

## Polymerization of Phenylacetylenes. IX. Polymerization of $\beta$ -Naphthylacetylene by $WCl_6$ and $MoCl_5$ \*

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**ABSTRACT:** The polymerization of  $\beta$ -naphthylacetylene by  $WCl_6$ - and  $MoCl_5$ -based catalysts was investigated. The  $WCl_6$  and  $MoCl_5$  catalysts were both found to be highly active. The polymer obtained with  $WCl_6$  [poly( $\beta$ NA)-W] was soluble, and its highest molecular weight was 9,200, which is by far the highest value reported so far. The polymer formed with  $MoCl_5$  [poly( $\beta$ NA)-Mo] was hardly soluble. According to the results from IR spectroscopy and differential thermal analysis, poly( $\beta$ NA)-W was rich in *trans* structure, whereas poly( $\beta$ NA)-Mo was *cis*-rich. The X-ray diffraction patterns showed that poly( $\beta$ NA)-W was amorphous, while poly( $\beta$ NA)-Mo was crystalline. The heat treatment of poly( $\beta$ NA)-Mo caused *cis*-to-*trans* isomerization, and rendered the polymer more soluble. The electric conductivity and paramagnetic property of the polymers are also described.

**KEY WORDS** Coordination Polymerization /  $\beta$ -Naphthylacetylene / Tungsten Hexachloride / Molybdenum Pentachloride / Geometric Structure / Heat Treatment / Crystallinity / Electric Conductivity /

We reported earlier that poly(phenylacetylene) [poly(PA)] having high molecular weights of 5,000—15,000 can be obtained from phenylacetylene in the presence of  $WCl_6$  and  $MoCl_5$  as catalysts.<sup>1</sup> It seems very probable that  $WCl_6$  and  $MoCl_5$  can also catalyze the high polymerization of various acetylenic monomers other than phenylacetylene.

Naphthylacetylenes ( $\alpha$ - and  $\beta$ -) have bulky substituents and large conjugated systems, compared with phenylacetylene. Therefore, it is expected that the reactivities of naphthylacetylenes in polymerization and the properties of polymers formed will be different from those of phenylacetylene.

$\beta$ -Naphthylacetylene ( $\beta$ NA) has been polymerized by use of several catalysts.<sup>2,3</sup> Among these, the Ziegler-type catalysts and phosphine complexes of transition metals have most often been used; the former catalysts provide an insoluble polymer as the main product,<sup>2,3</sup> while the latter give a methanol-soluble oligomer as well as a methanol-insoluble polymer.<sup>3</sup> The highest molecular weight of soluble poly( $\beta$ -naphthylacetylene) [poly( $\beta$ NA)] reported so

far is only 2,100. The polymerization of  $\alpha$ -naphthylacetylene has also been investigated.<sup>4-7</sup> Also, the highest molecular weight of the polymer is as low as 2,000. Recently, the solid-state photopolymerization of 1,4-diethynyl-naphthalene was reported,<sup>8,9</sup> and is believed to proceed by a radical mechanism.

In this paper, we describe the synthesis of soluble high molecular weight poly( $\beta$ NA) using  $WCl_6$  and  $MoCl_5$  as polymerization catalysts. The structure and properties of poly( $\beta$ NA) obtained are also reported.

### EXPERIMENTAL

#### Materials

$\beta$ NA was prepared by a modification of Robin's procedure,<sup>10</sup> as follow: After chlorination of  $\beta$ -naphthyl methyl ketone with phosphorus pentachloride, the reaction mixture was poured onto crushed ice to decompose the phosphorus oxychloride and phosphorus pentachloride, and the chlorination product was extracted with ether. The dehydrochlorination was performed in 2-propanol using potassium hydroxide instead of potassium ethoxide.

\* Part VIII: T. Masuda and T. Higashimura, *Macromolecules*, **12**, 9 (1979).

The  $\beta$ NA produced was purified by distillation; 78—82°C/ $<1$  mmHg (133 Pa); yield, *ca.* 20%. The purity of  $\beta$ NA was greater than 99% according to gas chromatography.

$WCl_6$ ,  $MoCl_5$ , and iron (III) acetylacetonate [ $Fe(acac)_3$ ] were commercially available (purity  $>99\%$ ), and were used without further purification. Tetraphenyltin ( $Ph_4Sn$ ) was purified by recrystallization from carbon tetrachloride. Triethylaluminum ( $Et_3Al$ ) was commercially obtained as a solution in hexane (15%), and was used after determination of its concentration. Bis(triphenylphosphine)nickel (II) bromide [ $(PPh_3)_2NiBr_2$ ] was prepared according to the usual method. The solvents for polymerization were purified by the usual methods.

### Procedures

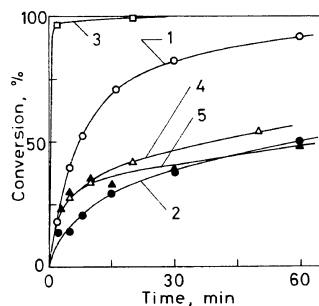
The preparation of the catalyst solutions and polymerization were carried out under a dry nitrogen atmosphere. The catalyst solutions were prepared as follows. The  $WCl_6 \cdot (1/2)CH_3OH$  and  $MoCl_5 \cdot (1/2)CH_3OH$  catalysts were prepared by mixing the chlorides and a half amount of methanol in solution, and were used after aging at 30°C for 30 min. The  $WCl_6 \cdot Ph_4Sn$  catalyst was obtained by mixing equimolar amounts of  $WCl_6$  and  $Ph_4Sn$  in solution, and this was also aged at 30°C for 30 min before use. These catalysts were all soluble. An Fe–Al catalyst was prepared by mixing  $Fe(acac)_3$  and a three-fold excess of  $Et_3Al$  in toluene, the solution being aged at 80°C for 30 min before use. The catalyst formed was a slurry of fine black particles in toluene. The polymerizations were performed as described before.<sup>11</sup>

The IR, UV-visible, and electron spin resonance (ESR) spectra of polymers were observed as described in a previous paper.<sup>11</sup> The X-ray powder diffraction patterns were obtained using a Shimadzu GX-3B. Differential thermal analysis (DTA) was performed on a Shimadzu-20B analyzer under nitrogen at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Polymerization of $\beta$ NA

Figure 1 shows the time–conversion curves for the polymerization of  $\beta$ NA catalyzed by  $WCl_6$  and  $MoCl_5$  at 30°C in benzene or in methylene chloride. Methanol, as a cocatalyst, only increased the polymerization rate, and did not affect the molecular



**Figure 1.** Time–conversion curves for the polymerization of  $\beta$ NA: 30°C,  $[M]_0 = 1.0 \text{ mol dm}^{-3}$ ; 1 (○),  $[WCl_6 \cdot (1/2)CH_3OH]_0 = 10 \text{ mmol dm}^{-3}$ ,  $C_6H_6$ ; 2 (●),  $[WCl_6 \cdot (1/2)CH_3OH]_0 = 10 \text{ mmol dm}^{-3}$ ,  $CH_2Cl_2$ ; 3 (□),  $[WCl_6 \cdot Ph_4Sn]_0 = 10 \text{ mmol dm}^{-3}$ ,  $C_6H_6$ ; 4 (△),  $[MoCl_5 \cdot (1/2)CH_3OH]_0 = 15 \text{ mmol dm}^{-3}$ ,  $C_6H_6$ ; 5 (▲),  $[MoCl_5 \cdot (1/2)CH_3OH]_0 = 15 \text{ mmol dm}^{-3}$ ,  $CH_2Cl_2$ .

weight of polymers formed.  $\beta$ NA was polymerized to high conversions by  $WCl_6$ - and  $MoCl_5$ -based catalysts. The  $WCl_6 \cdot Ph_4Sn$ -catalyzed polymerization in benzene showed the highest reaction rate. The polymerization by  $WCl_6 \cdot (1/2)CH_3OH$  was faster in benzene than in methylene chloride. In the polymerization by  $MoCl_5 \cdot (1/2)CH_3OH$ , the difference in reaction rates with respect to solvents was small.

Results for the polymerization of  $\beta$ NA performed in this study are listed in Table I. The polymerizations catalyzed by  $WCl_6$  and  $MoCl_5$  were carried out at 30°C for 2 h. The conversion in the  $WCl_6$ -catalyzed polymerization reached over 90% in benzene and in carbon tetrachloride, and it decreased with increasing solvent polarity, for example, in methylene chloride. The ratios of the yields of methanol-insoluble polymer to the conversions were 0.7–0.9. The methanol-soluble fraction of the product is assumed to consist of oligomers. The conversion of the  $MoCl_5$ -catalyzed polymerization was usually about 50–60% irrespective of solvent polarity. The conversion in carbon tetrachloride was unusually low, due to the low solubility of  $MoCl_5$  in carbon tetrachloride. The catalytic activity of  $MoCl_5$  was generally lower than that of  $WCl_6$ . The ratios of the polymer yields to the conversions were 0.4–0.8, indicating that a larger quantity of oligomers was formed than in the polymerization by  $WCl_6$ .

For the sake of comparison, an Fe–Al catalyst (a mixture of  $Fe(acac)_3$  and a threefold excess of  $Et_3Al$ ) and  $(PPh_3)_2NiBr_2$  were also used for the polymerization of  $\beta$ NA. The former is a Ziegler-type catalyst,

Polymerization of  $\beta$ -Naphthylacetylene

**Table I.** Polymerization of  $\beta$ -NA<sup>a</sup>

No.	Catalyst	[Cat]	Solvent	Time	Conversion	Polymer <sup>b</sup> Yield/%	Yield
		mol dm <sup>-3</sup>		h	%		Conversion
1	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	10	C <sub>6</sub> H <sub>6</sub>	2	92.5	78.8	0.85
2	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	10	CCl <sub>4</sub>	2	91.9	75.5	0.82
3	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	10	CHCl <sub>3</sub>	2	80.7	68.3	0.85
4	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	10	CH <sub>2</sub> Cl <sub>2</sub>	2	73.7	51.7	0.70
5	WCl <sub>6</sub> ·Ph <sub>4</sub> Sn	10	C <sub>6</sub> H <sub>6</sub>	2	99.9	89.1	0.89
6	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	15	C <sub>6</sub> H <sub>6</sub>	2	62.5	48.0	0.77
7	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	15	CCl <sub>4</sub>	2	19.5	8.3	0.43
8	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	15	CHCl <sub>3</sub>	2	51.3	37.3	0.73
9	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	15	CH <sub>2</sub> Cl <sub>2</sub>	2	61.0	33.7	0.55
10	Fe(acac) <sub>3</sub> ·3Et <sub>3</sub> Al	20	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	24	26.4	13.1	0.50
11	(PPh <sub>3</sub> ) <sub>2</sub> NiBr <sub>2</sub>	70	—	6	90.2	80.2	0.89

<sup>a</sup> Polymerized at [M]<sub>0</sub> 1.0 mol dm<sup>-3</sup>, 30°C (No. 11: Bulk, 140°C).

<sup>b</sup> Yield of CH<sub>3</sub>OH-insoluble polymer against monomer feed.

**Table II.** Properties of poly( $\beta$ -NA)

No. <sup>a</sup>	Catalyst	Solvent	$M_n$	Color	Softening point/°C	$D_{770}$
						$D_{740}$
1	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	C <sub>6</sub> H <sub>6</sub>	9200	Dark brown	235—244	0.034
2	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	CCl <sub>4</sub>	6300	"	231—238	0.037
3	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	CHCl <sub>3</sub>	6600	"	234—244	0.030
4	WCl <sub>6</sub> ·(1/2)CH <sub>3</sub> OH	CH <sub>2</sub> Cl <sub>2</sub>	4200	"	235—244	0.018
5	WCl <sub>6</sub> ·Ph <sub>4</sub> Sn	C <sub>6</sub> H <sub>6</sub>	9100	"	238—243	0.027
6	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	C <sub>6</sub> H <sub>6</sub>	Insol <sup>b</sup>	Red	232—235	0.128
7	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	CCl <sub>4</sub>	"	"	225—237	0.119
8	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	CHCl <sub>3</sub>	"	"	235—237	0.077
9	MoCl <sub>5</sub> ·(1/2)CH <sub>3</sub> OH	CH <sub>2</sub> Cl <sub>2</sub>	"	"	229—236	0.047
10	Fe(acac) <sub>3</sub> ·3Et <sub>3</sub> Al	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	"	"	235—242	0.197
11	(PPh <sub>3</sub> ) <sub>2</sub> NiBr <sub>2</sub>	—	640	Yellow	137—158	0.016

<sup>a</sup> These numbers correspond to those in Table I.

<sup>b</sup> The polymer formed was hardly soluble.

and the latter, a phosphine complex of the transition metal, both of which have been reported in the literature.<sup>3</sup> Results of the polymerizations are shown in Table I. The polymerization by the Fe–Al catalyst was slow, the polymer yield after 24 h being only 13%. The polymerization by (PPh<sub>3</sub>)<sub>2</sub>NiBr<sub>2</sub> did not proceed near room temperature, but required a high temperature such as 140°C. Thus, it is concluded that WCl<sub>6</sub> and MoCl<sub>5</sub> are much more active than these known catalysts.

#### Molecular Weight and Some Properties of Poly( $\beta$ NA)

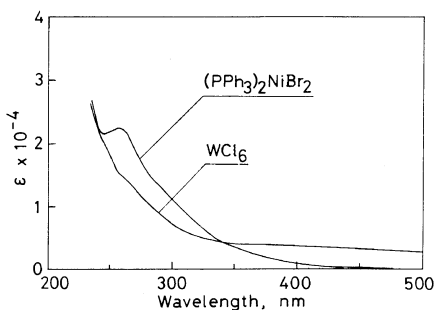
Poly( $\beta$ NA) obtained with WCl<sub>6</sub> is denoted as poly( $\beta$ NA)–W. In the same manner, abbreviations of poly-( $\beta$ NA)–Mo, poly( $\beta$ NA)–Fe·Al, poly-( $\beta$ NA)–Ni, poly(PA)–W, and poly(PA)–Mo are also used. Poly( $\beta$ NA)–W and poly( $\beta$ NA)–Ni were soluble in benzene. The major part of poly-( $\beta$ NA)–Mo was insoluble, and poly( $\beta$ NA)–Fe·Al was essentially insoluble. On the other hand poly((PA)–Mo is completely soluble;<sup>1</sup> the insolubility of poly( $\beta$ NA)–Mo might be due to either the  $\beta$ -naphthyl group which is bulkier than phenyl group or its geometric structure which could be different from that of poly(PA)–Mo.

The molecular weight of poly( $\beta$ NA)-W obtained in benzene was about 9,000 (Table II). This is by far the highest value for poly( $\beta$ NA) obtained to date; the highest molecular weight reported so far is only 2,100 as mentioned in the Introduction. It is evident from Table II that  $\text{Ph}_4\text{Sn}$  as a cocatalyst only accelerates the polymerization to a great extent but does not affect the polymer molecular weight. When carbon tetrachloride, chloroform and dichloromethane were used as solvents instead of benzene, the polymer molecular weights ranged from 4,000 to 7,000. The molecular weight of poly( $\beta$ NA)-Ni was only 640. The degree of polymerization (DP) of 60 for poly( $\beta$ NA), which corresponds to the molecular weight of 9,000, is lower than the DP of *ca.* 150 attained for poly(PA).<sup>1</sup> This appears to arise as a result of the steric effect of the  $\beta$ -naphthyl group.

Polymer colors are shown in Table II. Poly( $\beta$ NA)-W was dark brown, whereas poly( $\beta$ NA)-Mo and poly( $\beta$ NA)-Fe-Al were red. Thus polymer color depends on the kind of catalyst. Figure 2 shows the UV-visible spectra of polymers. The absorption of poly( $\beta$ NA)-W continued as far as 600 nm, indicating that the conjugated system is fairly long. On the other hand, poly( $\beta$ NA)-Ni had no absorption in the range where wavelength is greater than 450 nm. This is reasonable if its molecular weight is taken into account.

When the same polymerization catalyst is used, the color of poly( $\beta$ NA) obtained is darker than that of poly(PA) (*e.g.*, poly( $\beta$ NA) red, poly(PA) yellow, with  $\text{MoCl}_5$  as a catalyst).<sup>11</sup> In accordance with this, the absorption of poly( $\beta$ NA) in the visible region is large and shows a red shift (see Figure 2), compared with that of poly(PA).<sup>11</sup>

The softening points of polymers produced with

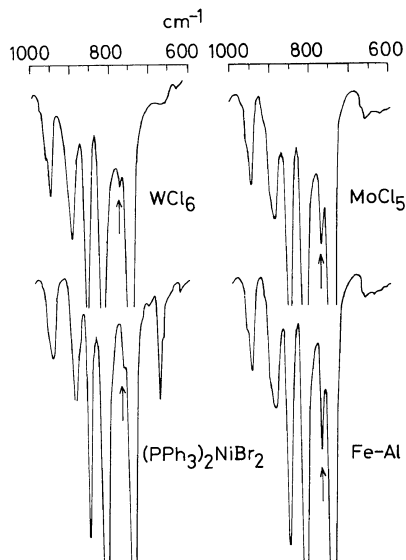


**Figure 2.** UV-visible spectra of poly( $\beta$ NA). The samples of  $\text{WCl}_6$  and  $(\text{PPh}_3)_2\text{NiBr}_2$  correspond to No. 1 and 11 in Table I, respectively; in  $(\text{CH}_2\text{Cl})_2$ .

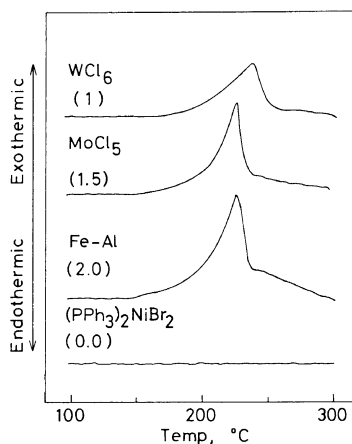
$\text{WCl}_6$ ,  $\text{MoCl}_5$  and the Fe-Al catalyst were all in a range of 225–245°C (Table II). Only poly( $\beta$ NA)-Ni showed an exceptionally low softening point.

#### Structure of Poly( $\beta$ NA)

Figure 3 shows part of the IR spectra of poly( $\beta$ NA) prepared with various catalysts. The intensity of the absorption at  $770\text{ cm}^{-1}$  depended on the reaction conditions. It decreased in the following



**Figure 3.** IR spectra of poly( $\beta$ NA). Samples of  $\text{WCl}_6$ ,  $\text{MoCl}_5$ , Fe-Al, and  $(\text{PPh}_3)_2\text{NiBr}_2$  correspond to No. 1, 6, 10 and 11 in Table I, respectively.



**Figure 4.** DTA curves of poly( $\beta$ NA). See the caption of Figure 3 for the samples.

catalyst order: Fe-Al > MoCl<sub>5</sub> > WCl<sub>6</sub> > (PPh<sub>3</sub>)<sub>2</sub>NiBr<sub>2</sub>. This absorption has been attributed to the *cis* structure of the double bond in the main chain.<sup>3</sup> Values for the ratio of absorbances at 770 cm<sup>-1</sup> and 740 cm<sup>-1</sup> ( $D_{770}/D_{740}$ ) are given in Table II. The *cis* contents of various polymer samples can be compared with each other using these values. The *cis* content tended to decrease with increasing polarity of polymerization solvent, in conjunction with the above-mentioned catalyst effect. The observed influence of catalyst and solvent on polymer geometric structure shows the same trend as seen in poly(PA).<sup>11,12</sup>

DTA curves of the polymers are shown in Figure 4. The polymers formed with WCl<sub>6</sub>, MoCl<sub>5</sub>, and the Fe-Al catalyst showed exothermic peaks at around 230°C. It has been reported that polyacetylene shows an analogous exothermic peak;<sup>13</sup> this peak in

polyacetylene is concluded to result from the *cis-to-trans* isomerization in the main chain. Consequently, it is inferred that the exothermic peaks observed in poly( $\beta$ NA) are due also to the *cis-to-trans* isomerization in the main chain. The relative isomerization heat was evaluated from the peak area, taking the value of poly( $\beta$ NA)-W as unity. These values are shown in parentheses in Figure 4. The isomerization heat decreased in the following order: Fe-Al > MoCl<sub>5</sub> > WCl<sub>6</sub> > (PPh<sub>3</sub>)<sub>2</sub>NiBr<sub>2</sub>. This order corresponds to that of the *cis* content estimated from IR spectra, thus supporting the fact that the observed exothermic peaks are due to *cis-to-trans* isomerization.

Figure 5 shows the X-ray diagrams of polymers formed with several catalysts. Poly( $\beta$ NA)-Fe-Al and poly( $\beta$ NA)-Mo which were insoluble, exhibited crystalline patterns. On the other hand, the soluble

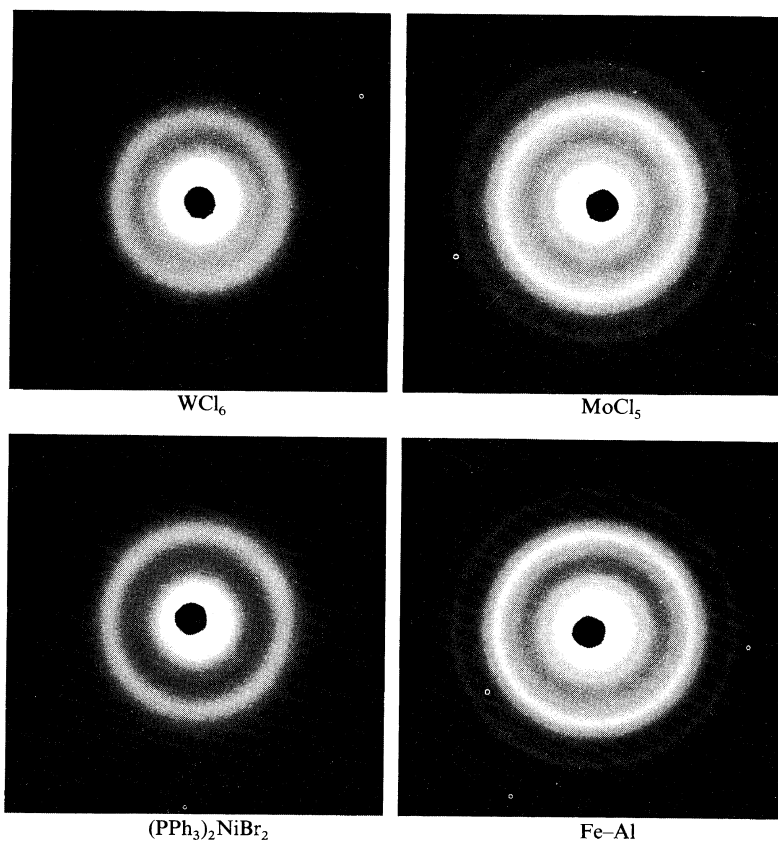


Figure 5. X-ray diagrams of poly( $\beta$ NA). See the caption of Figure 3 for the samples.

**Table III.** Heat treatment of poly( $\beta$ -NA)<sup>a</sup>

Sample No. <sup>b</sup>	Polymerization conditions	C <sub>6</sub> H <sub>6</sub> -sol Fraction/%	$D_{770}$	$M_n$	Color	
			$D_{740}$			
6	MoCl <sub>5</sub> -C <sub>6</sub> H <sub>6</sub>	11.1 → 53.7	0.128 → 0.022	Insol → 3400	Red	→ Yellow
9	MoCl <sub>5</sub> -CH <sub>2</sub> Cl <sub>2</sub>	45.9 → 80.3	0.047 → 0.010	Insol → 1700	"	→ "
1	WCl <sub>6</sub> -C <sub>6</sub> H <sub>6</sub>	100 → 100	0.034 → 0.017	9200 → 4900	Dark Brown	→ Orange Yellow
4	WCl <sub>6</sub> -CH <sub>2</sub> Cl <sub>2</sub>	100 → 100	0.018 → 0.013	4200 → 2900	"	→ "

<sup>a</sup> Performed in *o*-dichlorobenzene at 150°C for 5 h under a nitrogen atmosphere.

<sup>b</sup> These numbers correspond to those in Table I.

poly( $\beta$ NA)-W and poly( $\beta$ NA)-Ni were amorphous.

As observed in DTA, the *cis*-to-*trans* isomerization in the main chain occurred when poly( $\beta$ NA) was heated. Accordingly, it is anticipated that heat treatment of insoluble polymers having high *cis* content will bring about *cis*-to-*trans* isomerization to give soluble polymers. The heat treatment was tried in *o*-dichlorobenzene at 150°C for 5 h under a nitrogen atmosphere. Over 50% of poly( $\beta$ NA)-Mo became soluble in benzene by heat treatment (Table III). At the same time the *cis* content appreciably decreased, as is obvious from the ratio,  $D_{770}/D_{740}$ , indicating why some of the poly( $\beta$ NA) is insoluble, *i.e.*, high crystallinity due to *cis* structure without crosslinking. It has been reported that the heat treatment of insoluble poly(PA) also causes *cis*-to-*trans* isomerization, rendering polymer soluble.<sup>12</sup> Following the treatment, the molecular weight of the soluble fraction of the poly( $\beta$ NA)-Mo obtained in benzene reduced to 3,400. In the heat treatment of poly( $\beta$ NA)-W performed under the same conditions, the polymer molecular weight decreased to about a half. Consequently, it is reasonable to assume that poly( $\beta$ NA)-Mo obtained in benzene has a molecular weight of 5,000-6,000 prior to the heat treatment. Poly( $\beta$ NA)-Mo changed from red to yellow as a result of the heat treatment, and poly( $\beta$ NA)-W from dark brown to orange yellow. These color changes suggest that the conjugated systems in polymers became shorter due to the molecular weight decrease and certain side reactions.

#### Electric Conductivity and Paramagnetic Property of Poly( $\beta$ NA)

The electric conductivities at 20°C ( $\sigma_{20}$ ) and spin densities of poly( $\beta$ NA) are shown in Table IV. The electric conductivities of poly( $\beta$ NA)-W were in a

**Table IV.** Electric conductivity and spin density of poly( $\beta$ NA)

No. <sup>a</sup>	Polymerization	$\sigma_{20}$	Unpaired spin/g <sup>-1</sup>
		S cm <sup>-1</sup>	
1	WCl <sub>6</sub> -C <sub>6</sub> H <sub>6</sub>	$6.8 \times 10^{-14}$	$6.6 \times 10^{16}$
4	WCl <sub>6</sub> -CH <sub>2</sub> Cl <sub>2</sub>	$6.9 \times 10^{-15}$	$4.1 \times 10^{16}$
6	MoCl <sub>5</sub> -C <sub>6</sub> H <sub>6</sub>	$1.4 \times 10^{-17}$	$3.2 \times 10^{17}$
9	MoCl <sub>5</sub> -CH <sub>2</sub> Cl <sub>2</sub>	$2.3 \times 10^{-17}$	$2.8 \times 10^{17}$
10	Fe·Al-C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	$4.4 \times 10^{-15}$	$2.4 \times 10^{17}$
11	(PPh <sub>3</sub> ) <sub>2</sub> NiBr <sub>2</sub> -Bulk	$1.7 \times 10^{-18}$	$2.6 \times 10^{17}$

<sup>a</sup> These numbers correspond to those in Table I.

range of  $10^{-14}$ – $10^{-15}$  S cm<sup>-1</sup> and those of poly( $\beta$ NA)-Mo were about  $10^{-17}$  S cm<sup>-1</sup>; the former polymer exhibited a higher conductivity than the latter, though the reason is not obvious.

Poly( $\beta$ NA) showed a broad singlet signal in ESR, whose *g* value was 2.0021 and the peak-to-peak width was 8–11 G. The *g* value and spin densities of polymers were determined using 1,1-diphenyl-2-picrylhydrazyl as a reference. The spin densities were  $10^{16}$ – $10^{17}$  g<sup>-1</sup>, which are similar to the values of poly( $\beta$ NA) so far reported (*ca.*  $10^{16}$  g<sup>-1</sup>).<sup>2</sup>

No large difference is found in the electric conductivities and spin densities of poly( $\beta$ NA) and poly(PA).<sup>11</sup>

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