

프로파길 에테르들로부터 전도성 고분자의 합성과 특성 조사

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Preparation and Characterization of Conductive Polymers from Propargyl Ethers

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요약 : 여러가지 프로파길 에테르들 (치환기=메틸, 에틸, *n*-프로필, *n*-부틸, 및 2-테트라히드로푸릴)을 합성하고 WCl_6 , $MoCl_5$, $PdCl_2$ 등을 포함 한 전이금속촉매를 사용하여 이들을 중합시켰다. W- 및 Mo- 계 촉매를 사용했을 경우 중합수율은 $PdCl_2$ 을 촉매로 사용했을 경우보다 일반적으로 낮았다. 중합수율은 치환기에 따라 다음순서로 증가하였다: 메틸>에틸>*n*-프로필>*n*-부틸> 2-테트라히드로푸릴. $PdCl_2$ 를 사용하여 합성한 중합체들은 DMF나 DMSO에 용해하였으나 W- 및 Mo- 계 촉매를 사용하여 합성한 중합체들은 어떤 유기용매에도 전혀 용해하지 않았다. 프로파길 에테르들로부터 합성한 중합체들을 I_2 로 도핑한 후 측정된 전기전도도는 $1.7 \times 10^{-3} \Omega^{-1} cm^{-1}$ 에서 $1.32 \times 10^{-5} \Omega^{-1} cm^{-1}$ 범위였다. 합성한 중합체들의 색, 용해도, 열적특성 및 결정성에 관해서도 연구하였다.

Abstract : Various propargyl ethers (Substituent=methyl, ethyl, *n*-propyl, *n*-butyl, and 2-tetrahydrofuryl) were synthesized and polymerized by transition metal catalysts including WCl_6 , $MoCl_5$, $PdCl_2$, etc. The polymer yield in the polymerization by W- and Mo-based catalysts was generally lower than that by $PdCl_2$. The polymer yield increased in the following order : methyl>ethyl>*n*-propyl>*n*-butyl>2-tetrahydrofuryl, according to substituents. The polymers prepared by $PdCl_2$ were soluble in DMF and DMSO, but the polymers prepared by W- and Mo-based catalysts were not soluble in any organic solvents. The electrical conductivities of polymers (iodine-doped) from propargyl ethers were in the range of $1.7 \times 10^{-3} \Omega^{-1} cm^{-1}$ and $1.32 \times 10^{-5} \Omega^{-1} cm^{-1}$. The color, solubility, thermal property and crystallinity of the resulting polymers were also studied.

INTRODUCTION

The conjugated olefinic polymers formed by homo and copolymerization of acetylenes are interesting because they are generally organic semiconductors. Acetylene itself has been polymerized successfully to a polymer film by use of Ziegler-Natta catalysts such as a mixture of titanium tetra-*n*-butoxide and triethyl aluminum [Ti(*o*-*n*-Bu)₄, Et₃Al (1:4)].^{1,2}

The high conductivity of doped polyacetylenes was first observed by Shirakawa et al. about a decade ago,³ and now research on the applications of polyacetylene to such uses as polymer batteries and solar cells are in progress in many laboratories.

The polymerization of substituted acetylenes has been attempted by various methods: heat, light, radiation, and radical, ionic or transition-metal catalysts.^{4,5} In most cases, however, the products are not high polymers but linear oligomers and/or cyclotrimers.⁵ In 1974, Masuda et al. examined various transition-metal halides as catalysts for the polymerization of phenylacetylene to find eventually that WCl₆ and MoCl₅ (group 6 transition metal chlorides) are particularly effective.⁶ Since then, various acetylene derivatives have been polymerized and characterized.⁷⁻¹⁰ However, there have been no systematic study for the polymerization of propargyl derivatives and the characterization of the resulting polymers.

In recent years, we have studied the polymerization of propargyl derivatives¹¹⁻¹³ such as propargyl bromide, propargyl chloride, etc. and the cyclopolymerization of dipropargyl derivatives¹⁴⁻¹⁶ such as dipropargyl sulfide, dipropargyl silanes, etc.

The present paper deals with the polymerization of various propargyl ethers [methyl propargyl ether (MPE), ethyl propargyl ether (EPE), *n*-propyl propargyl ether (PPE), *n*-butyl propargyl ether (BPE), and 2-tetrahydrofuryl propargyl ether (TPE)] and the physical properties of the resulting polymers.

EXPERIMENTAL

Materials

Propargyl alcohol (Aldrich Chemicals) was fractionally distilled by the recommended procedures. Alkyl bromides (alkyl=ethyl, *n*-propyl, and *n*-butyl) and 2,3-dihydrofuran (Aldrich Chemicals) were dried with calcium hydride and fractionally distilled. Dimethyl sulfate, sodium hydroxide, and potassium hydroxide were used as received.

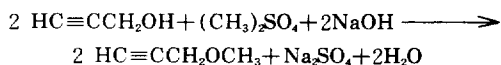
Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemicals, resublimed, 99+%), titanium(IV) chloride (Hayashi Pure Chemicals, EP grade), tetraalkyltin and organoaluminum compounds (Aldrich chemicals) and palladium chloride (Aldrich Chemicals) were used as received. Solvents used all analytical grade materials. They were dried and fractionally distilled.

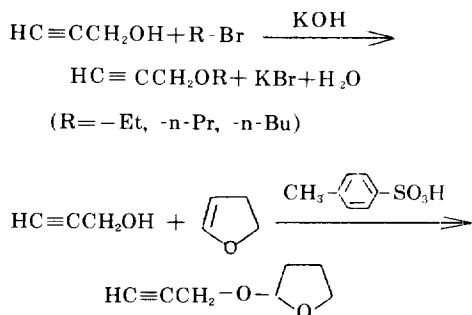
Instruments and Measurements

¹H-NMR spectra were taken on a Varian T-60A spectrophotometer and a Varian FT T-80A NMR spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer, Model 267 grating spectrometer using potassium bromide pellets. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min up to 700°C with Perkin-Elmer TGS-1 Thermobalance. Electrical conductivity of doped polymers was determined by 4-point probe DC method using hp 3434A digital multimeter (Hewlett Packard). X-ray diffraction analyses were performed on JEOL X-ray diffractometer with Cu-K α radiation at a scan speed of 4°/min. Inherent viscosity measurements were carried out at a concentration of 0.5g/dl of the polymers in DMSO at 30°C.

Preparation of Propargyl Ethers

The preparation of monomers, propargyl ethers, were performed as following reaction scheme 1.





Scheme 1. Preparation of Propargyl Ethers

Preparation of Methyl Propargyl Ether (MPE)

To a mixture of 1 mole of propargyl alcohol and 15ml of water was added with cooling in ice water, a solution of 59g of sodium hydroxide in 100ml of water. Subsequently, 74g of dimethyl sulfate were added at such a rate (in about 2 hours) that the temperature was maintained between 50~55°C.

After the addition the mixture was heated under reflux during 2 hours. The reflux condenser was then replaced by a 40cm vigreux column, which was connected to a descending condenser and a receiver, cooled at 0°C.

The products was distilled off as quickly as possible, stirring being continued. The distillation was stopped when the thermometer in the top of the column indicated 95°C.

The contents of the receiver were washed 2 times with a saturated NH₄Cl solution in order to remove some methanol, and were dried over MgSO₄. Pure MPE was obtained in a yield of 82.4% bp, 61°C / 760mmHg (lit.¹⁷ 61°C / 760mmHg) ; ¹H-NMR (δ, ppm) : 2.25(1H), 2.9(3H), 3.6(2H); IR (NaCl disk, cm⁻¹), 3260(≡C-H stretching band), 2105(C≡C stretching band).

Preparation of Ethyl Propargyl Ether (EPE)

A mixture of 0.4mole of propargyl alcohol and 0.3 mole of ethyl bromide was warmed to about 40°C in a three necked flask which equipped with an addition funnel for solid, a stirrer and a reflux condenser. Machine-powdered KOH (0.5mole) was added with vigorous stirring at such a rate that the ethyl bromide gently refluxed.

After the addition which took about 30min, the mixture was heated during 1 hour under reflux.

It was then cooled in an ice-water bath and 150ml of ice water and 100ml of ether were added. The organic layer was separated and the aqueous layer was extracted twice with ether.

The extracts were washed with water and dried over MgSO₄. The greater part of ether was distilled off at normal pressure through a 40cm vigreux column. The residue was distilled at normal pressure after drying with calcium hydride. EPE was obtained in a yield 86% : bp. 75°C / 760mmHg ; ¹H-NMR (δ, ppm), 0.9~1.2(3H), 2.4(1H), 3.2~3.5(2H), 3.9(2H) ; IR (NaCl disk, cm⁻¹), 3315 (≡C-H stretching band), 2860~3000 (C-H (aliphatic) stretching band), 2127(C≡C stretching band).

Preparation of n-Propyl Propargyl Ether (PPE)

In the three necked flask which equipped with an addition funnel for solid, a stirrer, and a thermometer, 0.3mole of propargyl alcohol and 0.2mole of n-propyl bromide was added.

Then machined-powdered KOH (0.4mole) was added in 30 min to the vigorously stirred mixture. The reaction temperature rose gradually but was kept below 70°C. Stirring and warming at 70°C were continued for an additional hour after the exothermic reaction had subsided. The mixture was then cooled and 500ml of ice-water were added. The layers were separated and the aqueous layer extracted one time with a very small amount of ether. Extract and main portion were combined, washed with water and dried over MgSO₄. PPE was obtained in a yield 83.6%, bp, 96°C / 760mmHg ; ¹H-NMR (δ, ppm), 0.65~1(3H), 1.2~2(2H), 2.5(1H), 3.2~3.55(2H), 4.05(2H) ; IR (NaCl disk, cm⁻¹), 3300(≡C-H stretching band), 2860~3000 (C-H (aliphatic) stretching band), 2124 (C≡C stretching band).

Preparation of n-Butyl Propargyl Ether (BPE)

In the three-neck flask were placed 0.4mole of propargyl alcohol and 0.3mole of n-butyl bromide. Powdered KOH (0.5mole) was added over a period of 30min to the vigorously stirred mixture. The temperature rose gradually but was kept

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100°C by occasional cooling. Stirring and warming at 95~98°C were continued for an additional hour after the exothermic reaction had subsided. The mixture was then cooled to 30°C and 500ml of icewater were added. The layers were separated and the aqueous layer was extracted one time with a very small amount ether.

Extract were washed with water and dried over MgSO₄. Ether was removed by rotary evaporator. The residue was distilled in vacuo. BPE was obtained in a yield 81.8% ; bp. 50-51°C / 50mmHg (lit.¹⁸ 35.5~7°C / 23mmHg) : ¹H-NMR (δ ppm) : 0.7~1.1(3H), 1.15~2(4H)2.45(1H), 3.33~3.6 (2 H), 4.1(H) : IR (NaCl disk, cm⁻¹), 3310(≡C-H stretching band), 2860-3000 (C-H (aliphatic) stretching band), 2125(C≡C stretching band).

Preparation of 2-Tetrahydrofuryl Propargyl Ether (TPE)

In the flask were placed 1 mole of freshly distilled dihydrofuran and were added 70mg of powdered *p*-toluenesulfonic acid. Immediately thereafter 0.05mole of the propargyl alcohol was added and the cooling bath was temporarily removed.

In most case a rapid rise in temperature to about 10°C within 2 min was observed. The mixture was then again cooled and the remainder of the 0.5mole of propargyl alcohol was added over a period of 15-20 min, while the internal temperature was maintained between 0°C and 10°C.

After the addition the cooling bath was removed and the temperature was allowed to rise : it should, however, be kept below 20°C, stirring was continued for an additional hour at room temperature, after about 50mg of the acid catalyst had been added. The solution was then cooled to 5~10°C and 5ml of a saturated K₂CO₃ solution were added with vigorous stirring After 5min a sufficient amount of powdered K₂CO₃ was added likewise with stirring in order to remove the water.

The solution was sucked through a sintered-glass funnel and the salt was rinsed well with ether. A vigorous stream of gaseous ammonia was blown for 2~3 sec into the solution after ether and excess of dihydrofuran were distilled off at normal pressure or were removed in vacuo.

TPE was obtained in a yield 91.3% ; bp. 67°C / 30mmHg) : ¹H-NMR(δ, ppm), 1.5~2.2(4H), 2.5 (1H), 3.4~3.9(2H), 4.05(2H), 5.1(1H) ; IR(NaCl disk, cm⁻¹), 3290 (≡C-H stretching band), 2870 ~ 3010 (C-H(aliphatic) stretching band), 2121 (C≡C stretching band).

Polymerization Procedures

All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere because of the active species are sensitive to moisture or oxygen. Catalyst system preparation and all polymerizations were carried out as the same procedures described elsewhere.¹² The polymer yield was calculated by gravimetry.

Measurement of Electrical Conductivity

The polymer powder was pressed under 1500 psi pressure into compaction pellets. The electrical conductivity of the sample was determined using a standard four-point probe measurement.¹⁹⁻²⁰

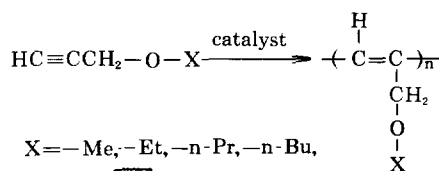
Doping

The iodine doping (gas-phase) was done by exposing the polymer pellet to the vapors of iodine in a vacuum desiccator (initial vacuum : 10mmHg) at 20°C. The dopant concentration was estimated from weight uptake method.²¹

RESULTS AND DISCUSSION

Polymerization

Propargyl ethers were polymerized by the various transition metal catalyst as following polymerization Scheme 2.



X = -Me, -Et, -n-Pr, -n-Bu,



Catalyst : PdCl₂, WCl₆, MoCl₅,

WCl₆-cocatalyst,

MoCl₅-cocatalyst, etc.

Scheme 2. Polymerization of Propargyl Ethers

Table 1 shows the results for the polymerization of MPE by various transition metal catalysts. As compared with those of other propargyl derivatives such as propargyl bromide and propargyl chloride, the polymer yields are generally low. When WCl_6 alone or WCl_6-Me_4Sn were used as catalyst system, the polymer yield was only 2%. However, the polymer yield was increased to 17% when $EtAlCl_2$ is used as cocatalyst in the polymerization by WCl_6 . The cocatalytic activity order of organoaluminum compounds in the polymerization of MPE by WCl_6 was as follows : $EtAlCl_2 > Et_2AlCl > Et_3Al$. Similar results were also observed in the polymerization of 2-ethynylpyridine.²² The polymerization of MPE by $WCl_6-EtAlCl_2$ (-10, -78°C), $MoCl_5$ or $MoCl_5-Me_4Sn$ gives nearly no polymer. However, the polymer yield was 24% when $EtAlCl_2$ is used as cocatalyst in the polymerization by $MoCl_5$. $TiCl_4$ -based catalysts, which are effective for the polymerization of propargyl bromide and propargyl chloride,¹² give no polymer.

Table 2 shows the results for the polymerization

Table 1. Polymerization of Methyl Propargyl Ether by Various Transition Metal Catalysts^a

Exp. No.	Catalyst System ^b (mole ratio)	Temp. (°C)	Solvent	P.Y. ^c (%)
1	WCl_6	40	Chlorobenzene	2
2	$WCl_6-Me_4Sn(1:2)$	40	Chlorobenzene	2
3	$WCl_6-Et_3Al(1:4)$	40	Chlorobenzene	5
4	$WCl_6-Et_2AlCl(1:4)$	40	Chlorobenzene	14
5	$WCl_6-EtAlCl_2(1:4)$	40	Chlorobenzene	17
6	$WCl_6-EtAlCl_2(1:4)$	-10	Chlorobenzene	3
7	$WCl_6-EtAlCl_2(1:4)$	-78	Toluene	0
8	$MoCl_5$	40	Chlorobenzene	0
9	$WCl_6-Me_4Sn(1:2)$	40	Chlorobenzene	0
10	$MoCl_5-EtAlCl_2(1:4)$	40	Chlorobenzene	24
11	$TiCl_4$	40	Benzene	0
12	$TiCl_4-EtAlCl_2(1:4)$	40	Benzene	0

^a Polymerization was carried out for 24hrs. Monomer to catalyst mole ratio(M/C) and initial monomer concentration([M]₀) were 50 and 1.5, respectively.


^b Mixture of catalyst and cocatalyst was aged at 30°C for 15min. before use.

^c Methanol-insoluble polymer (mostly insoluble in any organic solvents).

of propargyl ether by $WCl_6-EtAlCl_2$ catalyst system according to substituent bulkiness. The polymer yield was decreased as the bulkiness of substituent was increased. The polymer yield was only 4% when substituent is 2-tetrahydrofuran, the highest bulky group.

Table 3 shows the results for the polymerization of propargyl ethers by $PdCl_2$ in DMF. It was generally known that $PdCl_2$ is less effective than W- and Mo-based catalysts for the polymerization of acetylene derivatives. However the polymer yields in the polymerization of propargyl ethers


Table 2. Polymerization of Propargyl Ether Derivatives by $WCl_6-EtAlCl_2(1:4)$ Catalyst System^a

Exp. No.	$HC\equiv C-CH_2-O-X$ X	P. Y. ^b (%)
1	-Me	17
2	-Et	13
3	-n-Pr	12
4	-n-Bu	7
5		4

^a Polymerization was carried out in chlorobenzene for 24hrs at 40°C. Monomer to catalyst mole ratio(M/C) and initial monomer concentration, [M]₀ were 50 and 1.5, respectively. Mixture of WCl_6 and $EtAlCl_2$ was aged for 15 min. before use.

^b Methanol-insoluble polymer (mostly insoluble in any organic solvents).

Table 3. Polymerization of Propargyl Ether Derivatives by $PdCl_2$ in DMF^a

Exp. No.	$HC\equiv C-CH_2-O-X$ X	P.Y. ^b (%)
1	-Me	60
2	-Et	49
3	-n-Pr	36
4	-n-Bu	32
5		30

^a Polymerization was carried out at 90°C for 24hrs. Monomer to catalyst mole ratio(M/C) and initial monomer concentration, [M]₀ were 30 and 0.25, respectively.

^b Methanol-insoluble polymer

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by PdCl_2 are generally higher than that by other transition metal-based catalysts such as WCl_6 , $\text{WCl}_6\text{-EtAlCl}_2$, $\text{MoCl}_5\text{-EtAlCl}_2$, etc.

The polymer yield was also decreased as the bulkiness of substituent is increased with same as $\text{WCl}_6\text{-EtAlCl}_2$ catalyst system.

Identification of Polymer Structure

Figure 1 shows the IR spectra of poly(methyl propargyl ether) (PMPE) obtained by various catalyst systems: A (obtained by PdCl_2), B (obtained by $\text{WCl}_6\text{-EtAlCl}_2$), and C (obtained by $\text{MoCl}_5\text{-EtAlCl}_2$). Spectra A, B, and C give an aliphatic C-H stretching band at $2800\sim 3000\text{cm}^{-1}$. And they also show absorption bands at $1550\sim 1750\text{cm}^{-1}$ owing to the conjugated double bond stretching and the carbonyl $\text{C}=\text{O}$ stretching caused by spontaneous air oxidation. Absorption band at about 1100cm^{-1} are due to the C-O-C stretching.

Figure 2 and Figure 3 show the IR spectra of poly(ethyl propargyl ether) (PEPE) and poly(*n*-propyl propargyl ether) (PPPE). These show a similar spectral properties with those of PMPE.

Figure 4 shows the IR spectra of poly(*n*-butyl propargyl ether) (PBPE) and poly(2-tetrahydrofuryl propargyl ether) (PTPE).

These give an aliphatic C-H stretching band at $2800\sim 3000\text{cm}^{-1}$. And they also show absorption bands at $1550\sim 1750\text{cm}^{-1}$ owing to the conjugated double bond

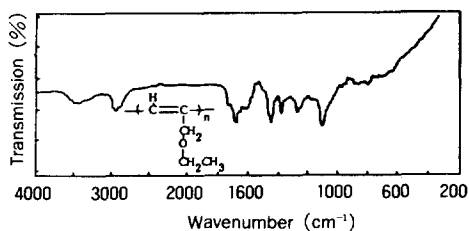


Fig. 2. IR spectra of poly(ethyl propargyl ether) prepared by $\text{WCl}_6\text{-EtAlCl}_2$.

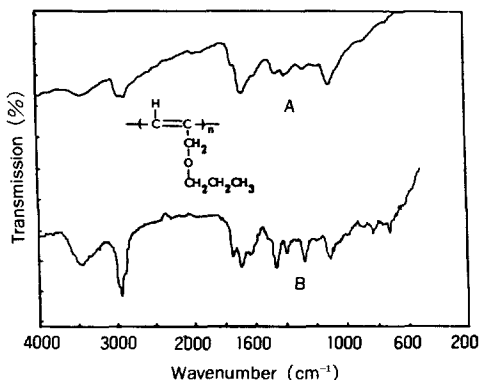


Fig. 3. IR spectra of poly(*n*-propyl propargyl ether) s: A (by PdCl_2) and B (by $\text{WCl}_6\text{-EtAlCl}_2$).

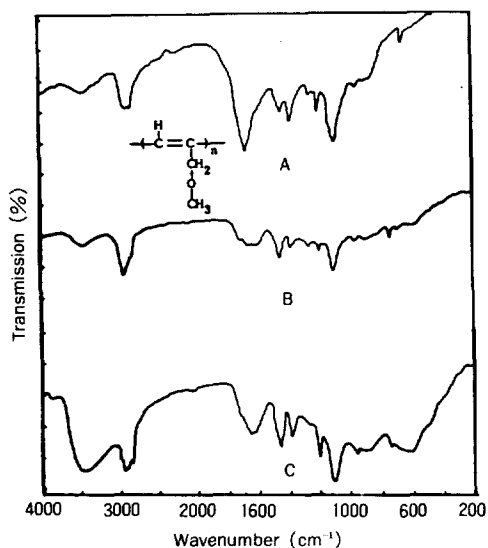


Fig. 1. IR spectra of poly(methyl propargyl ether) s: A (by PdCl_2), B (by $\text{WCl}_6\text{-EtAlCl}_2$), C (by $\text{MoCl}_5\text{-EtAlCl}_2$).

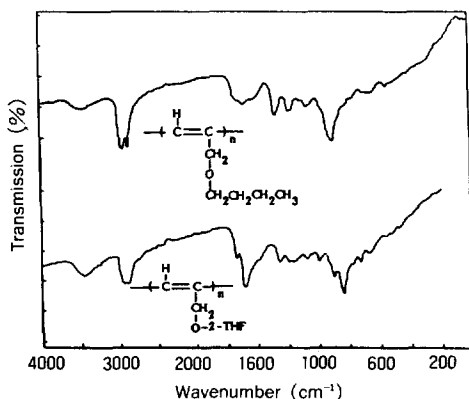


Fig. 4. IR spectra of poly(*n*-butyl propargyl ether) (by $\text{MoCl}_5\text{-EtAlCl}_2$) and poly(2-tetrahydrofuryl propargyl ether) (prepared by MoCl_5).

stretching and the carbonyl C=O stretching frequency. The absorption at about 1100cm^{-1} is due to the C-O-C stretching. The C-O-C stretching of tetrahydrofuryl substituent is shown at 1050cm^{-1} . The $^1\text{H-NMR}$ spectrum of PTPE prepared by PdCl_2 showed a broad and featureless peaks at vinyl proton region (5~9ppm) and aliphatic proton region (0.5~5ppm).

Physical Properties

The color of polymers from propargyl ethers by W- and Mo-based catalysts was yellow or brown, whereas that by PdCl_2 was black.

Table 4 shows the solubility behaviors of the polymers from propargyl ethers. The polymers prepared by PdCl_2 show a relatively good solubility. These samples are soluble in DMF and DMSO, but insoluble in methanol, ethyl ether, chlorobenzene, etc. However, the polymers prepared by W- and Mo-based catalysts were not soluble in any organic solvents including conc. sulfuric acid. This insolubility may be due to the cross-linking by active methylene hydrogen adjacent oxygen atom during the polymerization. Table 5 shows the inherent viscosities of soluble polymers prepared by PdCl_2 . The inherent viscosity was increased from 0.17 to 0.21 as the size of substituent increases.

Figure 5 shows the TGA thermogram of PMPE prepared with PdCl_2 .

It retains 90% of its original weight at 277°C ,

80% at 400°C , and 60% at 700°C .

The TGA thermograms of other polymers (PEPE, PPPE, PBPE, PTFE) from propargyl

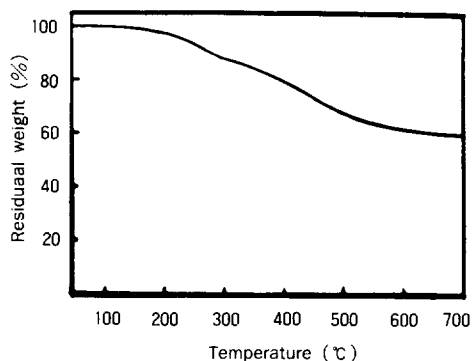


Fig. 5. TGA thermograms of poly(methylpropargyl ether) (PMPE).

Table 5. Inherent Viscosities of the Polymers from Propargyl Ethers ^a

Exp. No	Polymers	η_{inh}^b
1	PMPE	0.17
2	PEPE	0.18
3	PPPE	0.18
4	PBPE	0.20
5	PTPE	0.21

^a Prepared by PbCl_2 at DMF.

^b Measured at a concentration of 0.5g/dl in DMSO at 30°C .

Table 4. Solubility Behavior of Polymers from Propargyl Ether Derivatives ^a

Polymer	Catalyst	Solvent							
		Chlorobenzene	Toluene	Chloroform	CCl_4	DMF	DMSO	MeOH	Ethyl ether
PMPE	PdCl_2	-	-	-	-	+	+	-	-
PEPE	PdCl_2	-	-	±	±	+	+	-	-
PPPE	PdCl_2	-	-	±	±	+	+	-	-
PBPE	PdCl_2	±	±	±	±	+	+	-	-
PTPE	PdCl_2	-	-	±	±	+	+	-	-
PMPE	$\text{WCl}_6\text{-EtAlCl}_2$	-	-	-	-	-	-	-	-
PEPE	$\text{WCl}_6\text{-EtAlCl}_2$	-	-	-	-	-	-	-	-
PPPE	$\text{WCl}_6\text{-EtAlCl}_2$	-	-	-	-	-	-	-	-
PBPE	$\text{WCl}_6\text{-EtAlCl}_2$	-	-	-	-	-	-	-	-
PTPE	$\text{WCl}_6\text{-EtAlCl}_2$	-	-	-	-	-	-	-	-

^a Solubility test was performed for powdery samples in excess solvent (+ = soluble, ± = partially soluble, - = insoluble).

ethers were similar with that of PMPE. As compared with TGA thermograms of other polymers from propargyl bromide, propargyl chloride, and propargyl alcohol, the polymers from propargyl ethers was found to be more thermally stable.

X-ray diffractograms of polymers from propargyl ethers all showed a featureless broad peak. The ratios of half-height width to diffraction angle ($\Delta 2\theta / 2\theta$) are all larger than 0.20. The value for amorphous polyethylene is similar to these values, while those of crystalline polyethylene and cis-polyacetylene are much smaller. This must be due to the presence of bulky substituents and/or the non-selective geometric structure of the main chain. In conclusion, the polymers from propargyl ethers are mainly amorphous. The electrical conductivities of undoped polymers were in the range of $1.5 \times 10^{-12} \sim 3.7 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$ (1.5×10^{-12} for PMPE, 2.7×10^{-12} for PEPE, 3.1×10^{-12} for PPPE, 7.0×10^{-12} for PBPE, $3.7 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$ for PTEE).

Table 6 shows the electrical conductivity of I₂-doped poly(alkyl propargyl ether)s. It was found that the smaller the substituent, the higher the electrical conductivity.

Table 6. Electrical Conductivity of I₂-doped Poly(alkyl propargyl ethers)^a

Polymer	Composition of doped polymer ^b	Electrical Conductivity ($\Omega^{-1} \text{cm}^{-1}$) ^c
PMPE	(C ₄ H ₆ O) ₁ (I ₂) _{0.18}	1.7×10^{-3}
PEPE	(C ₅ H ₈ O) ₁ (I ₂) _{0.30}	3.2×10^{-4}
PPPE	(C ₆ H ₁₀ O) ₁ (I ₂) _{0.32}	6.6×10^{-5}
PBPE	(C ₇ H ₁₂ O) ₁ (I ₂) _{0.35}	1.54×10^{-5}
PTEE	(C ₇ H ₁₀ O ₂) ₁ (I ₂) _{0.27}	1.32×10^{-5}
PTMA ^d	(C ₃ HF ₃) ₁ (I ₂) _{0.98}	9.5×10^{-5}

^a: Pressed pellets of these polymers were doped by exposing to the vapor of iodine at 20°C for 24 hrs.

^b: Extent of doping was obtained by weight uptake method.

^c: Measured with 4-point probe method.

^d: Poly(trifluoromethylacetylene)²³.

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