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CYCLOPOLYMERIZATION OF *BIS*(3-TRIMETHYLSILYL-2-PROPYNYL ETHER) BY TRANSITION METAL CATALYSTS

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ABSTRACT

The cyclopolymerization of bis(3-trimethylsilyl-2-propynyl) ether was carried out by Mo- and W-EtAlCl₂ catalyst system. The polymer yields were very low (maximum polymer yield: 13%). The resulting polymer was a white powder and insoluble in common organic solvents. The polymer was found to have a partially desilylated polymer structure. The most probable polymer structure was proposed on the basis of the cyclopolymerization mechanism and its stability.

INTRODUCTION

During the past three decades, a large effort has produced a wide range of mono- and di-substituted polyacetylenes with various pendant groups.¹⁻⁴ It was reported that 1-(trimethylsilyl)-1-propyne [MeC≡CSiMe₃], a Si-containing disubstituted acetylene, polymerizes with TaCl₅ and NbCl₅ to produce a high molecular weight polymer in high

yields, and that the resulting polymer shows extremely high oxygen permeability.⁵⁻⁷

In recent series of papers,^{4,8-15} we have reported that Mo- and W-based catalyst systems are very effective for the cyclopolymerization of 1,6-heptadiyne and dipropargyl derivatives yielding a highly π -conjugated double bond in the cyclic recurring unit. Dipropargyl ether was easily polymerized with transition metal catalysts to give the polymer in high yield.⁸ Also, 2-propynyl 3-trimethylsilyl-2-propynyl ether, an acetylenic monomer, was polymerized to give a moderate yield of polymer.¹⁶

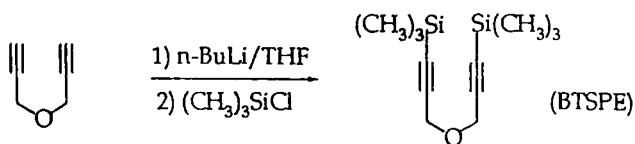
We now report an attempted cyclopolymerization of disubstituted dipropargyl ether, bis(3-trimethylsilyl-2-propynyl)ether [BTSPE], which has a highly bulky substituent ($-\text{SiMe}_3$) by transition metal catalysts and the characterization of the resulting poly(BTSPE).

EXPERIMENTAL

Materials: Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemical Co., resublimed, 99.9%) were used without further purification. Palladium(II) chloride and ethyl aluminum dichloride (Aldrich Chemical Co.) were also used as received. Propargyl bromide (Aldrich Chemical Co., 80 wt% solution in toluene) was dried over calcium hydride and fractionally distilled by recommended procedures. Propargyl alcohol (Aldrich Chemical Co., 99%) was used as received. The polymerization solvents were analytical grade materials. They were dried with appropriate drying agents and fractionally distilled.

Instruments for Characterization: ^1H - and ^{13}C -NMR spectra were recorded with the use of a Bruker AM-200 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as the internal standard. FT-IR spectra were measured with neat oils or KBr pellets on a Bomem MB-100 spectrometer, and frequencies are given in reciprocal centimeters. A Shimadzu UV-3100S spectrometer was used for UV-visible spectral data.

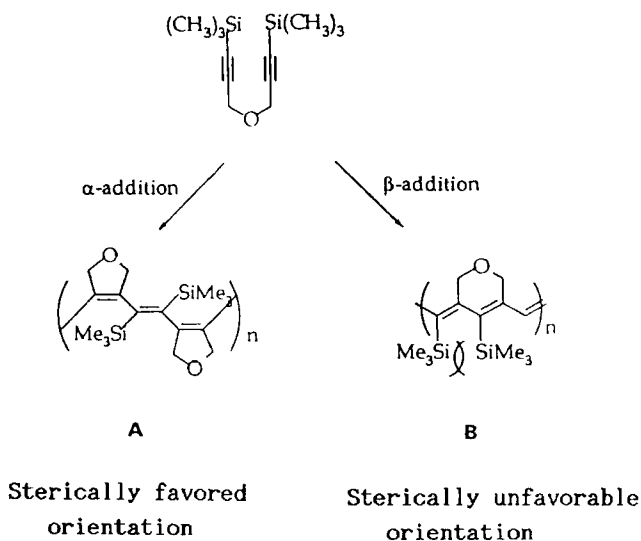
2-Propynyl ether^{8,17}: 2-Propynyl ether was prepared by the reaction of propargyl bromide and propargyl alcohol with sodium hydroxide according to the literature. b.p.:67°C/85mmHg, yield: 85%.



Scheme I. Preparation of Bis(3-trimethylsilyl-2-propynyl) ether

Bis (3-trimethylsilyl-2-propynyl)ether (BTSPE, Scheme I): The reaction flask was charged with 2-propynyl ether (4.7g, 0.05 mol) and THF (40mL). *n*-Butyllithium (1.6M in hexane solution, 0.1 mol) was added over a few min to the reaction mixture cooled to $-60\sim-50^\circ\text{C}$. After an additional 5 min, freshly distilled chlorotrimethylsilane (10.8g, 0.1 mol) was added over 5 min to the clear solution with vigorous stirring while carefully keeping the temperature within this range. After this addition, the cooling bath was occasionally removed and the temperature was allowed to rise gradually over 1 hour to room temperature. The white suspension was poured into 250mL of ammonium chloride solution and then the water phase was extracted with hexane. The combined organic phase was dried with anhydrous magnesium sulfate. The product was isolated by distillation at reduced pressure. b.p.: $102^\circ\text{C}/10\text{mmHg}$, yield:72%; $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 0.15 (s, 18H), 4.21 (s, 4H), $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): -0.23 [$-\text{Si}(\text{CH}_3)_3$], 56.36 ($\text{CH}_2\text{-O-}$), 91.98 ($\equiv\text{C-}$), 100.6 ($\text{SiC}\equiv$), IR (wavenumbers, cm^{-1}): 2175 ($\text{C}\equiv\text{C-Si}$).

Polymerization Procedures: Catalyst solution preparation and polymerization were carried out under dry nitrogen atmosphere. Transition metal chlorides and ethyl aluminum dichloride were dissolved in chlorobenzene to make 0.1 and 0.2M solutions prior to use. A polymerization ampule equipped with rubber septum was flushed with dry nitrogen. A typical polymerization procedure was as follows: chlorobenzene, catalyst solution, and when needed, cocatalyst solution were injected into the polymerization ampule in the order given. When cocatalyst was used, the catalyst system was aged at 30°C for 15min. Finally, the monomer was injected into the polymerization ampule. After the reaction mixture was allowed to react at 70°C for 24 hours, the polymerization was terminated by adding a small amount of methanol and 10mL of chloroform was added. The resulting polymer was precipitated into a large excess of methanol. The polymer was filtered from the solution and dried under vacuum at 40°C for 6 hours. The polymer yield was calculated by gravimetry.



Scheme II. Polymerization of BTSPE

RESULTS AND DISCUSSION

The attempted cyclopolymerization of BTSPE, a diacetylenic monomer disubstituted with highly bulky substituent, was carried out by transition metal catalysts (Scheme II).

Table 1 shows the results for the polymerization of BTSPE by transition metal catalysts. MoCl_5 , $\text{Mo}_5\text{-Ph}_4\text{Sn}$, and WCl_6 catalyst systems fail to polymerize the BTSPE. Molybdenum and tungsten chloride- EtAlCl_2 catalyst systems give only a low yield of polymer even at the condition of high initial monomer concentration ($[\text{M}]_0$). When $\text{MoCl}_5\text{-EtAlCl}_2$ and $\text{WCl}_6\text{-EtAlCl}_2$ catalyst systems were used for the polymerization, the polymer yields were 13% and 5%, respectively. The resulting polymer was a white powder and insoluble in common organic solvents.

Fig. 1 shows the FT-IR spectra of BTSPE and Poly(BTSPE). In the IR spectrum of poly(BTSPE), acetylenic $\text{C}\equiv\text{C}$ stretching peak (2175cm^{-1}) disappeared and the $\text{C}=\text{C}$ double bond stretching peak in the conjugated polymer backbone observed at about 1640cm^{-1} . However, a small amount of acetylene functional group was also observed even in the IR spectrum

TABLE I
Cyclopolymerization of Bis (3-trimethylsilyl-2-propynyl) ether by
Transition Metal Catalysts^a

Exp. No	Catalyst System ^b (mole ratio)	[M] ₀ (M)	Polymer Yield ^c (%)	Polymer Color
1	MoCl ₅	1.5	-	-
2	MoCl ₅ -Ph ₄ Sn(1:1)	1.5	-	-
3	MoCl ₅ -EtAlCl ₂ (1:4)	0.5	trace	white
4	MoCl ₅ -EtAlCl ₂ (1:4)	1.5	13	white
5	WCl ₆	1.5	-	-
6	WCl ₆ -EtAlCl ₂ (1:4)	1.5	7	white

^aPolymerization was carried out at 70°C for 24 hours in chlorobenzene. The mole ratio of monomer to catalyst was 50. ^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min. before use. ^cThe precipitated polymers were gravimetrically estimated.

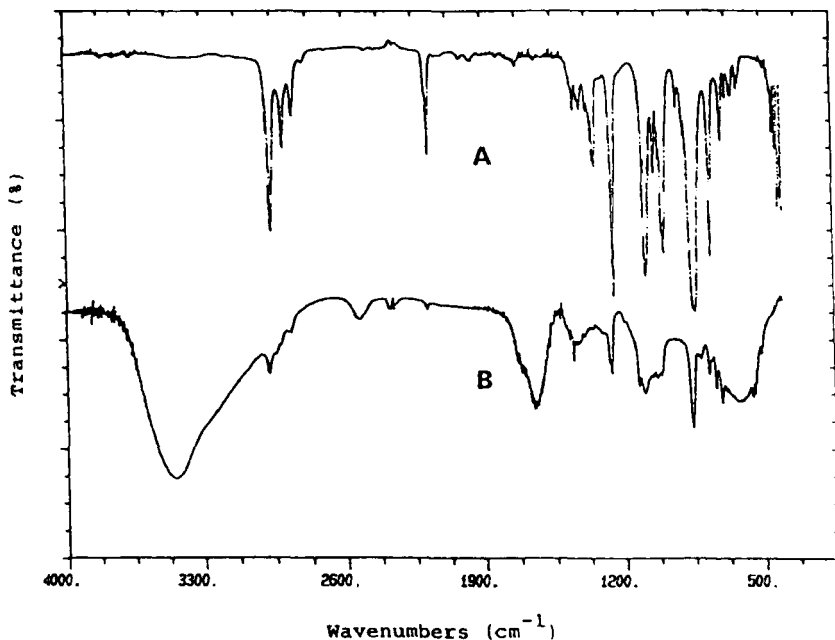


Fig. 1. FT-IR spectra of BTSPE [A] and poly(BTSPE) [B] in KBr pellet.

of polymer. From these observations, the present poly(BTSPE) was thought to have the conjugated polymer structure with a small amount of unreacted acetylene group. It can be proposed that the polymer structure A is formed by α -addition mechanism in view of the cyclopolymerization mechanism and stereochemistry of the resulting polymer.¹⁸⁻²⁰ In addition, it was found that the resulting polymers were partially desilylated, judging from the observation of the Si-C peak intensity at 848cm^{-1} in the IR spectrum and the integration ratio of $-\text{Si}(\text{CH}_3)_3$ functional group in the $^1\text{H-NMR}$ spectrum of slightly soluble products. The desilylation phenomenon of disubstituted polyacetylene having trimethylsilyl functional group was also observed in the polymerization of 1-aryl-2-trimethylsilylacetylenes (aryl: phenyl, 2-thienyl, 2-furyl, and 2-pyridyl).²¹

The resulting poly(BTSPE)s were insoluble in common organic solvents. This polymer insolubility may originate from the crosslinking by the activated allyl protons and/or the unreacted acetylenic functions. The white polymer color is originated from the highly twisted polymer backbone structure.

Further works on the increase of polymer yield and the copolymerization with other acetylenic monomers are in progress.

CONCLUSIONS

In this article, we presented the attempted cyclopolymerization results of disubstituted dipropargyl ether, having a bulky trimethylsilyl substituent. Mo- and W-EtAlCl₂ catalyst systems can polymerize BTSPE to give a low yield of polymer. The low polymer yield was thought to be due to the high steric hinderance of the bulky substituent. The polymer structure was thought to have five-membered cyclic recurring unit majorly by α -addition polymerization mechanism.

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