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Catalysts

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Microstructure of Polyphenylacetylene Obtained by $MoCl_5$ and WCl_6 Type Catalysts

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Dedicated to Prof. H.-J. Cantow in honor of his 60th birthday

SUMMARY

The microstructure of polyphenylacetylenes prepared with $MoCl_5$ and WCl_6 catalysts under different reaction conditions was determined by 200 MHz ^1H-NMR spectroscopy. Cis, trans and cyclohexadiene sequences were evidenced in all polymers. Two mechanisms are responsible for the polymer microstructure: isomerization prior to double bond formation, and thermal isomerization after double bond formation. When trans sequences are formed mainly through the first mechanism, the polymer is almost void of cyclohexadiene structural units and its molecular weight is very high. This can be explained through a unimolecular termination mechanism, i.e., intramolecular cyclization of the cis-polymer chain end. The control of polyphenylacetylene microstructure by these two mechanisms explains why a cis-cisoidal polymer could not be obtained by using $MoCl_5$ or WCl_6 catalysts.

INTRODUCTION

In spite of the increasing interest in the synthesis and applications of acetylenic polymers, their microstructure and polymerization mechanism are still not completely elucidated.

The difficulties encountered in the studies carried out on the simplest homolog of this series, i.e., polyacetylene, are due to its insolubility. The first homolog from the arylacetylenes series, i.e., phenylacetylene (PA) presents the advantage that at least two of its geometric isomers, i.e., cis-transoidal and trans-cisoidal, are soluble, and consequently their microstructural analyses can be approached by solution NMR spectroscopy. Previous studies showed that at least with Ziegler-Natta type catalysts, the opening of the triple bond takes place in cis position and the microstructure, as well as the physical properties, of the obtained polymers are strongly dependent on the thermal history of the polymer synthesis (1-10). Two geometric isomers are obtained when the caloric effects responsible for thermally induced reactions are removed: cis-cisoidal (crystalline and insoluble) and cis-transoidal (soluble and amorphous) (1,5-8,10). Thermally induced isomerization of both cis-cisoidal and cis-transoidal polyphenylacetylenes (PPA) (1,5-9) leads to intramolecular cyclization reactions (1,3-cyclohexadiene sequences), and trans structural units seem to appear only by double bond migration as a side reaction. Thermal treatment at higher temperatures than 120°C leads to aromatization of the polymer main chain (polyphenylenic sequences), accompanied by chain scission and cyclic trimers release. Because of the numerous overlappings of the proton resonances in the aromatic region of the spectrum, ^1H-NMR structural analyses was successful only on poly(pentadeuterophenylacetylene) (6). The pure trans isomers could not be obtained by polymerization. Consequently, the trans-cisoidal isomer was synthesized by chemical isomerization only (9).

A few years ago, Higashimura et al. (11) showed that $MoCl_5$ and WCl_6 based catalysts polymerize PA to high molecular weight polymers having predominantly cis ($MoCl_5$) or trans (WCl_6) configurations. They also proposed a mechanism of polymerization similar to that encountered in the ring opening polymerization of cycloolefins in the presence of metathesis catalysts. It was clearly demonstrated by Katz et al. (12,13) and more recently by Farona et al. (14) that, indeed these polymerizations proceed via metal carbene and a metallacyclobutene intermediate. Katz et al. also proposed a mechanism of geometric structure control (12, 13). This mechanism was used by Higashimura et al. (15) to explain the difference in geometric structure of t-butylacetylene polymers obtained by $MoCl_5$ and WCl_6 catalysts in different solvents.

Although the structure of a poly(pentadeuterophenylacetylene) obtained in the presence of $MoCl_5$ at 60°C showed a microstructure based mainly on cyclohexadiene sequences (6), there are a few unclear aspects which prompted us to investigate the structure of PPA obtained with Higashimura type catalysts.

1. When Ziegler-Natta type catalysts are used for the polymerization of phenylacetylene, both cis-cisoidal and cis-transoidal configurations are obtained. Only a cis-transoidal configuration is obtained by using $MoCl_5$ as catalysts (11). WCl_6 leads mainly to PPA containing trans sequences.
2. The polymerization of β-ethynylnaphthalene by Ziegler-Natta type catalysts (16) as well as by $MoCl_5$ (17) gives rise in both cases to cis-cisoidal as well as cis-transoidal polymers. Trans-cisoidal polymers with low contents of cis-transoidal sequences could only be obtained by using WCl_6 type catalysts. This last comment is valid for the polymerization of diphenylacetylene also (18).
3. If the mechanism controlling the polymer microstructure is that proposed by Katz et al., then by using Higashimura type catalysts, pure trans polymers would have to be obtained directly by polymerization under proper reaction conditions.

This paper presents the microstructural analysis of PPA obtained in the presence of $MoCl_5$ and WCl_6 type catalysts and different polymerization solvents.

EXPERIMENTAL

Phenylacetylene (Aldrich) was distilled from CaH_2. Polymerization solvents: toluene (T), anisole (A) and dioxane (D) were first distilled from sodium and then from CaH_2. $MoCl_5$ and WCl_6 (Alfa) were used as received. The polymerization conditions were as follows: phenylacetylene, 1 mole/l; catalyst, 20 mmole/l. When $MoCl_5$-$SnPh_4$ (1:1) was used as a catalyst, it was aged for 30 minutes at 25°C prior to polymerization. In all cases PA was added over the catalytic systems and the polymerizations were carried out under dried argon. The polymers were recovered by precipitation in methanol and purified by reprecipitation with methanol from THF solutions.

^{1}H-NMR spectra were recorded on Varian EM 360A (60 MHz) and Varian XL 200 (200 MHz) instruments in CCl_4 (TMS internal standard) solutions at 60°C. Twenty scans were recorded at 200 MHz in order to allow the integration of all the resonance areas. Molecular weights were determined by GPC using Microstyragel columns of 10^5, 10^4, 10^3, 500, 100Å, and a calibration plot constructed with polystyrene standards.

RESULTS AND DISCUSSION

Figures 1 and 2 present the 200 MHz ^{1}H-NMR spectra of PPA corresponding to the numbers in Table 1. Attempts to characterize the PPA microstructure by using 60 MHz ^{1}H-NMR spectroscopy failed because of the very low protonic concentration of the signal at δ = 3.6 ppm. The spectra recorded at 200 MHz allow the integration of the signals at δ = 3.6 ppm and δ = 5.82 ppm in comparison with the total protonic area. The assignements of these signals are made on Figure 1. In addition, the trans sequences present the polyenic protons at δ = 6.85 ppm and the aromatic protons at δ = 6.92 ppm (6-8). The calculation of the molar fraction of cyclohexadiene sequences (fcx), cis sequences (fc) and trans sequences (ft) presented in Table 1 were carried out as follows.

$$\frac{\mathrm{Acx}(3.6)}{\mathrm{A}(5\text{-}9)} = \frac{\mathrm{fcx}}{2\mathrm{fcx} + \mathrm{fc} + 5\mathrm{fc} + 6\mathrm{ft} + 15\mathrm{fcx}} \qquad (1)$$

where Acx(3.6) = area of cyclohexadienic protons at δ = 3.6 ppm (1, methinic); A(5-9) = area of the protons at δ = 5-9 ppm i.e., A(5-9) = Ac(5.82) + Acx(5.82) + Ac(6.82) + Acx(6.82) + At(6.82); Ac(5.82) = area of cis sequences at δ = 5.82 ppm (1, olefinic); Acx(5.82) = area of cyclohexadienic protons at δ = 5.82 ppm (2, olefinic); Ac(6.82) = area of cis protons at δ = 6.82 ppm (5, aromatic); Acx(6.82) = area of cyclohexadienic protons at δ = 6.82 ppm (15 aromatic); and At(6.82) = area of trans protons at δ = 6.82 ppm (6, both olefinic and aromatic protons).

By replacing ft with:

$$\mathrm{ft} = 1 - \mathrm{fc} - \mathrm{fcx} \qquad (2)$$

in eq(1), one obtains eq(3) which was used to calculate the molar fraction of cyclohexadiene sequences, fcx.

$$\mathrm{fcx} = \frac{6\mathrm{Acx}(3.6)}{\mathrm{A}(5\text{-}9) - 11\mathrm{Acx}(3.6)} \qquad (3)$$

$$\frac{\mathrm{Acx}(3.6)}{\mathrm{Ac}(5.82) + \mathrm{Acx}(5.82)} = \frac{\mathrm{fcx}}{\mathrm{fc} + 2\mathrm{fcx}} \qquad (4)$$

where

$$\mathrm{Ac}(5.82) + \mathrm{Acx}(5.82) = \mathrm{Aol}(5.82) \qquad (5)$$

i.e., Aol(5.82) = total area of the signal at δ = 5.82 ppm.

From eq(4), fc can be calculated by using eq(6) and the value of fcx determined with eq(3).

$$\mathrm{fc} = \frac{\mathrm{fcx}[\mathrm{Aol}(5.8) - 2\mathrm{Acx}(3.6)]}{\mathrm{Acx}(3.6)} \qquad (6)$$

ft was calculated from eq(2).

As we can see in Table 1, all obtained polymers contain cyclohexadiene sequences. This means that pure cis PPA can be obtained only by using Ziegler-Natta catalysts (6). The cis-cisoidal configuration is thought to appear through the isomerization of the cis-transoidal one during the propagation reaction (1). The impossibility of obtaining a pure cis-transoidal configuration for PPA, explains why cis-cisoidal configuration is not obtained when phenylacetylene is polymerized in the presence of $MoCl_5$ or WCl_6. The fact that the polymers obtained with $MoCl_5$-$SnPh_4$ catalysts and short reaction times contain a very low concentration of cyclohexadiene sequences and a high concentration of trans sequences, clearly demonstrates that in this case trans sequences are obtained only by thermal isomerization as in Ziegler -Natta polymerizations.

The solvent plays a double role in the mechanism of polymerization with $MoCl_5$ and WCl_6 based catalysts. First, it can, for example, increase the rate of polymerization. This means that the heat of polymerization is released in a shorter period of time. This will lead to a higher probability of the thermally induced reactions during propagation. On the other hand, the solvent can affect the polymer configuration according to the Katz and Higashimura mechanism, i.e., through a different degree of coordination with the metal carbene chain end. This mechanism is briefly outlined in Figure 3. The propagation occurs through a metallacyclobutene intermediate.

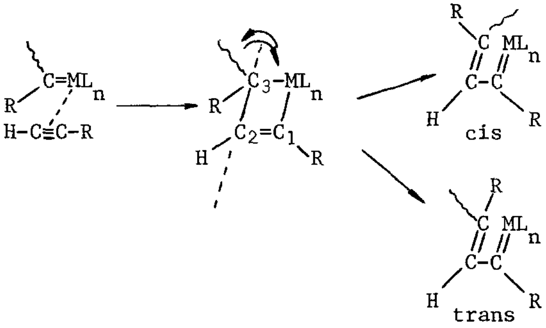

Figure 3. Mechanism of Geometric Structure Control

The metallacyclobutene then undergoes ring scission (cleavage of the C_3-metal linkage), and during this step the C_3-C_2 bond rotates around its axis to form a coplanar double bond (isomerization prior to double bond formation). According to Katz's mechanism, the polymer configuration is determined by this rotation because the C_3-C_2 bond would rotate in the way which will minimize the steric interaction between the coordinated metal (MLn) and the substituent R of the polymer chain. When oxygen or nitrogen containing solvents are used for polymerization, they will coordinate with the catalyst metal and consequently the coordinated active center should be bulky and susceptible to steric effects as compared with an uncoordinated one (15). In the case of t-butylacetylene polymerization, the coordinating solvent makes the t-butyl group exerts a greater steric effect than does the polymer chain and cis polymers form in these solvents (15).

Consequently, when PA is polymerized with $MoCl_5$, anisole in comparison with toluene increases the PPA cis content by a Katz mechanism, and at the same time it increases the rate of polymerization. The consequence of higher rate of polymerization will be an increase of cyclohexadiene sequences by a thermally induced intramolecular cyclization. As we already shown, the decrease in cis content at room temperature is as high as 15%/day for a PPA containing 80% cis sequences (7), and this rate is higher if the reaction takes place during propagation. Consequently, part of the cis sequences are transformed into cyclohexadiene and trans sequences under these reaction conditions.

Comparing the microstructure of PPA's obtained with $MoCl_5$-type catalysts in different reaction conditions (Table 1), we see that the polymers obtained in anisole present a concentration of trans sequences which is less than twice the concentration of cyclohexadiene sequences. On the other hand, the PPA obtained in toluene shows a much higher concentration of trans sequences than cyclohexadiene sequences. This difference can be explained by the difference in the mechanism of geometrical structure control. In anisole, most of the trans sequences are obtained due to thermal intramolecular cyclization, when at least one or two double bonds vicinal to the cyclohexadiene ring changes their configuration from cis to trans

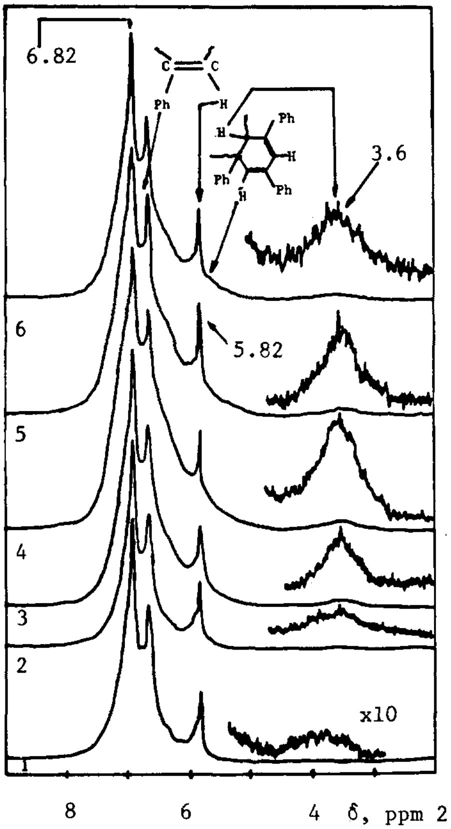

Figure 1. ^{1}H-NMR (CCl_4, TMS, 60°C) Spectra of PPA nos. 1-6 from Table 1

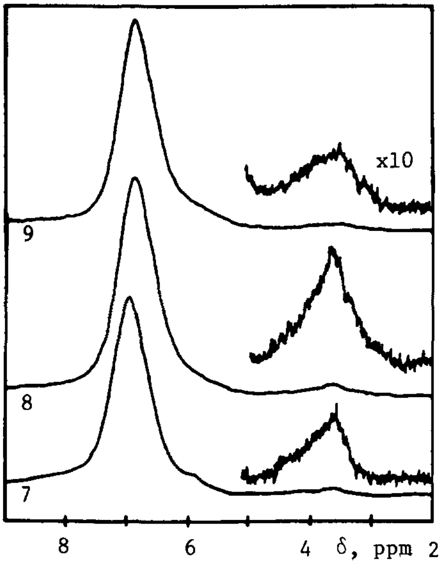

Figure 2. ^{1}H-NMR (CCl_4, TMS, 60°C) Spectra of PPA nos. 7-9 from Table 1

Table 1. Microstructure of PPA Obtained by $MoCl_5$ and WCl_6 Based Catalysts

No.	Catalyst	Polym. Solvent	Reaction Time hrs.	Polymer Yield %	Polym. Temp. °C	Polymer Composition fcx	fc	ft
(1)	$MoCl_5$-$SnPh_4$	T	2	10	25	0.03	0.54	0.43
(2)	$MoCl_5$-$SnPh_4$	T-A(1:1,V/V)	2	15	25	0.06	0.44	0.50
(3)	*$MoCl_5$-$SnPh_4$**	A	2	18	25	0.14	0.62	0.24
(4)	$MoCl_5$	A	24	20	25	0.21	0.47	0.32
(5)	$MoCl_5$	T	24	15	25	0.12	0.53	0.35
(6)	$MoCl_5$	A	24	15	5	0.22	0.50	0.28
(7)	WCl_6^a	T	2	15	25	0.30	0.00	0.70
(8)	WCl_6**	A	2	25	25	0.45	0.00	0.55
(9)	WCl_6^b	D	24	60	25	0.13	0.00	0.87

*monomer over catalyst; **exothermal reactions; $^a\bar{M}_n$ = 12,000; $^b\bar{M}_n$ = 90,000.

(8). In order to explain the high trans content concentration for the PPA obtained in toluene, we have to consider the second mechanism of geometric structure control, i.e., isomerization prior to double bond formation.

PPA obtained with WCl_6 catalyst contains only cyclohexadiene and trans sequences. It has been already shown by Higashimura et al. (11,15) that $MoCl_5$ leads to polymers containing higher concentrations of cis sequences than the polymers obtained in the presence of WCl_6. The explanation proposed was based on the difference in the atomic radius of these two metals (Mo shorter than W) which will give rise to different degrees of interaction with the monomer pendant groups.

The lowest concentration in cyclohexadiene sequences is obtained by using dioxane as a solvent. This demonstrates that most of the trans sequences are obtained through a Katz mechanism and only a very few by thermal isomerization. This polymer contains the highest trans content obtained so far by direct polymerization and has the highest molecular weight at the same time (19) (Table 1). The same polymer prepared in toluene, on the other hand, has a molecular weight ten times lower. The major structural difference between these two polymers is their content of cyclohexadiene sequences (Table 1).

A pertinent reason for this difference in the PPA molecular weight seems to be due to the difference in the initial cis content of these two polymers (formed by Katz mechanism). This is reflected in their final content of cyclohexadiene sequences as shown in Table 1. The termination reaction in the radical polymerization of PA is first order (20), and is considered to occur through the intramolecular cyclization of the cis-transoidal polymer chain end (10). The radical polymerization of PA also takes place with the opening of the triple bond in cis position (10), as in Ziegler-Natta catalyst polymerizations. On the other hand trans sequences can not lead to intramolecular cyclization reactions. Consequently, the higher the content in trans sequences obtained by isomerization prior to double bond formation, the higher should be the molecular weight of the obtained polymer. The experimental data confirmed this assumption (19). An even higher molecular weight (160,000) is obtained from β-ethynylnaphthalene (19) due to the fact that during propagation reactions, the intramolecular cyclization of the chain end is much more hindered than in the case of PPA.

By increasing the size of the acetylenic monomer pendant group, i.e., from phenyl to naphthyl, etc., the rate of thermally induced reactions decreases (8) and perhaps the control of stereochemistry is mainly by a Katz type mechanism. In the case of β-ethynylnaphthalene polymerization by $MoCl_5$ catalyst, mainly cis-configurations are obtained due to the fact that the interactions existing between naphthyl and MLn are higher than those between polymer chain and MLn. This explain why cis-cisoidal structures can be obtained by the polymerization of β-ethynylnaphthalene with $MoCl_5$ type catalysts (17).

CONCLUSIONS

By using 200 MHz ^{1}H-NMR spectroscopy it was possible for the first time to analyze the microstructure of PPA. Previously, the microstructural characterization was possible only on poly(pentadeuterophenylacetylene) (6). The microstructure of PPA obtained by metathesis catalysts is controlled both by isomerization prior to double bond formation as well as by thermally induced reactions after double bond formation. Isomerization prior to double bond formation can be controlled by the nature of the polymerization solvent. For example the polymerization of PA with $MoCl_5$ in anisole forms mainly polymer with cis sequences while the trans sequences are obtained basically by a thermal mechanism. In the case of the polymerization of PA with WCl_6 in dioxane, the thermal reactions are less important because the polymer contains a very high concentration of trans sequences obtained by isomerization prior double bond formation. This behavior explains why cis-cisoidal PPA could not be obtained by using metathesis catalysts, and also offers a plausible explanation for the high molecular weight of the polymer prepared with WCl_6 in dioxane. It is thought that metathesis type catalysts can lead to pure cis or trans polymers under reaction conditions in which thermally induced reactions would be completely avoided. Research is in progress to prove this.

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