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Communications to the Editor

Cyclopolymerization of 2,5-Bis(methoxycarbonyl)-1,5-hexadiene by Group-Transfer Polymerization

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Various polymerization techniques have been developed to meet the challenges of finding new monomer-to-polymer systems. Cyclopolymerization, first established by Butler[1] is a technique which can give a ring-fused structure in the polymer main chain. Cyclopolymerization is normally carried out by free-radical, cationic, and anionic methods.[2] In the cyclopolymerization of 1,6-diene, there were ambiguities as to whether cyclization involves six- and/or five-membered ring formations. We have recently reported that cyclopolymerization of dimethacrylic 1,6-dienes by group-transfer polymerization (GTP) can be controlled in such a manner as to produce only the six-membered ring formation[3,4] since GTP allows for only a head-to-tail mechanism.

In an organic reaction of simple molecules, it is well-known that, 1,5-diene cannot be cyclized by a nucleophile, because of stereoelectronic effects,[5] and the examples of anionic cyclopolymerization of 1,5-diene monomers are not reported in the literature. However, we were able to show that a 1,5-diene monomer, namely, 2,5-bis(methoxycarbonyl)-1,5-hexadiene (DCHXD), can be cyclopolymerized by GTP. This work presented in this paper describes the group-transfer polymerization of DCHXD, and the possibility of its being an anionic polymerization is examined.

DCHXD used in this investigation was prepared in the manner described earlier in the literature[6] and was purified by repeated distillation under a reduced pressure [bp 72–73 °C (1 mmHg)]. The GTP initiator (I) and catalyst were prepared as described in the literature.[7,8] Other reagents used were commercially available, and they were purified by distillation under a nitrogen atmosphere.

^{1}H and ^{13}C NMR spectra were recorded on Varian FT-80A and Bruker AM-300 spectrometers. 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 (10^5, 10^4, 10^3, and 500 Å) connected in series. The standard was polystyrene, and THF was used as the eluent at a flow rate of 1 mL/min at 30 °C.

A typical group-transfer polymerization was as follows (Scheme I). A 50-mL reactor fitted with an argon inlet, a magnetic stirrer, and a thermocouple was charged with THF (6 mL), tetrabutylammonium bibenzoate (TBAB; 0.05 mL, 0.05 M in THF), and the initiator [1-methoxy-1-[(trimethylsilyl)oxy]-2,2-dimethylethylene] (0.1 mL). Then DCHXD (9.4 mmol) was added via syringe over a period of 5 min. After an interval, the reaction was terminated by methanol. The solvent was removed by evaporation, and the remaining residue was then dissolved in 20 mL of ethyl acetate and washed three times with 20-mL portions of water. The organic layer was dried over magnesium sulfate. GPC $\bar{M}_n$ = 4100 and $\bar{M}_w/\bar{M}_n$ = 1.38 (theoretical $\bar{M}_n$ = 3100).

During the GTP of DCHXD, there were no insoluble products due to side reactions such as cross-linking. Moreover, all the precipitated polymers were found to be soluble in choroform, methylene chloride, THF, and ethyl acetate. The results of the cyclopolymerization are

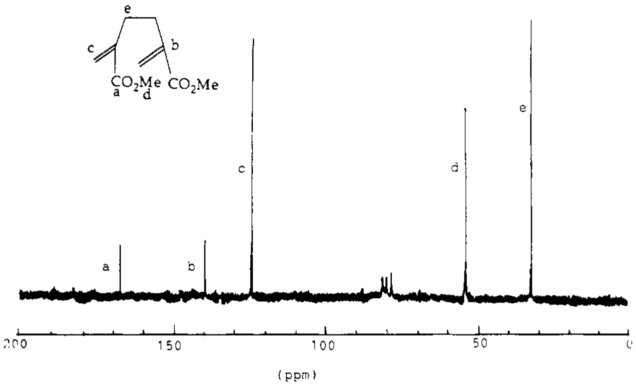

Figure 1. ^{13}C NMR at 50.4 MHz of DCHXD.

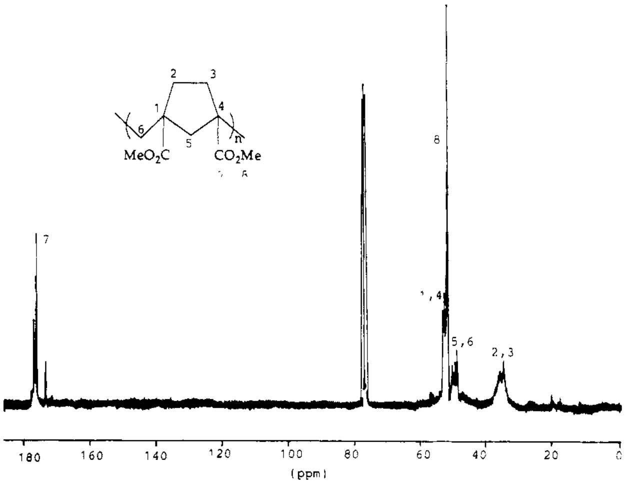

Figure 2. ^{13}C NMR at 75.8 MHz of poly(DCHXD) proton-decoupled in CDCl$_3$.

Scheme I

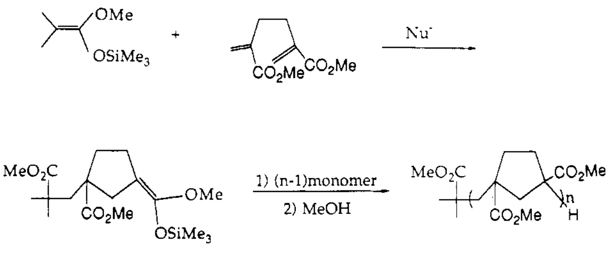

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Table I
Cyclopolymerization of DCHXD

expt no.	monomer DCHXD (mmol)	solvent (mL)	cat.[b] (mL)	init. (mmol)	$\bar{M}_n \times 10^{-3}$ calcd	$\bar{M}_n \times 10^{-3}$ obsd	$\bar{M}_w/\bar{M}_n$
1	9.4	THF (6)	TBAB (0.05)	1 (0.6)	3.1	4.1	1.38
2	9.4	THF (6)	$TASHF_2$ (0.1)	1 (0.6)	3.1	4.5	1.43
3	9.4	THF (4)	TBAB (0.05)	1 (0.6)	3.1	4.2	1.45
4	9.4	THF (4)	$TASHF_2$ (0.1)	1 (0.6)	3.1	4.7	1.51
5	9.4	toluene (10 mL)		9-fluorenyllithium (0.3)		no polymzn	

[a] All yields of the polymer were quantitative. The values for $\bar{m}_n$ and $\bar{M}_w/\bar{M}_n$ were determined by gel permeation chromatography with polysytrene standards. [b] $TASHF_2$ is tris(dimethylamino)sulfonium bifluoride (0.05 M in CH_3CN). TBAB is tetrabutylammonium bibenzoate (0.05 M in THF).

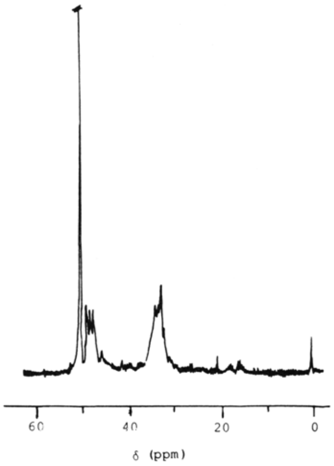


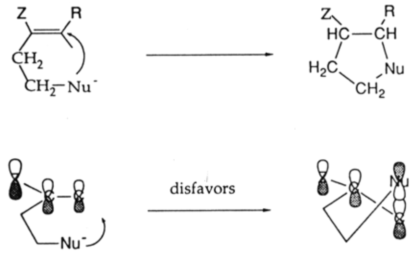
Figure 3. 75.8-MHz ^{13}C NMR DEPT spectrum of poly(DCHXD) for the methyl and methylene carbons only.

summarized in Table I. The polymer yield was quantitative. However, the measured molecular weights of poly(DCHXD) were somewhat greater than the theoretical values, which may be due to the fact that these values were calculated from a polystyrene calibration curve. The polydispersities ($D = \bar{M}_w/\bar{M}_n$) of the poly(DCHXD) were estimated to be in the range between 1.38 and 1.51, which is higher than those reported in the earlier works. This may be due to impurities in the reaction or to inherent reactivity of DCHXD during the cyclopolymerization.

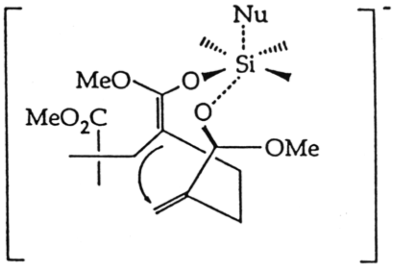
^1H and ^{13}C NMR spectra as well as IR measurements gave no indication of linear structure or olefinic moieties. ^{13}C NMR spectra of the monomer and the polymer product are shown in Figures 1 and 2. The assignments of the ^{13}C NMR of the polymer peaks were made based on monomer, model polymer spectra as well as on the results of additional DEPT experiments[9] (Figure 3), which allow for the differentiation between the methylene carbons and quaternary carbons in the ^{13}C NMR spectrum of the poly(DCHXD). The multiplet at 52 ppm, which is negative, corresponds to the quaternary carbons C1 and C4. We could therefore conclude that GTP of DCHXD yielded a cyclopolymer consisting of a cyclopentane moiety.

We also studied anionic cyclopolymerization of DCHXD for the purpose of comparing it with group-transfer polymerization. The polymerization was carried out by 9-fluorenyllithium, which is a typical initiator in an anionic polymerization of an acrylic monomer at low temperature (−78 °C).[10] As shown in Table I (expt no. 5), no polymer was obtained. No satisfactory explanations for this phenomenon are found in the literature. However, the difficulty of an anionic polymerization of DCHXD may be connected with the analogous organic reaction of low-molecular-weight compounds. Five-membered ring formation by nucleophiles, in an anionic polymerization of DCHXD, may be classified as the 5-endo-trigcyclization (Scheme II). Due to large distortion in the trajectory of the approaching nucleophiles, this cyclization is known to be too difficult to occur.[5] Hence, it may be assumed that the cyclopolymerization of DCHXD by anionic techniques cannot occur due to the above-mentioned stereoelectronic effects.

Scheme II
5-Endo-Cyclization



By contrast, cyclopolymerization of DCHXD can proceed by GTP. The explanation may be obtained by considering the cyclization mechanism, which involves a hypervalent intermediate with a catalyst and another carbonyl oxygen of the intramolecule. Such an intermediate can relax a large distortion during an intramolecular cyclization.



In conclusion, the application of GTP has been extended to cover 1,5-diene monomers of the type 2,5-bis(methoxycarbonyl)-1,5-hexadiene. The GTP of DCHXD has been shown to be a facile route to a cyclopentane structure containing two methacrylate moieties. A more detailed discussion on the description of this reaction will be given later.

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