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Cyclopolymerization of Dipropargylgermaniums by Transition-Metal Catalysts

Ok-Kyung Cho,[†] Yun-Hi Kim,[†] Kil-Yeong Choi,[‡] and Sam-Kwon Choi[*,†]

Department of Chemistry, Korea Advanced Institute of Science and Technology,
P.O. Box 150, Cheongryangri, Seoul 130-650, Korea.

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ABSTRACT: Cyclopolymerization of dipropargylgermaniums [$(CH_3)_2Ge(CH_2C\equiv CH)_2$, $(Ph)_2Ge(CH_2C\equiv CH)_2$] was examined for $MoCl_5$- and WCl_6-based catalysts. The WCl_6 and $MoCl_5$ catalysts are all effective in the polymerization of dipropargylgermaniums. Polymerization of diphenyldipropargylgermaniums by WCl_6 leads to soluble, highly colored polymers of a number-average molecular weight of ($\bar{M}_n$) 12 000. NMR (^1H and ^{13}C), IR, UV-visible spectroscopies showed that poly(diphenyldipropargylgermaniums) possess polyene structures having cyclic recurring units in the polymer backbone. Poly(dipropargylgermaniums) have been investigated in terms of physical properties, solubility, electrical conductivity, and thermal and oxidative stability. Fairly good thermal and oxidative stability and solubility of the present cyclopolymer are notable characteristics.

Introduction

Cyclopolymerization (ring-forming polymerization) is any type of chain growth addition polymerization that leads to the introduction of cyclic structures into the main chain of the polymer.[1]

Since the discovery of polymerization of 1,6-heptadiyne using Ziegler–Natta catalyst in 1961,[2] there have been many studies on the cyclopolymerization of nonconjugated diynes giving the conjugated double bonds in the polymer backbone and cyclic recurring unit. However, this catalyst leads to insoluble polymer films.[3] It was known that group VI metal-based catalysts exhibit a high catalytic activity for the polymerization of substituted acetylenes.[4] Recently, we have found that Mo- and W-based catalyst systems are very effective for the cyclopolymerization of dipropargyl sulfide,[5] dipropargyl ether,[6] and dipropargylsilanes.[7] The latter polymer is generally soluble, thermally stable, and has high electrical conductivity.

We have now investigated the cyclopolymerization of dipropargylgermaniums [$(CH_3)_2Ge(CH_2C\equiv CH)_2$, $(Ph)_2Ge(CH_2C\equiv CH)_2$] by $MoCl_5$- or WCl_6-based catalysts. The physical and spectroscopic properties of the resulting polymer will be discussed.

Experimental Section

Monomers were prepared by a Grignard reaction.[8] Dimethyldipropargylgermanium (DMPGe), 1.22 mol of magnesium turnings, and 1.49 mol of propargyl bromide were reacted with 0.5 mol of dichlorodimethylgermanium. Yield: 66%. Bp: 70–72 °C (20 mmHg). Anal. Calcd for $C_8H_{12}Ge$: C, 53.15; H, 6.69. Found: C, 53.02; H, 6.47. ^1H NMR ($CDCl_3$): δ 0.40 (3 H, s, CH_3), 1.67 (2 H, d, $C\equiv CCH_2$), 1.90 (1 H, t, $C\equiv CH$). IR (NaCl): 3300, 2970, 2120 cm^{-1}.

Diphenyldipropargylgermanium (DPPGe). Yield: 60%. Bp: 104–106 °C (0.1 mmHg). Anal. Calcd for $C_{18}H_{16}Ge$: C, 70.90; H, 5.29. Found: C, 70.75; H, 5.11. ^1H NMR ($CDCl_3$): δ 7.2–7.7 (5 H, m, ArH), 1.90 (1 H, t, $C\equiv CH$), 2.27 (2 H, d, $C\equiv CCH_2$). IR (NaCl): 3310, 3100, 2910, 2120 cm^{-1}.

Polymerization. All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere. The cyclopolymers were synthesized by the same method as described in a previous paper.[7]

Polymer Characterization. ^1H NMR and ^{13}C NMR spectra were recorded with a Varian T-60A spectrometer and a Bruker AM-200 spectrometer. IR and UV-vis spectra were taken on a Perkin-Elmer 283B spectrometer and Cary 17 spectrometer. The number-average molecular weights ($\bar{M}_n$) of polymers were determined by GPC (150C of Waters) using a polystyrene calibration. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 °C/min with a Du Pont 1090 analyzer. Thermal transitions were measured with a Du Pont 990 thermal analyzer. Electrical conductivities were measured by 2-point probe dc method with a Hewlett-Packard 6216A power supply and Keithley 485 picoammeter.

[†] Korea Advanced Institute of Science and Technology.
[‡] Korea Research Institute of Chemical Technology.

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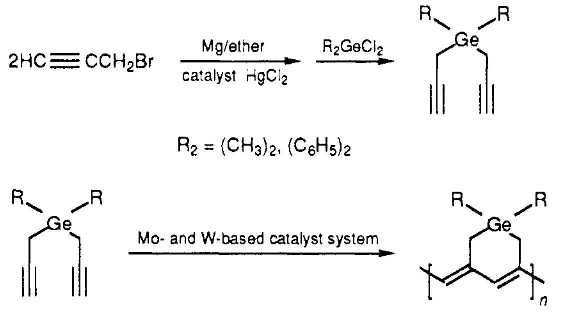
Table I
Polymerization of Dipropargylgermaniums by Various Catalyst Systems[a]

exp. no.	catalyst system[b] (mole ratio)	M/C	solvent	polym yield, % R = CH_3	polym yield, % R = C_6H_5
1	$MoCl_5$	50	PhCl	20	55
2	$MoCl_5/(n\text{-}Bu)_4Sn$ (1:2)	50	PhCl	12	46
3	$MoCl_5/EtAlCl_2$ (1:4)	50	PhCl	22	98
4	WCl_6	50	PhCl	15	44
5	$WCl_6/(n\text{-}Bu)_4Sn$ (1:2)	50	PhCl		36
6	$WCl_6/EtAlCl_2$ (1:2)	50	PhCl	24	46
7	$PdCl_2$[c]	30	DMF		32
8	$PdCl_2$	50	DMF		18

[a] Polymerization was carried out at 60 °C for 24 h. Initial monomer concentration ($[M]_0$) was 2 M. [b] Mixture of catalyst and cocatalyst in chlorobenzene was aged at 30 °C for 15 min before use as catalyst. [c] Polymerization was carried out at 90 °C.

Scheme I



Results and Discussion

The process for the preparation of dipropargylgermaniums is reported in Scheme I.

Table I shows the results for the polymerization of dipropargylgermaniums by various catalysts. The W and Mo catalysts are all effective in the polymerization of dipropargylgermaniums. WCl_6 exhibits less effective catalytic activity by itself than $MoCl_5$, but highly colored (brownish red) poly(diphenyldipropargylgermanium) was obtained having a number-average molecular weight ($\bar{M}_n$) of 12 000 by GPC (polystyrene calibration) and $[\eta] = 0.195$ dL/g by viscosity measurement at 25 °C in THF. It was known that the addition of a small amount of reducing agent such as $(n\text{-}Bu)_4Sn$ increases polymer yield and molecular weight.[9] However, cyclopolymerization of dipropargylgermaniums is slightly decreased. Especially for the present polymerization, organoaluminium compounds exhibit high cocatalytic activities. The best result is obtained when $MoCl_5/EtAlCl_2$ is used as catalyst. However, it gives a yellow solid having a number-average molecular weight ($\bar{M}_n$) of 6000 by GPC (polystyrene calibration) and $[\eta] = 0.135$ dL/g by viscosity measurement at 25 °C in THF. Catalytic activity order is hardly affected by substituent bulkiness; however, polymerizability increases with bulkier substituent (DMPGe < DPPGe). This tendency is similar to that reported for polymerization of dipropargylsilanes.[7]

To test the effectiveness of polymerization solvent, we have polymerized monomers in various solvents. It was reported that the most suitable solvents for polymerization by metal chloride based catalysts are aromatic hydrocarbons, especially toluene and chlorobenzene.[10] In our study, high polymer yields were generally achieved in aromatic and halogenated hydrocarbons. As to oxygen-containing solvent, high yield is obtained with THF.

Polymer structure was identified by NMR (^1H and ^{13}C), IR, UV-vis spectroscopy. Figure 1 shows the ^{13}C NMR and IR spectra of poly(DPPGe). In the ^{13}C NMR spectrum, the chemical shift at 136–140 ppm is due to the polyconjugated carbon and another peak at about 20 ppm is due to the methylene carbon adjacent to the germanium atom. IR spectra show the conjugated carbon–carbon double bond stretching at 1600–1650 cm^{-1}. On the other hand, the acetylenic hydrogen (3300 cm^{-1}) and carbon–carbon triple bond (2120 cm^{-1}) stretching of the monomer is not seen at all in the polymer. In the ^1H NMR spectrum, a broad peak at 6.0–7.8 ppm is due to the protons on the conjugated double bond and phenylic protons. Also, a characteristic peak of conjugated polyene, broad and weak $\pi \rightarrow \pi^*$ absorption, which are absent in monomer, appeared in the visible region (300–600 nm) with maximum at 430 nm.

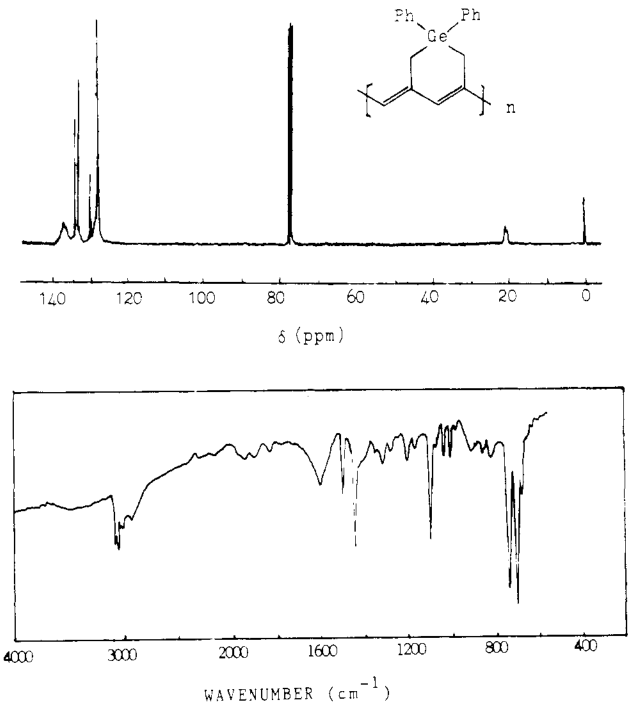


Figure 1. ^{13}C NMR and IR spectra of poly(diphenyldipropargylgermanium).

The polymer is powdery and is easily soluble in aromatic hydrocarbons (benzene, toluene, xylene), halogenated hydrocarbons (CCl_4, $CHCl_3$, $(CH_2Cl)_2$, PhCl), and THF. A dark red, less brittle film is prepared by casting the polymer from toluene solution. However, poly(DMPGe) is only partially soluble in organic solvents. From the above results, poly(dipropargylgermaniums) possess polyene structures, having cyclic recurring units in the polymer backbone.

The TGA thermogram of poly(DMPGe) shows that it retained 95% of its original weight at 180 °C. Also, poly(DPPGe) retained 95% of its original weight at 350 °C. This temperature is higher than that of dipropargylsilanes.[7]

When poly(DPPGe) was left standing exposed to air at room temperature for 1 mo, there was no indication of air oxidation such as new carbonyl band in IR spectra. Thus, cyclopolymers having a germanium atom are more stable to thermal and air oxidation than those having a silicone atom.[7]

The DSC curve shows two irreversible exothermic processes, one peaking at 112 °C and the other at 260 °C. This behavior at 112 °C is attributed to the rearrangement of the exo double bond of poly(DPPGe), converting the polymer from a helical structure to a nearly planar polyene backbone configuration. This process may be compared to the poly(1,6-heptadiyne)[3] and poly(dipropargyl sulfide)[5] at 107 and 160 °C, respectively.

The electrical conductivity of poly(DPPGe) at 25 °C is 2.9×10^{-11} S cm^{-1}.

Fairly good thermal, oxidative stability and solubility of the present polymer are notable characteristics. We are now attempting to increase electrical conductivity by various doping methods.

Acknowledgment. We thank the Korea Science and Engineering Foundation for support of this work.

Registry No. DMPGe, 123639-65-6; DMPGe (homopolymer), 123639-66-7; DPPGe, 6262-84-6; DPPGe (homopolymer), 29317-06-4; $(n\text{-Bu})_4Sn$, 1461-25-2; $EtAlCl_2$, 563-43-9; $PdCl_2$, 7647-10-1; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; propargyl bromide, 106-96-7; dichlorodimethylgermanium, 1529-48-2.

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A Study of Solution Polymerization of Polyphosphazenes

Ashutosh N. Mujumdar, Scott G. Young, Robert L. Merker, and Joseph H. Magill*

Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261. *Received October 3, 1988; Revised Manuscript Received May 1, 1989*

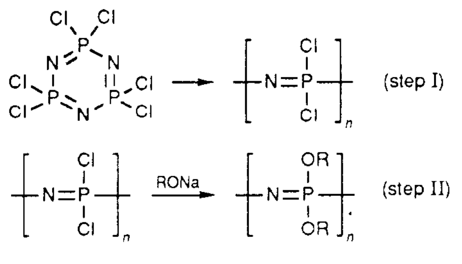
ABSTRACT: Several alkoxy/aryloxy-substituted phosphazene polymers $[P(OR)_2{=}N]_n$ (R = CH_3, C_6H_5, $C_6H_4CH_3$, CH_2CF_3, $C_6H_4C_6H_5$, C_6H_4Cl, C_6H_4Br, C_8H_{10}) were prepared by the reaction of poly(dichlorophosphazene) with their corresponding sodium salts. The poly(dichlorophosphazene) was obtained by the solution polymerization of hexachlorocyclotriphosphazene in 1,2,4-trichlorobenzene. Sulfamic acid and ammonium sulfamate were used as catalysts. Apparently sulfamic acid functions as a catalyst through its acid group in some decomposed form. Toluenesulfonic acid and sulfobenzoic acid were new catalysts developed for solution polymerization. The polymerization favors a cationic mechanism. Promoters were found to speed up to polymerization reaction. Effects of different parameters including dilution, catalyst concentration, and promoter concentration on the properties of the final polymer were investigated. The changes in molecular weight and molecular weight distribution of the polymer as a function of polymerization reaction time were noted. The nucleophilic reaction was studied, and the effect of reaction time and temperature on the properties of the final polymer was investigated. Ring opening on fully substituted cyclotriphosphazenes at elevated pressures and temperatures was unsuccessful. The polymers were characterized by differential scanning calorimetry, gel permeation chromatography, infrared spectroscopy, and ^{31}P solution nuclear magnetic resonance spectroscopy.

Introduction

Inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms, known as polyphosphazenes, have attracted growing attention in recent years. They comprise a relatively new class of polymers that show promise for further development. Many such polymers with a variety of substituents at the phosphorus have been prepared, and they often exhibit useful properties including fire retardancy, low-temperature flexibility, resistance to chemical attack, and biocompatibility among others.[1-3]

The most commonly used synthetic route to linear polyphosphazene is a two-step process developed by Allcock in the mid-1960s.[4] It involves ring-opening polymerization of cyclic trimer, hexachlorocyclotriphosphazene, to produce linear high molecular weight poly(dichlorophosphazene) (step I) and subsequent replacement of the chlorine groups with the nucleophilic substituents (step II).

Scheme I



This synthetic route is different than conventional polymer synthesis in that a variety of polymers can be prepared from one polymer source, namely, poly(dichlorophosphazene).

Cyclic phosphazene trimer is polymerized to linear poly(dichlorophosphazene)[5,6] (step I) by either solution polymerization[7] or melt polymerization.[8,9] The melt poly-

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