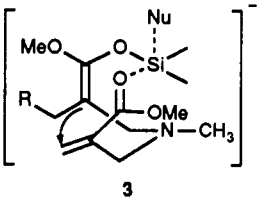
Scheme III



(ca. <2%) in weight, however, was observed after stirring overnight. Thus the product is considered to consist of ABA triblock copolymer. The results of homopolymerization of DCMA and its copolymerization with methyl methacrylate (MMA) or BMA were summerized in Table I. The polydispersities ($D = \bar{M}_w/\bar{M}_n$) of the PDCMA are estimated to be 1.31–1.42, which show that molecular weight distribution is somewhat broader than typically observed for polymers by GTP.[3,8] We can attribute this to the two different rates of mechanisms (intramolecular and intermolecular mechanism). It has been known that the intramolecular mechanism is faster than the intermolecular mechanism in radical cyclopolymerizations of other difunctional monomers.[1] The measured molecular weights of the polymers are somewhat higher than those of theory, which is probably due to the fact that values are calculated by a polystyrene calibration curve. It was found that the elution curves of the block copolymers in GPC were unimodal, which indicates effective initiation of DCMA with living PMMA (Figure 1) as well as of BMA with living PDCMA (Figure 2). During the GTP of DCMA, there was no insoluble product due to a side reaction, e.g., cross-linking. The precipitated polymer, PDCMA was subsequently soluble in chloroform, methylene chloride, THF, and acetone but insoluble in ethyl ether, hexane, and methanol. The IR spectrum of PDCMA showed no vinyl peaks at 1630 cm^{-1}. Strong ester bands were observed at 1735 and 1256 cm^{-1}. No residual unsaturation due to pendent vinyl groups was observed in the ^1H NMR and ^{13}C NMR spectra of the polymer sample, which proved the complete cyclopolymerization. The ^1H NMR spectrum of the polymer contained broad, over-

Figure 4. ^{13}C NMR spectrum of PDCMA in $CDCl_3$ (75.8 MHz), carbon a/c/d/e region in Figure 3.

lapping peaks at 1.2–2.8 ppm and one peak of a methyl proton of ester at 3.6 ppm. ^{13}C NMR spectra are given in Figures 3 and 4, and the peak assignment is based on comparison to monomer. The carbon atoms represented by b and c show doublets that may be due to tacticity. The peaks at 60.79 and 44.99 ppm were assigned as mr (heterotactic) triads and 58.94 and 44.65 ppm as rr (syndiotactic) triads by analogy[11] of PMMA, that is, a polymer being expected to show similar ^{13}C NMR splitting patterns with PDCMA by its tacticity. It is assumed that the



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structure of the polymer must be cyclic repeating units with a piperidine moiety by considering the fact that GTP allows only a head-to-tail mechanism. When the nondissociative mechanistic rationale of GTP is used, it seems likely that the formation of the cyclopolymer by GTP can proceed via the intermediate 3 that permits an intramolecular reaction. In a TGA experiment of PDCMA obtained by GTP, 95% of the initial weight remained at 310 °C, which reduced to 15% at 420 °C. The DSC of PDCMA (exp. no. 3 in Table I) showed a T_g at 140 °C, and two T_g's at 35 and 140 °C were shown in the DSC of the triblock copolymer, poly(BMA-*b*-DCMA-*b*-BMA) (exp. no. 6 in Table I).

In conclusion, GTP of DCMA is an example of living cyclopolymerization, which gives a new cyclopolymer of well-defined structure possessing two methacrylate functionalities and an amine functionality in one repeating unit. A more detailed description of these reactions, as well as characterization of the different new product through this novel route, will be discussed elsewhere.

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References and Notes

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Registry No. 1, 31469-15-5; 2, 56920-00-4; DCMA, 130434-50-3; PDCMA (homopolymer), 130434-52-5; PDCMA (SRU), 130434-55-8; TBAB, 130434-59-2; $TASHF_2$, 85248-37-9; (MMA)(DCMA) (block copolymer), 130434-53-6; (BMA)(DCMA) (block copolymer), 130434-54-7; methylamine, 74-89-5; methyl 2-chloromethylacrylate, 922-15-6.