

MoCl₅에 의한 페닐아세틸렌의 중합에서 2-프로핀-1-올의 영향

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The Effect of 2-Propyn-1-ol on the Polymerization of Phenylacetylene by MoCl₅

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요 약 : MoCl₅-HC≡CCH₂OH 촉매 시스템을 사용한 페닐아세틸렌의 중합을 여러가지 반응조건하에서 시도하였다. MoCl₅에 대한 HC≡CCH₂OH의 몰비, 활성화 온도 및 중합온도의 영향을 연구하였다. MoCl₅에 대한 HC≡CCH₂OH 몰비가 5일 경우 가장 좋은 결과(중합수율=58%, $\overline{M}_w=7,200$)를 얻었다. HC≡CCH₂OH에 대한 MoCl₅의 활성화 온도에 관계없이 넓은 온도범위에서 중합이 잘 진행되어 비교적 높은 수율을 보였다. HC≡CCH₂OH가 MoCl₅의 염소원소를 치환시켜 중합시에 활성 촉매종으로 작용하는 몰리브덴의 알콕사이드를 만드는 것으로 판단되었다. MoCl₅-HC≡CCH₂OH 촉매 시스템에 의해 합성된 폴리페닐아세틸렌의 구조를 NMR(¹H-, ¹³C-), IR, UV-visible 등과 같은 분석장비로 규명하였으며 합성한 폴리(페닐아세틸렌)의 열특성에 관해서도 연구하였다.

Abstract : The polymerization of phenylacetylene using MoCl₅-HC≡CCH₂OH catalyst system was carried out at various reaction conditions. The effects of the mole ratio of HC≡CCH₂OH to MoCl₅, the activation and polymerization temperatures, etc. were studied. The best result (polymer yield=58%, $\overline{M}_w=7200$) was obtained when the mole ratio of HC≡CCH₂OH to MoCl₅ was 5. In a wide temperature range (20~90°C), the polymerizations were well proceeded to give a relatively good yield, regardless of the activation temperature of MoCl₅ by HC≡CCH₂OH. It was concluded that the hydroxyl group of HC≡CCH₂OH substituted the chlorine atom of MoCl₅ to make an alkoxide derivative of molybdenum, which plays a role as an active catalytic species. The polymer structure of poly(phenylacetylene) prepared by MoCl₅-HC≡CCH₂OH catalyst system was also characterized by various instrumental methods such as NMR(¹H-, ¹³C-), IR, UV-visible spectroscopies. The thermal properties were also studied.

INTRODUCTION

The Mo- and W- based catalysts have been used as the catalyst for the olefin metathesis reaction and the metathesis polymerization of cyclic olefins.¹⁻³ In 1974, it was found that phenylacetylene was polymerized with WCl_6 and MoCl_5 .⁴ In this case, the MoCl_5 -based catalysts were found to be less effective than WCl_6 -based catalysts and to give a low yield of polymer (conversion : <20%).

Mo-based catalysts are of three main types⁵ : support oxides, generated in various ways ; MoCl_5 , activated with a suitable cocatalyst ; Mo complexes, also activated by a cocatalyst. It was known that the cocatalyst used in most homogeneous systems plays essential part in the whole process of metathesis. Besides its first action as alkylating and reducing agent for the transition metal compound, the cocatalyst may interact with active centers during propagation and may act upon metal ligands, labilizing and then creating vacant sites for coordination. In general, the metathesis cocatalysts have Lewis acid properties. They interact with the transition metal complex or are converted into more active species which are involved in the process. This interaction depends upon the nature of the transition metal and its ligands, the nature of cocatalyst metal, the solvent and the reaction conditions.

The Mo-based catalyst systems used in the olefin metathesis reaction and the polymerization of acetylenes are as follows : $\text{MoCl}_5/\text{Et}_3\text{Al}$ for cyclopentene,⁶ $\text{MoCl}_2(\text{NO})_2(\text{PPh}_3)_2/\text{EtAlCl}_2$ for tetradec-1-ene/4-methylpent-1-ene,⁷ $\text{Mo}(\text{CO})_6/4$ -bromophenol for $\text{BuC}\equiv\text{CPh}$,⁸ $\text{MoCl}_5/\text{NaBH}_4/\text{DMF}$ for C_2H_2 and C_2H_4 ,⁹ $\text{MoO}(\text{OPh})_4/\text{Et}_3\text{Al}/\text{PhOH}$ for non-4-yne,¹⁰ $\text{MoCl}_5/\text{Ph}_4\text{Sn}$ for alk-2-ynes (C_6 - C_{10}),¹¹ etc.

The living polymerizations of some acetylene derivatives such as 1-chloro-2-alkynes¹² and *o*-(trifluoromethyl)phenylacetylene¹³ using $\text{MoOCl}_4/n\text{-Bu}_4\text{Sn}/\text{EtOH}$ catalyst system, were carried out.

In recent years, we found that the MoCl_5 alone is very active catalyst for the polymerization of

$\text{HC}\equiv\text{CCH}_2\text{OH}$ to give a quantitative yield of polymer.¹⁴ There have been some viewpoints that $\text{HC}\equiv\text{CCH}_2\text{OH}$ activates the MoCl_5 .

In our previous communication,¹⁵ we briefly reported on the cocatalytic activity of $\text{HC}\equiv\text{CCH}_2\text{OH}$ for the polymerization of phenylacetylene by MoCl_5 . This paper deals with the full accounts for the polymerization of phenylacetylene by MoCl_5 - $\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system, and the characterization and physical properties of the resulting polymers.

EXPERIMENTAL

Materials. Phenylacetylene (PA, Aldrich Chemicals, 98%, bp 142~144°C) was dried with calcium hydride and fractionally distilled. 2-Propyn-1-ol (Aldrich Chemicals, 99%) was used after simple distillation. Molybdenum pentachloride (Aldrich Chemicals, resublimed, 99+%) and ethylaluminum dichloride (Aldrich Chemicals, 25 wt% solution in toluene) were used as received. Solvents used were all analytical grade materials. They were dried and fractionally distilled.

Instruments and Measurement. NMR (^1H -, ^{13}C -) spectra were recorded on a Bruker AM-200 spectrophotometer using CDCl_3 . Infrared (IR) spectra were taken on a Bio-Rad Digilab FTS-60 spectrometer using KBr pellets. UV-visible spectra were recorded on a Beckman DU-6 Spectrometer in THF. The average molecular weights (\overline{M}_w) of the resulting polymers were measured by means of GPC-150C of Waters using a calibration curves for polystyrene. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min with Dupont 951 Thermogravimetric Analyzer. Thermal transitions were measured with Dupont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/min.

Preparation of Catalyst Systems. Catalyst system preparations were carried out under nitrogen atmosphere because the active species are sensitive to moisture or oxygen. Transition metal chlorides, organometallic compounds, and 2-propyn-1-

ol were dissolved in as 0.05 M, 0.2 M, and 0.4 M chlorobenzene solutions before use.

Polymerization Procedures. Typical examples of the polymerization are described below. The obtained polymers were dissolved in chloroform followed by the precipitation into excess methanol. The precipitated polymers were filtered from the solution and dried to constant weight under vacuum at 40°C for 24 hr. The polymer yield was calculated by gravimetry.

Polymerization of PA by MoCl_5 . A solution of MoCl_5 (1.96 ml 0.05 M chlorobenzene solution, 0.0979 mmol) and chlorobenzene (2.39 ml, $[\text{M}]_0 = 1 \text{ M}$) was prepared. To this solution was added PA (0.5 g, 4.9 mmol) at room temperature and the polymerization was carried out at 60°C for 24 hr. Polymer yield was 34%.

Polymerization of PA by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/5). A catalyst solution was prepared by mixing MoCl_5 (1.96 ml 0.05 M chlorobenzene solution, 0.0979 mmol), $\text{HC}\equiv\text{CCH}_2\text{OH}$ (1.225 ml 0.4 M chlorobenzene solution, 0.490 mmol), and chlorobenzene (1.17 ml, $[\text{M}]_0 = 1 \text{ M}$), and aged at 30°C for 15 min. To this solution was added PA (0.5 g, 4.9 mmol). Polymerization was carried out at 60°C for 24 hr. Polymer yield was 58%.

Polymerization of PA by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}/\text{EtAlCl}_2$ (1/5/2). A catalyst solution was prepared by mixing MoCl_5 (1.225 ml 0.05 M chlorobenzene solution, 0.0979 mmol), $\text{HC}\equiv\text{CCH}_2\text{OH}$ (0.98 ml 0.4 M chlorobenzene solution, 0.392 mmol), EtAlCl_2 (0.98 ml 0.2 M chlorobenzene solution, 0.196 mmol), and chlorobenzene (0.19 ml, $[\text{M}]_0 = 1 \text{ M}$) in this order and aged at 30°C for 15 min. To this solution was added PA (0.5 g, 4.9 mmol). Polymerization was carried at 60°C for 24 hr. Polymer yield was 33%.

RESULTS AND DISCUSSION

The polymerization of PA by transition metal chlorides (MoCl_5 and WCl_6) activated by $\text{HC}\equiv\text{CCH}_2\text{OH}$ was carried out at various reaction conditions.

Table 1 shows the results for the polymerization

of PA by transition metal chloride- $\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst systems. MoCl_5 alone gave 34% yield of polymer. When $\text{HC}\equiv\text{CCH}_2\text{OH}$, a new activator, was used with MoCl_5 in the polymerization of PA, the polymer yield was increased from 34% to 58%. Organoaluminum compounds, which have been used in the metathesis of *cis*-2-pentene by $\text{MoCl}_5/2,6$ -diisopropylphenol and $\text{MoCl}_5/\text{PhCH}_2\text{CHOHCH}_2\text{Ph}$,¹⁶ were used as a third component. Thus in the present study, EtAlCl_2 , which have been found to be a effective cocatalyst for the polymerization of 1-chloro-2-thienylacetylene,¹⁷ 2-ethynylpyridine,¹⁸ and dipropargyl sulfide¹⁹ by WCl_6 and MoCl_5 , was also used. But, the polymer yield was slightly increased in comparison to that of MoCl_5 alone used. $\text{Mo}(\text{OEt})_5$ and $\text{Mo}(\text{OEt})_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst systems were also used for the present polymerization. However these catalyst systems gave no polymers. In WCl_6 -based catalysts, WCl_6 alone gave a good yield of polymer (84%) as reported in 1974 by Masuda et al.²⁰ However, in the WCl_6 -catalyzed polymerization of PA using $\text{HC}\equiv\text{CCH}_2\text{OH}$, $\text{HC}\equiv\text{CCH}_2\text{OH}$ deactivated WCl_6 to give only low

Table 1. Polymerization of Phenylacetylene by Transition Metal Chloride/ $\text{HC}\equiv\text{CCH}_2\text{OH}$ Catalyst System^a

Experiment Number	Catalyst System ^b (mole ratio)	Polymer	
		Yield ^c (%)	\bar{M}_w
1	MoCl_5	34	6850
2	$\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/5)	58	7200
3	$\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}/$ EtAlCl_2 (1/5/2)	41	6840
4	$\text{Mo}(\text{OEt})_5$	0	—
5	$\text{Mo}(\text{OEt})_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/4)	0	—
6	WCl_6	84	10800
7	$\text{WCl}_6/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/4)	8	—
8	$\text{WCl}_6/\text{HC}\equiv\text{CCH}_2\text{OH}/$ EtAlCl_2 (1/4/2)	2	—
9	$\text{WCl}_6/\text{EtAlCl}_2$ (1/2)	71	10100

^a Polymerization was carried at 60°C for 24 hr in chlorobenzene. Initial monomer concentration ($[\text{M}]_0$) and monomer to catalyst mole ratio (M/C) were 1 M and 50, respectively.

^b Mixture of MoCl_5 and cocatalyst was aged at 30°C for 15 min before use.

^c Methanol-insoluble polymer.

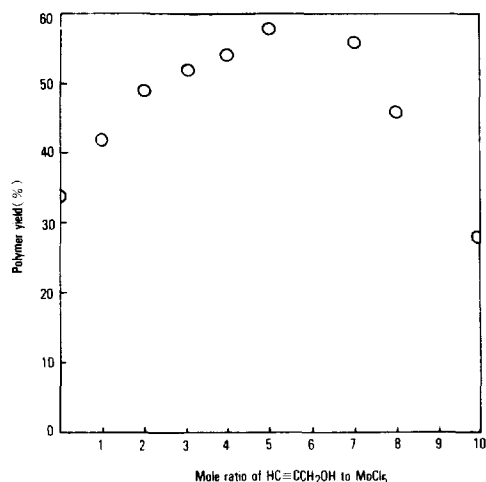


Fig. 1. The effect of HC≡CCH₂OH to MoCl₅ mole ratio on the polymerization of phenylacetylene.

yield of polymer.

Fig. 1 shows the effect of HC≡CCH₂OH to MoCl₅ mole ratio on the polymerization of PA. The polymer yields were gradually increased as the mole ratio of HC≡CCH₂OH to MoCl₅ was increased. And then above [MoCl₅]/[HC≡CCH₂OH]=5, the polymer yield was somewhat decreased. The best results (polymer yield=58%) was obtained when the mole ratio of HC≡CCH₂OH to MoCl₅ was 5. The role of HC≡CCH₂OH in the activation of MoCl₅ was deduced to be due to the substitution of the chlorine atom of molybdenum by HC≡CCH₂OH to some extents although the exact molecular structure of molybdenum complex activated by HC≡CCH₂OH was not elucidated. In the preparation of catalyst solution, the initial purple color of MoCl₅ solution was disappeared as soon as the HC≡CCH₂OH solution was added.

Table 2 shows the temperature effect for the polymerization of PA by MoCl₅/HC≡CCH₂OH(1/5) catalyst system. The polymerization at 5°C did not yield any polymer. However, in the wide temperature ranges between 20°C and 90°C, the polymerization was well proceeded to give a similar polymer yield. The average molecular weights (\bar{M}_w) of poly(PA) according to the polymerization temperature, were ranged between 5210 and 11700.

Table 2. The Temperature Effect on the Polymerization of Phenylacetylene by MoCl₅/HC≡CCH₂OH(1/5) Catalyst System^a

Experiment Number	Temperature (°C)	Polymer Yield (%)	\bar{M}_w
1	5	0	—
2	20	47	11700
3	40	51	8370
4	60	58	7200
5	90	49	5210

^a Polymerization was carried out for 24 hr in chlorobenzene. Initial monomer concentration([M]₀) and monomer to catalyst mole ratio(M/C) were 1 M and 50, respectively. Mixture of MoCl₅ and cocatalyst was aged for 15 min at 30°C before use.

^b Methanol-insoluble polymer.

Table 3. The Activation Temperature Effect of MoCl₅/HC≡CCH₂OH(1/5) Catalyst System for the Polymerization of Phenylacetylene^a

Experiment Number	Activation Temperature (°C)	Polymer Yield ^b (%)	\bar{M}_w
1	20	55	7210
2	30	58	7200
3	40	55	7030
4	60	53	6980
5	90	57	6450

^a Polymerization was carried out at 60°C for 24 hr in chlorobenzene. Initial monomer concentration([M]₀) and monomer to catalyst mole ratio(M/C) were 1 M and 50, respectively. Mixture of MoCl₅ and cocatalyst was aged for 15 min at 30°C before use.

^b Methanol-insoluble polymer.

In the polymerization of PA catalyzed by MoCl₅/HC≡CCH₂OH system, the effect of temperature on the activation of MoCl₅ and HC≡CCH₂OH solution was also tested. (Table 3) Similar polymerization results were observed in most activation temperature ranges. From these observations, it was known that the activation temperature of MoCl₅ by HC≡CCH₂OH is not a important variable for the present polymerization.

In the polymerization of PA, it can be deduced that the HC≡CCH₂OH have two functional groups, which activate the molybdenum chloride, i. e. the acetylenic hydrogen and the hydroxy group. These

two functional groups are thought to act as an activator of molybdenum chloride. It was also reported that the catalytic activity of Mo-based catalysts was greater than that of W-based catalysts when the organic compounds containing oxygen atom are used as monomer or solvent.^{21,22} From these viewpoints, it may be deduced that the contribution of hydroxy functional group is greater than that of acetylenic hydrogen functional group for the activation of molybdenum chloride.

The polymer structure of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system was characterized by NMR(^1H -, ^{13}C -), IR, UV-visible spectroscopies, and elemental analysis. The elemental analysis agreed well with the calculated value(e.g., poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/5), calculated for $(\text{C}_8\text{H}_6)_n$: C, 94.08%; H, 5.92%. found: C, 93.21%; H, 5.83%).

Fig. 2 shows the ^1H -NMR spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system. A broad peak at 5.0~8.0 ppm is due to the vinyl protons on the conjugated chain and phenyl substituents. This spectrum was similar to that of poly(PA) prepared by WCl_6 .²³

The differences in chemical shifts of aromatic protons were qualitatively estimated by theoretical calculations according to Johnson and Bovey²⁴ and Haigh and Mallion.²⁵ The conformation of macromolecular chains was reproduced by using atomic model. Taking into account the distance from the center of the phenyl ring to the hydrogen atom in question and the distance between the planes of these rings, the chemical shifts were estimated.

The theoretical NMR studies of the four helicoi-

dal structure models(*cis*-cisoidal, *cis*-transoidal, *trans*-cisoidal, and *trans*-transoidal) of poly(PA) indicated that for the *trans*-transoidal(12/1) structure, two aromatic protons must be shifted to the lower values of δ ; for the *cis*-cisoidal(3/1) structure, one aromatic proton must be shifted to lower value of δ , while in the case of the *cis*-transoidal(3/1) structure, two protons(one aromatic and one from the main chain) must be shifted to the lower values of δ . Only for the *trans*-cisoidal(3/1) structure must all protons appear in the same field.^{26,27}

The present poly(PA) shows only one broad peak at 5~8 ppm. The shoulder peak at 5.82 ppm may be correlated with that of *cis*-transoidal structure. Moreover, the present NMR spectrum shows a weak, wide resonance peaks at 1.0~4.5 ppm. These signals may be due to a low content of aliphatic(methyl, ethyl) protons, which arise from the initiation step(migratory insertion of monomer into the metal-alkyl bond).²⁸

Fig. 3 shows the ^{13}C -NMR spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$. The chemical shifts of the carbons on the phenyl substituent were observed at 125~130 ppm, whereas those of the carbons on the conjugated double bond were observed at 138~144 ppm.

Fig. 4 shows the IR spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system. It shows the aromatic $=\text{C}-\text{H}$ stretching frequencies of phenyl substituents at 3011~3045 cm^{-1} and the vinyl $\text{C}=\text{C}$ stretching frequencies at 1600 cm^{-1} . The absorption frequencies at 755 and 693 cm^{-1} are due to the $\text{C}-\text{H}$ out-of-plane deformation of mono-substituted benzene. Further, the polymer posses-

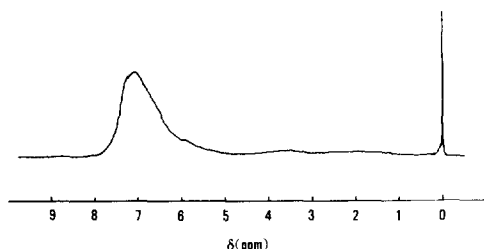


Fig. 2. ^1H -NMR spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/5).

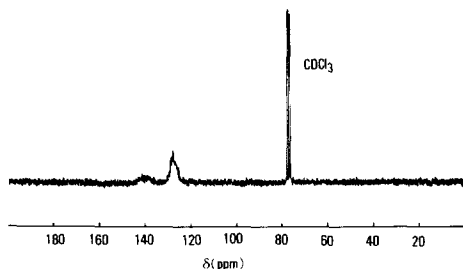


Fig. 3. ^{13}C -NMR spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ (1/5).

sed three absorptions at 910, 880, and 840 cm^{-1} . It has been known that the absorption at 880 cm^{-1} is a characteristic of *cis* structure in poly(PA)^{29,30} and a ratio D_{880}/D_{910} can be used as a measure of *cis*-structure content. The D_{880}/D_{910} ratio of present poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ was 0.72.

The UV-visible spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system is given in Fig. 5. A characteristic peak of conjugated polymer, a wide broad $\pi \rightarrow \pi^*$ absorption of poly(PA) was observed as far as ca. 550 nm.

The poly(PA)s prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system were mostly soluble in aromatic and halogenated hydrocarbons such as benzene, chlorobenzene, chloroform, methylene chloride, but insoluble in methanol, ethyl ether, formic acid, etc. The color of poly(PA) prepared by $\text{MoCl}_5/$

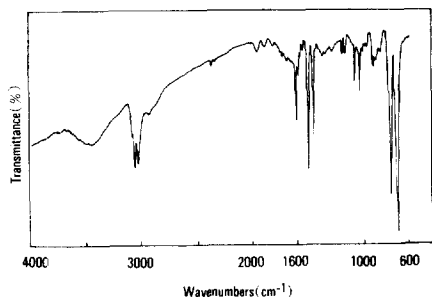


Fig. 4. IR spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}(1/5)$.

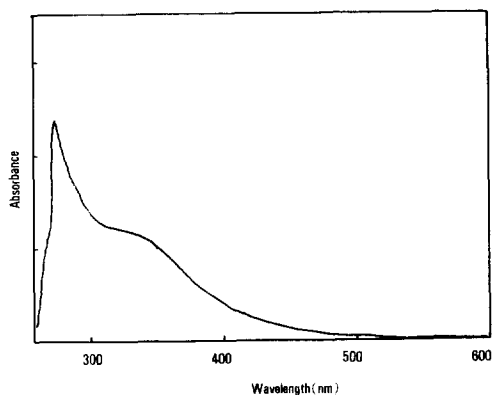


Fig. 5. UV-visible spectrum of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}(1/5)$.

$\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system was light brown or yellow.

Fig. 6 shows the TGA thermogram of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system. It showed that it retains 95% of its original weight at 278°C, 57% at 400°C, 36% at 500°C, and 30% at 700°C.

Fig. 7 shows the DSC thermogram of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system. The two exothermic peaks at 208 and 225°C were observed. In the case of poly(β -ethynylnaphthalene)³¹ and poly(N-ethynylcarbazole),³² it was also reported that the exothermic peak at similar temperature was due to the isomerization from *cis*-cisoidal structure to *trans*-cisoidal structure. And the present poly(PA) starts to fuse at about 295°C. This process involved the decomposition of the polymer to low molecular-weight oligomers and a cross-linked solid.³³

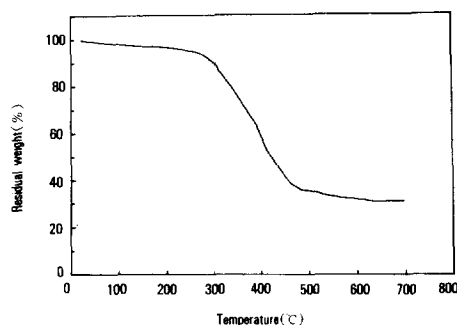


Fig. 6. TGA thermogram of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}(1/5)$.

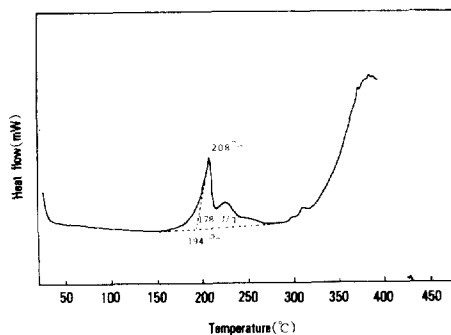


Fig. 7. DSC thermogram of poly(PA) prepared by $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}(1/5)$.

CONCLUSIONS

A new activator, 2-propyn-1-ol, for the polymerization of PA by MoCl_5 was tested and evaluated. The activator, $\text{HC}\equiv\text{CCH}_2\text{OH}$, increased the polymer yield from 34% to 58% in the polymerization of PA by MoCl_5 . It was found that the catalytic activity of $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system was greater than that of $\text{WCl}_6/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system. The activation temperature of MoCl_5 by $\text{HC}\equiv\text{CCH}_2\text{OH}$ and the polymerization temperature was found to be not important factor for the present polymerization. The high catalytic activity of $\text{MoCl}_5/\text{HC}\equiv\text{CCH}_2\text{OH}$ catalyst system was deduced that the partially substituted molybdenum compounds by $\text{HC}\equiv\text{CCH}_2\text{OH}$ are active species though the mechanism is not fully understood. It was concluded that the contribution of the hydroxyl functional group of $\text{HC}\equiv\text{CCH}_2\text{OH}$ was greater than that of acetylenic hydrogen functional group of $\text{HC}\equiv\text{CCH}_2\text{OH}$ for the activation of molybdenum chlorides.

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