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Cyclopolymerization of 2,6-Dicarbomethoxy-1,6-heptadiene by Group-Transfer Polymerization

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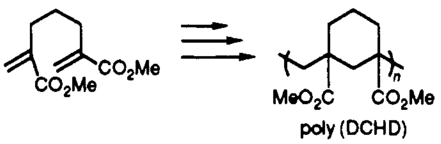
ABSTRACT: A difunctional methacrylate monomer, 2,6-dicarbomethoxy-1,6-heptadiene (DCHD), was cyclopolymerized by group-transfer polymerization (GTP). The polymerization could be initiated by silyl enol ether in the presence of bifluoride or bibenzoate salt as a catalyst. "Living" cyclopolymerization was achieved to give a linear polymer of a cyclohexane repeat unit without any network structure. The polydispersity of poly(DCHD) was in the range of 1.23–1.28. The structure of the resulting polymer was characterized by ^{13}C NMR, ^1H NMR, and IR spectroscopy. Block copolymers with controlled sequence lengths were prepared from methyl methacrylate and *n*-butyl methacrylate.

Introduction

Cyclopolymerization is a relatively new area of polymer science, which has important theoretical and practical implications. There are numerous examples of cyclopolymers[1] prepared by free-radical, cationic, and anionic techniques. However, controlled living polymerization for cyclopolymerization has not been fully investigated, and only a few were reported. Living polymerization is actually a very powerful pathway when the fine control of molecular weight, molecular weight distribution, and polymer architecture is required.[2-5] We reported preliminary studies of cyclopolymerization of bis[2-(carbomethoxy)allyl)]methylamine by group-transfer polymerization.[6] It was the first example of a cyclopolymer that was obtained by a truly living system, e.g., group-transfer polymerization (GTP).[7] As another example, we found that 2,6-dicarbomethoxy-1,6-heptadiene (DCHD) could be cyclopolymerized by GTP. This dimethacrylate monomer and its derivatives were cyclopolymerized under free-radical conditions by Marvel and Vest.[8] Milford[9] also prepared soluble homopolymer and copolymer with monofunctional active monomer of DCHD by radical polymerization. But those polymerizations were not living systems, and the structure of poly(DCHD) was not identified.

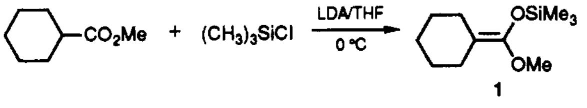


The present paper describes the preparation of homopolymer and block copolymers, with methyl methacrylate and *n*-butyl methacryltae, of DCHD by GTP and characterization of the structure of the resulting polymers.

Experimental Section

Materials. Monomer. Methyl methacrylate and *n*-butyl methacrylate were purchased from Aldrich Chemical Co. 2,6-Dicarbomethoxyheptadiene (DCHD) was prepared according to a published procedure.[8]

Initiators. 1-Methoxy-1-[(trimethylsilyl)oxy]-2,2-dimethylethylene (2) and difunctional initiator 1,6-dimethoxy-2,5-dimethyl-1,6-bis(trimethylsilyl)-1,5-hexadiene (3) were prepared according to procedures in the literature respectively.[7,11] [1-Methoxy-1-[(trimethylsilyl)oxy]methylene]cyclohexane (1) was synthesized by the following procedure.



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Yield: 86%. Bp: 65–68 °C (15 mmHg). Anal. Calcd for $C_{11}H_{22}O_2Si_1$: C, 61.08; H, 11.19; Si, 12.98. Found: C, 61.13; H, 11.08; Si, 12.91. IR: 1697 cm^{-1} (C=C). ^1H NMR (CDCl$_3$, 80 MHz): 0.2 (s, 9 H, Si(CH$_3$)$_3$), 1.4 (m, 6 H, (CH$_2$CH$_2$CH$_2$)), 2.0 (m, 4 H, =C(CH$_2$)(CH$_2$)), 3.4 (s, 3 H, OCH$_3$).

Catalysts. Tetrabutylammonium bibenzoate (TBAB)[10] and tris(dimethylamino)sulfonium (TAS) bifluoride[7] were prepared and purified as described earlier.

Solvent. Tetrahydrofuran (THF) was distilled from sodium benzophenone immediately prior to use.

Polymerization. All glassware was dried prior to assembly by storing overnight in a 180 °C oven. A typical homopolymerization procedure is as follows (exp no. 1 in Table I); a 50-mL reactor fitted with an argon inlet, a magnetic stirred, and a thermocouple was charged with THF (4 mL), TBAB (0.05 mL, 0.05 M in THF), and initiator 1 (0.6 mmol). Then DCHD (9.4 mmol) was added via syringe over 5 min. After a certain interval, the reaction was terminated by methanol. The resulting polymer solution was precipitated in a large amount of methanol, filtered off, and vacuum dried to give 2.14 g of poly(DCHD). Block copolymerization was carried out by adding methyl methacrylate under dry argon to a completely polymerized DCHD solution, which was prepared as described above (exp no. 4 in Table I).

Polymer Characterization. The molecular weight and polydispersity ($D = \bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) using a Waters GPC 150C with a refractive index detector and four μ-Styragel columns with pore sizes of 10^5, 10^4, 10^3, and 500 Å connected in series. The standard used was polystyrene, and the eluent was THF at a flow rate of 1 mL/min (30 °C). ^1H and ^{13}C NMR spectra were recorded on a Varian FT-80A and Bruker AM-300 spectrometers. Infrared spectra were taken on a Bomem Michelson MB-100 spectrometer in a potassium bromide pellet. Thermogravimetric analysis (TGA) was performed with a Du Pont 951 TGA in nitrogen atmosphere at 10 °C/min.

Results and Discussion

Homopolymerization of DCHD. As shown in Scheme I, the cyclopolymerization is carried out by using a GTP initiator in the presence of a catalyst to give quantitative yield. This reaction is a cyclopolymerization through an alternating "intermolecular–intramolecular" reaction, which is expected to produce recurring cyclohexane units by the fact that GTP allows only a head-to-tail mechanism[7] through intermediate 4. This is supported by the fact that GTP of DCHD does not give insoluble product due to a side reaction. Since it is known that the intramolecular mechanism is faster than the intermolecular mechanism in radical cyclopolymerizations of other difunc-

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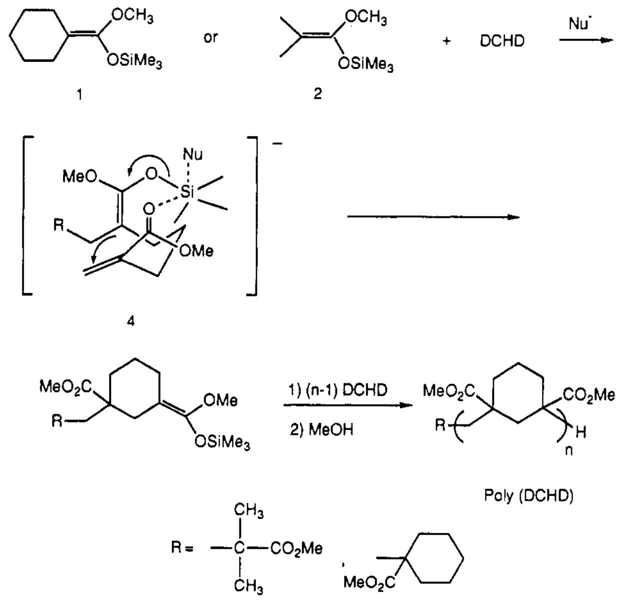
Table I
Homopolymerization and Copolymerization of DCHD[a]

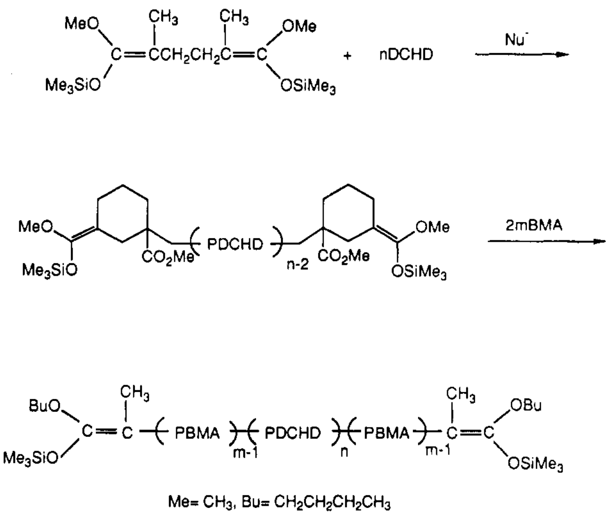
exp no.	monomer (mmol)	solvent THF, mL	cat.[b] (mL)	init. (mmol)	$\bar{M}_n \times 10^{-3}$ calcd[c]	$\bar{M}_n \times 10^{-3}$ obsd	$\bar{M}_w/\bar{M}_n$
1	DCHD (9.4)	4	TBAB (0.05)	**1** (0.6)	3.3	4.5	1.23
2	DCHD (9.4)	4	TBAB (0.05)	**2** (0.6)	3.3	4.7	1.25
3	DCHD (9.4)	4	TASHF (0.10)	**1** (0.6)	3.3	4.3	1.28
4[d]	DCHD (9.4)	7	TBAB (0.05)	**1** (0.6)	3.3	4.2	1.24
	MMA (14.0)				5.7	8.6	1.33
5[e]	MMA (14.0)	7	TBAB (0.05)	**3** (0.55)	2.5	3.8	1.12
	DCHD (9.4)				6.1	9.4	1.38
6[e]	DCHD (9.4)	7	TBAB (0.05)	**3** (0.55)	3.6	4.6	1.25
	MMA (12.7)				6.9	9.8	1.37

[a] Polymerization temperature was between 20 and 30 °C, with addition of monomer to a solution of initiator and catalyst. All yields of polymer were quantitative. The values for $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined by gel permeation chromatography with polystyrene standards. [b] $TASHF_2$ is tris(dimethylamino)sulfonium bifluoride (0.05 M in CH_3CN). TBAB is tetrabutylammonium bibenzoate (0.05 M in THF). [c] Theoretical $\bar{M}_n$ is calculated by [weight of reacted monomer]/[moles of initiator]. [d] AB diblock copolymer. [e] ABA triblock copolymer.

Scheme I



Scheme II



tional monomers,[1] the rate of propagation is considered to be determined by the rate of the intermolecular reaction. In order to study the differences of the rate of initiation and propagation, [1-methoxy-1-[(trimethylsilyl)oxy]methylene]cyclohexane, having a structure similar to that of the polymer end group, was used as a GTP initiator. However, there is no difference in polydispersities when using conventional GTP initiator **2** (see Table I, exp nos. 1 and 2). This suggests that the rate of initiation by **1** and **2** is not much slower than the rate of propagation,[12] during the GTP of DCHD. Similar instances of low rates of initiation relative to the rates of propagation leading to poor control of the molecular weight in GTP have been reported earlier for methacrylate with certain types of initiators.[13] The polydispersity ($D = \bar{M}_w/\bar{M}_n$) was estimated to be 1.23–1.28, which shows good molecular weight control. The measured molecular weight of the polymers are somewhat higher than those predicted from the monomer/initiator ratio, which is probably due to the fact that molecular weights are calculated by a polystyrene calibration curve.

Copolymerization with Methacrylates. As illustrated in Scheme II (exp no. 6 in Table I), an ABA triblock copolymer was prepared by adding *n*-butyl methacrylate, as the second monomer, to a completely polymerized DCHD solution. In a solvent extraction experiment with formic acid, which is a solvent for homopoly(DCHD) and a nonsolvent for poly(BMA), no soluble fraction was found. Thus the resulting polymer was identified to be an ABA triblock copolymer. These block copolymerizations resulted in quantitative yield and polymers with fairly low dispersities ($\bar{M}_w/\bar{M}_n$ = 1.33–1.38), as shown in Table I. The GPC eluogram of the polymer produced in a block copolymerization (Figure 1) clearly demonstrates the increase of the molecular weight after the second monomer addition without side reaction, e.g., chain transfer or termination.

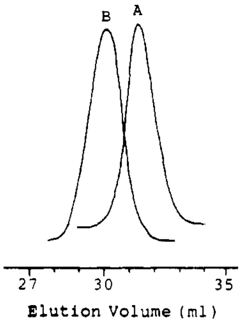


Figure 1. GPC curves for poly(DCHD) (A) and for poly(DCHD-*b*-MMA) (B); exp. no. 4 in Table I.

Polymer Characterization. No indication of linear structure or olefinic moieties was observed in the IR and NMR spectra of poly(DCHD). Thus, cycloaddition has exclusively occurred. The ^{13}C NMR spectrum of poly(DCHD) at 75.8 MHz is shown in Figure 2. The spectrum is relatively complicated, which may be due to tacticity or cis/trans ring substitution. The assignment of these resonances can be aided through the use of a DEPT experiment,[14] which permits us to differentiate between methylene and quaternary carbons. As shown in Figure 3, it turns out that the multiplet at 47 ppm, which was

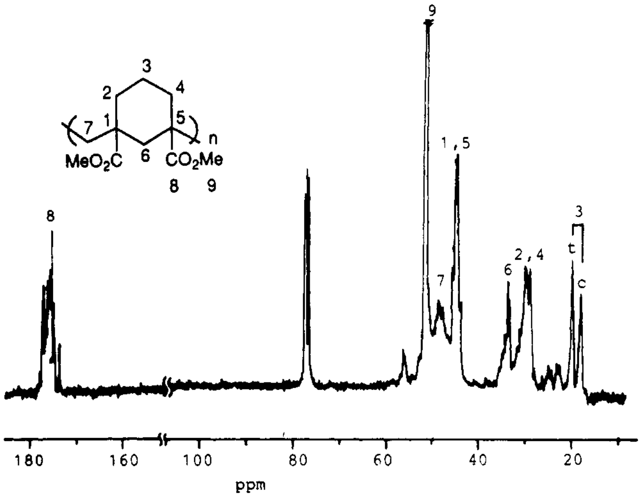


Figure 2. ^{13}C NMR at 75.8 MHz of poly(DCHD) proton-decoupled in $CDCl_3$.

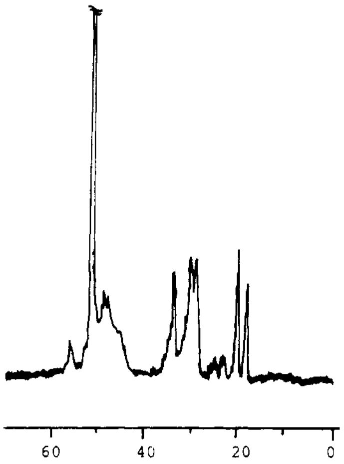
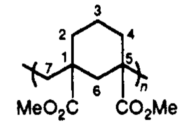
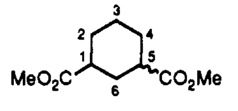


Figure 3. 75.8-MHz ^{13}C NMR DEPT spectra of poly(DCHE) for the methyl and methylene carbon only.

Table II
Comparison of Poly(DCHD) Assignments vs 1,3-Dicarbomethoxycyclohexane's ^{13}C Chemical Shifts[a]


poly(DCHD)


1,3-dicarbomethoxycyclohexane

Cn	poly(DCHD) (ppm)	1,3-dicarbomethoxycyclohexane (ppm)
C3	trans (19.9)	trans (25.0)
	cis (17.9)	cis (22.2)
C2, C4	trans (29.9)	trans (28.5)
	cis (28.7)	cis (28.1)
C6	cis/trans (33.6)	trans (31.3)
		cis (29.6)

[a] *cis/trans*-1,3-Dicarbomethoxycyclohexane's chemical shifts were referred to the ^{13}C NMR of Sadtler Research Lab., Inc., 3725C.

negative and partially overlapped with a methylene resonance, is a correspondent to quaternary carbons C1 and C5. A complicated interpretation of the spectrum can be accomplished by referring to low molecular weight analogues (*cis/trans*-1,3-dicarbomethoxycyclohexane).[15] From the data in Table II, it appears that the ^{13}C chemical shifts of C2,4 of the poly(DCHD) are similar with the correspondents of 1,3-dicarbomethoxycyclohexane. The largest effect (ca. 2 ppm) of the cis/trans placement of substituents was found at the position C3 in both cases.

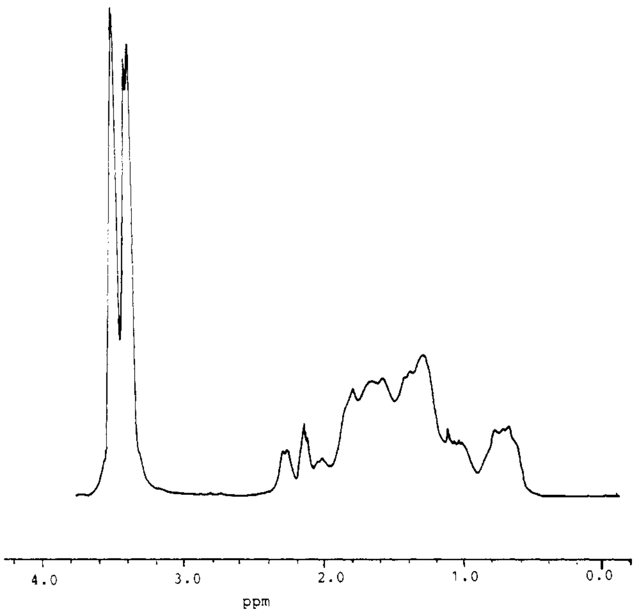


Figure 4. ^1H NMR spectrum of poly(DCHD) in $CDCl_3$ (300 MHz).

In addition, the presence of cis/trans ring substitutuion can be identified by two peaks of carbomethoxy methyl protons in the ^1H NMR spectrum (Figure 4). This ^1H doublet is estimated to be due to cis/trans isomerism and not to the chirality of the carbon of the next monomer unit by considering free orientation of the methylene bridge of the repeated cyclohexane units. The similar instance of a larger effect on the placement of substituents across a repeated ring unit rather than methylene bridges has been reported.[16]

The precipitated polymer, poly(DCHD), was soluble in chloroform, acetone, formic acid, and THF but insoluble in hexane, ether, and methanol. In a TGA experiment of poly(DCHD) obtained by GTP, 96% of the initial weight remained at 320 °C, which reduced to 17% at 450 °C. The DSC thermogram of poly(DCHD) showed the T_g at 111 °C.

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