Polymerization of N-(Propargyloxy)phthalimide by Transition Metal Catalysts

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This article deals with the synthesis and characterization of poly [N-(propargyloxy)phthalimide][poly (POPI)]. The polymerization of POPI was carried out by various transition metal catalysts. MoCl₅-based catalysts were found to be more effective than WCl₆-based catalysts. However, the polymer yield was relatively low (maximum 35%). The polymerization of POPI by PdCl₂ gave poly (POPI) in fair yields in DMF and pyridine. The resulting poly (POPI)s were mostly insoluble in organic solvents. The infrared spectrum of poly (POPI) showed no peak at 2135 cm⁻¹ due to acetylenic C≡C stretching frequency. Instead, the carbon-carbon double bond stretching frequency was observed at 1600-1650 cm⁻¹. The TGA thermogram showed that the present poly (POPI) is thermally stable up to 160℃.

Introduction

During the past three decades, extensive studies on the polymerization of acetylene and its derivatives have been made.[1] To date, various propargyl derivatives were polymerized and characterized. The following propargyl derivatives were polymerized: $HC\equiv CCH_2X(X=$ -Br, -Cl, -OH, -OMe, -O-*n*-Bu, -OPh, -OPh-*p*-NO₂, -OTHF, -NEt₂, OAc, etc.).[2] To our knowledge, there have been no reports for the polymerization of N-(propargyloxy)phthalimide (POPI). The polymerization of propargyl derivatives was attemped using catalyst systems such as PdCl₂,[3] γ-ray,[4] NiI₂(Ph₃P)₂,[5] W(CO)₆-CCl₄-hv,[6] MoCl₅,[2c] MoCl₅-polymer,[7] etc. In recent years, we reported[8] that WCl₆- and MoCl₅-based catalyst systems were very effective for the polymerization of some propargyl derivatives such as propargyl bromide, -chloride, and -alcohol. The present article deals with the polymerization of POPI by various transition metal catalysts and the characterization of the resulting poly (POPI).

Experimental

POPI (Aldrich Chemicals., 97%) was purified by recrystallizing twice from toluene. Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemicals, resublimed, 99+%) and palladium(II) chloride (Aldrich Chemicals, 99.999%) were used without further purification. Tetraphenyltin (Aldrich Chemical, 97%) was purified by recrystallizing twice from carbon tetrachloride. Tetra-*n*-butyltin (Aldrich Chemicals, tech., 93%) was used after fractional distillation. Organoaluminum compounds (Aldrich Chemicals, 25 wt% solution in toluene) were used as received. All polymerization solvents were EP grade and dried with appropriate drying agents (CaH₂ for chlorobenzene, toluene, DMSO and Pyridine; MgSO₄ for DMF and nitrobenzene) and then fractionally distilled. A typical polymerization procedure is as follows; Into a 20 ml ampule including solvent and POPI, sealed with rubber septum, the premixed catalyst solution (catalyst + cocatalyst) was added after shaking for 15 min at 30℃ to activate the transition metal chloride. After the ampule was stood for 24 hr at 90℃,

the polymerization was stopped by adding a small amount of methanol. Then 10 ml of chloroform was added to the ampule. This solution was poured into excess methanol, filtered from the solution, and then dried under vacuum at 40℃ for 24 hr to give a polymer. The polymer yield was calculated by gravimetry.

Infrared spectra were recorded on a Bio-Rad Digilab FTS-60 spectrometer using KBr pellet. Elemental analyses were performed with Carlo Erba EA 1108 Elemental Analyzer. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10℃/min up to 400℃ with Dupont 951 Thermogravimetric Analyzer. Thermal transitions were measured by a Dupont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10℃/min up to 300℃.

Results and Discussion

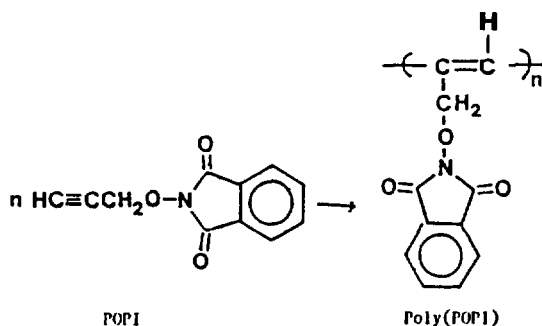The polymerization of POPI was carried out by various transition metal catalysts.

Table 1 shows the results for the polymerization of POPI by WCl₆-and MoCl₅-based catalysts. In general, WCl₆-based catalysts gave only low yield of polymers in comparison with MoCl₅-based catalysts. These results were consistent with those of some propargyl derivatives containing heteroatoms such as dipropargyl sulfur[9] and propargyl ether.[2d,2e]

Ph₄Sn[10] and EtAlCl₂,[8b,11] typical cocatalysts for the polymerization of acetylene derivatives by WCl₆ or MoCl₅, sho-

Table 1. Polymerization of POPI by Various Transition Metal Catalysts[a]

Exp. no.	Catalyst system[b] (mole ratio)	M/C[c] (mole ratio)	[M]o[d]	Polymer yield[e] (%)
1	WCl₆	30	0.5	0
2	WCl₆	30	0.5	0
3	WCl₆-EtAlCl₂(1 : 2)	50	1	4
4	WCl₆-Ph₄Sn(1 : 1)	50	1	0
5	MoCl₅	50	1	15
6	MoCl₅-Ph₄Sn(1 : 1)	50	1	19
7	MoCl₅-Et₃Al(1 : 2)	50	1	20
8	MoCl₅-Et₂AlCl(1 : 2)	50	1	27
9	MoCl₅-EtAlCl₂(1 : 2)	50	1	35

[a] Polymerization was carried out at 90℃ for 24 hr in chlorobenzene, [b] Mixture of catalyst and cocatalyst in chlorobenzene was aged at 30℃ for 15 min before use as catalyst, [c] Monomer to catalyst mole ratio, [d] Initial monomer concentration, [e] Methanolinsoluble polymer.

Table 2. Polymerization of POPI by PdCl₂[a]

Exp. no.	M/C[b] (mole ratio)	[M]o[d]	Solvent	Polymer yield[e] (%)
1	30	0.5	DMF	50
2	50	0.5	DMF	43
3	50	0.25	DMF	21
4	50	0.5	DMSO	29
5	50	0.5	Pyridine	42
6	50	0.5	Toluene	15
7	50	0.5	Nitrobenzene	17
8	50	0.5	Ethanol	11

[a] Polymerization was carried out at 90℃ for 24 hr, [b] Monomer to catalyst mole ratio, [c] Initial monomer concentration, [d] Methanolinsoluble polymer.

wed no enhanced cocatalytic activity. However, MoCl₅-based catalysts were found to be effective catalyst system. MoCl₅ itself gave a some moderate yield of polymer (15%). Organotin and organoaluminum compounds showed a cocatalytic activity. The polymer yield according to organoaluminum compound was as follows.

$$EtAlCl_2 > Et_2AlCl > Et_3Al$$

The higher catalytic activity of MoCl₅-based catalysts in comparison with those of WCl₆-based catalysts was consistent with that of acetylene derivatives containing oxygen (hydroxy,[8b] carboxylic acid[12]), bromine,[13] chlorine,[14] ester,[15] and fluoroalkyl.[16] These observations indicates that the polar functional group and halogen atom participates in the activation of MoCl₅, although the mechanism is not fully understood.[8b,12,14]

The relatively low polymer yield (maximum 35%) is due to the inhibition of polymerization by the poor solubility of the resulting polymers formed.

Table 2 shows the results for the polymerization of POPI by PdCl₂. Poly (POPI) was obtained in fair yields in DMF and pyridine. The polymer yields according to solvents were
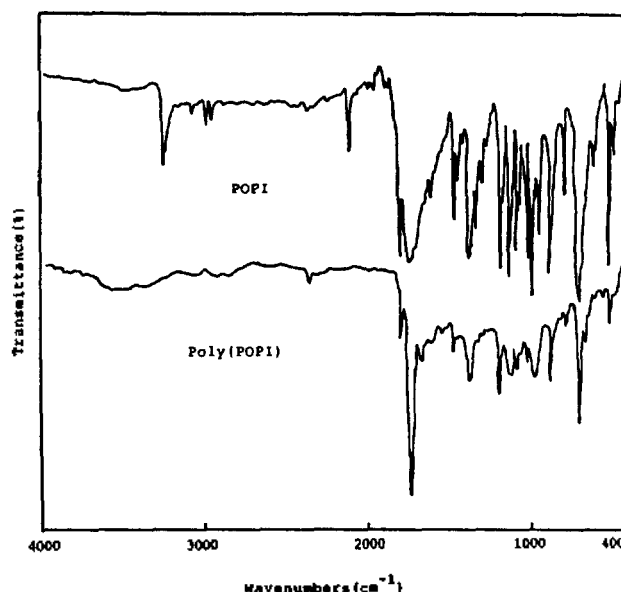
Figure 1. IR spectra of POPI and poly (POPI) in KBr pellet.

in the range of 11% and 50%. The polymerization at somewhat low temperatures was also carried out. However, the polymerization did not proceed at 30℃ and 60℃. This indicates that the present catalyst systems for POPI are activated at relatively high temperature (90℃). The resulting poly (POPI) prepared by PdCl₂ was dark black. On the other hand, the poly (POPI) prepared by W-and Mo-based catalysts was light brown and brown color.

The poly (POPI)s were insoluble in any organic solvents regardless of the catalysts used. The reason of insolubility is deduced to the crosslinking by active allyl protons of the resulting poly (POPI), during polymerization, by catalyst moiety. The similiar polymers obtained from some propargyl derivatives such as propargyl alcohol,[8] methyl propargyl ether[17] dipropargyl ether,[18] etc have been known to be insoluble in any organic solvents.

Figure 1 exhibits the infrared spectra of POPI and poly (POPI). The infrared spectrum of poly (POPI) showed no peaks at 2135 cm⁻¹ and 3300 cm⁻¹ due to the acetylenic C≡C and ≡C-H stretching frequencies, respectively. Instead, the carbon-carbon double bond (in the polymer backbone) stretching frequency was observed at 1600-1650 cm⁻¹, along with the aromatic double bond frequency.

The elemental analysis data for poly (POPI) agreed well with the theoretical value: Calcd for $(C_{11}H_7NO_3)_n$: C, 65.67%; H, 3.51; N, 6.96%; O, 23.86% Found: C, 65.26%; H, 3.50%; N, 6.95%; O, 24.29%.

The TGA thermogram (Figure 2) of poly (POPI) showed that poly (POPI) retained 98% of its original weight at 140℃, 60% at 257℃, and 34% at 400℃. The DSC thermogram of poly (POPI) did not show a characteristic peak of glass transition temperature. The broad endothermic peak at about 120℃ is deduced to be due to the increased side chain (methyleneoxyphthalimide) mobility.

In conclusion, this paper dealed with the systhesis and characterization of new conjugated polymer, poly (POPI). MoCl₅-based catalysts were more effective than those of WCl₆ -based catalysts. The polymerization of POPI by PdCl₂ gave
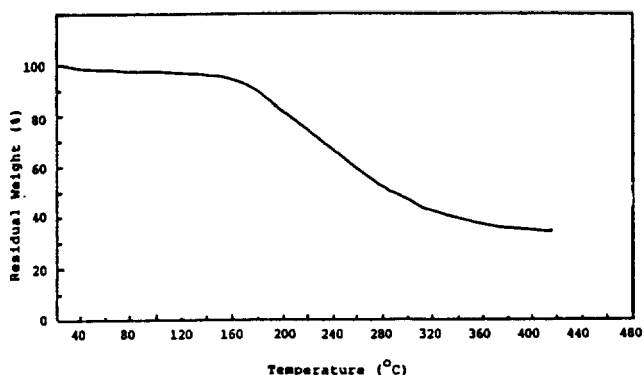
Iridium(III) Insertion Into an Aromatic C-H Bond

Bull. Korean Chem. Soc., Vol. 13, No. 6, 1992 627

Figure 2. TGA thermogram of poly (POPI).

poly (POPI) in fair yields in DMF and Pyridine solvents. The relatively low polymer yields in the polymerization are thought to be due to the inhibition of polymerization by the poor solubility of the resulting polymers formed. The insolubility of the poly (POPI) were deduced to be due to some cross-linking of active allyl protons of poly (POPI), during polymerization, by catalyst moiety.

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Iridium(III) Insertion into an Aromatic C-H Bond and Si-H Bond

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The dihydrido iridium(III) complex [Ir(PPh$_3$)$_2$H$_2$(ac)$_2$]BF$_4$ (ac=acetone) reacts with 2-phenylpyridine and 7,8-benzoquinoline to yield the C-H activated complexes [Ir(PPh$_3$)$_2$H(ac)(L)]BF$_4$ (L=phenylpyridine; 7,8-benzoquinoline). The dihydrido iridium(III) complex [IR(PPh$_3$)$_2$H$_2$(ac)$_2$]BF$_4$ also reacts with triaklysilane *via* an oxidative addition reaction to yield the trihydrido iridium complexes [IR(PPh$_3$)$_2$H$_3$SiR$_3$]BF$_4$ (R=Et and Ph). The structural configuration was studied by conventional spectroscopy.

Introduction

The activation of carbon-hydrogen bonds by homogeneous transition metal complexes is a topic that has received a great deal of attention[1]. Interest in reactions of alkanes and arenes with metal complexes has led to the discovery of