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A ^{13}C-NMR Study of the Microstructure of Polyphenylacetylenes Prepared with $MoCl_5$ and WCl_6

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SUMMARY

The microstructure of polyphenylacetylenes prepared with $MoCl_5$ and WCl_6 catalysts in several solvents was studied by ^{13}C-NMR spectroscopy. Use of $^{13}C\{^1H\}$ INEPT (insensitive nuclei enhanced by polarization transfer) experiment aids the resonance assignments of cis, trans and cyclohexadiene structural units. The NMR spectral data confirm our previous findings regarding the roles of isomerization prior to double bond formation and thermal isomerization after double bond formation in the mechanism responsible for the control of polymer microstructure and molecular weight.

INTRODUCTION

^{1}H-NMR spectroscopic studies carried out on polyphenylacetylenes (PPA) (1-7) and poly(pentadeuterophenylacetylenes) (4, 5, 7) prepared with Ziegler-Natta and other coordinative catalysts, indicated that the polymerization of phenylacetylene (PA) always occurs with the addition to the triple bond to form cis olefin. Three isomeric structures can be obtained for the PPA prepared with Ziegler-Natta catalysts: cis-cisoidal, cis-transoidal, and trans-cisoidal (1). The first one is crystalline and insoluble. Support for the cis-cisoidal configuration of crystalline PPA was recently obtained from solution and solid state ^{13}C-NMR studies (8,9). The cis-cisoidal isomer is thought to appear by the isomerization of a pure cis-transoidal isomer during the polymerization process (1).

Thermally induced reactions of cis-PPA include formation of 1,3-cyclohexadiene sequences by intramolecular cyclization reactions and formation of trans structural units, a side reaction which seems to occur mainly by double bond migration (3-6). Consequently, the trans-cisoidal isomer contains a large fraction of cyclohexadiene sequences. Thermal treatment at a temperature greater than 120°C leads to polymer aromatization, chain scission and release of cyclic trimers. The intramolecular cyclization of the polymer chain end is accepted as the cause of the first order termination reaction in the thermal polymerization of acetylenes (10,11).

A 200 MHz ^{1}H-NMR study of the microstructure of PPA prepared in different solvents with Higashimura type catalysts (i.e., $MoCl_5$ and WCl_6) (12, 13) was presented in a previous paper (7). The molecular weight differences between dissimilarly prepared PPA samples were explained by two mechanisms which are available for control of the polymer microstructure. These two mechanism are thermal isomerization after double bond formation (4), and isomerization prior to double bond formation (14,15). The latter mechanism is only valid for metathesis polymerization. It was shown that when trans sequences are primarily formed by the second mechanism, very high molecular weight PPA is obtained which is almost void of cyclohexadiene sequences.

The present paper presents a ^{13}C-NMR study of PPA prepared with $MoCl_5$ and WCl_6 in various solvents. The ^{13}C-NMR spectra provide additional experimental evidence for the formation of cyclohexadiene units upon thermal isomerization during the propagation step. The large ^{13}C-NMR spectral dispersion allows resolution of all the resonances from cis, trans, and cyclohexadiene units in PPA, and provides a direct measure of the relative amounts of these units.

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: PA, 3.33 mole/l; catalyst 66.6 mmole/l, polymerization temperature: 20°C. The polymers were recovered by precipitation with methanol and purified by precipitation with methanol from THF solutions. ^{1}H- and ^{13}C-NMR spectra were obtained using a Varian XL-200 instrument (200 and 50 MHz, respectively) in CCl_4 at 60°C (^{1}H) and in $CDCl_3$ at 20°C (^{13}C). ^{1}H chemical shifts were referenced relative to TMS, and ^{13}C chemical shifts were referenced relative to $CDCl_3$ (at 77.0 ppm). ^{13}C-NMR spectra were obtained using a 15 KHz sweep width, 4 μs (30°) pulse width, 0.4 s acquisition time, 0.4 s repetition rate, and 5,000 transients. Various exponential weighting factors (line broadening 5-50 Hz) were used to optimize the signal to noise (using matched filter) for each of the signals of interest. $^{13}C\{^1H\}$ INEPT spectra were obtained using the standard software provided by the instrument manufacturer. PPA's microstructure (Table 1) was determined from ^{1}H-NMR spectra as was previously reported (7). Gel Permeation Chromatograms were obtained with μ-Styragel columns of 10^5, 10^4, 10^3 Å and a calibration plot constructed with polystyrene standards.

Table 1: Microstructure of PPA obtained by $MoCl_5$ and WCl_6 Based Catalysts

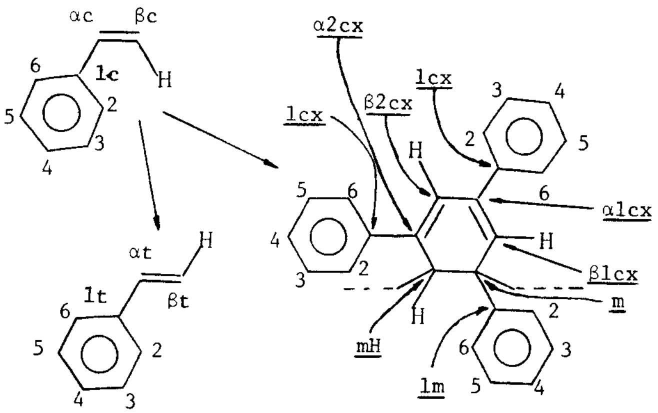
Polymer sample	Catalyst	Polymerization solvent	Reaction time, hr	Polymer color	Polymer composition		
					f_{cx}	f_c	f_t
MT	$MoCl_5$	T	3.5	orange	0.05	0.56	0.43
MA	$MoCl_5$	A	15.5	orange	0.18	0.40	0.42
WT	WCl_6	T	19.0	brick-red	0.30	0.00	0.70
WA	WCl_6	A	15.5	dark-orange	0.45	0.00	0.55
WD	WCl_6	D	19.0	brick-red	0.15	0.00	0.85

f = molar fraction, cx = cyclohexadiene, c = cis, t = trans.

RESULTS AND DISCUSSION

As shown in the previous paper (7), PPA-MT possesses the highest cis content, f_c = 0.56 (Table 1). Cis-transoidal PPA having ca. 95% cis sequences can be prepared with Ziegler-Natta catalysts without difficulty (1-6). When PA is polymerized by Ziegler-Natta type catalysts, the polymer cis content is largely dependent on the polymerization temperature. It was already demonstrated that the PPA microstructure is controlled by thermally induced reactions of the formed double bonds (1). In metathesis type polymerization, there is an additional mechanism which controls the polymer microstructure i.e., isomerization prior to double bond formation (7, 14, 15), so that trans double bonds are also formed by this mechanism and not only by thermal isomerization (7). Consequently, the solvent nature will strongly influence the polymer's cis, trans content. Figure 1 presents the ^{13}C-NMR spectra of PPA-MT, MA and MA-INEPT (MAi, vide infra). PPA-MT shows a spectrum almost identical with that of a cis-cisoidal polymer (8, 9). In addition we see two signals at 62.2 and 54.1 ppm which are due to sp^3 carbons. Our assignments of the aromatic resonances in Figure 1 differ from those of the previous workers (8,9). Insensitive nuclei enhanced by polarization transfer (INEPT) NMR experiments (16, 17) allow selective observation of only those carbons which have directly bonded protons. A typical INEPT spectrum is presented for sample MA (MAi, Figure 1). It demonstrates that the carbons at 142.8 and 139.2 ppm are quaternary. We have assigned these resonances to Cα (cis and trans; c,t) and C1 (cis and trans), respectively (Scheme 1). These assignments are based on the 137 ppm shift of C1 on styrene, the 137.2 ppm shift of C2 on 1,3-butadiene, and the fact that phenyl substitution on an olefinic carbon results in a large downfield shift of its carbon resonance (18). These assignments are confirmed by the disappearance of the 142.8 ppm resonance in thermally treated polymers which have been cyclized to lower the Cα (cis/trans) content. Similar use of the INEPT experiment allows identification of the resonances at 136.1, 131.7, 127.8 and 126.6 ppm as those arising from protonated carbons. The signal at **136.1 ppm is attributed to Cβ2cx, since the resonance of the methine carbons on butadiene are at 137.2 ppm.**

Scheme 1



PPA-MA possesses a lower content of cis sequences and a higher content of cyclohexadiene sequences (Table 1). This is confirmed by its ^{13}C-NMR spectrum (Figure 1). The aliphatic region of the PPA-MA increases in intensity in comparison with that of the PPA-MT spectrum. Again, application of the INEPT NMR experiment allows the assignment of the resonances at 62.2 and 54.1 ppm to methine and quaternary carbon atoms, respectively. These arise from the formation of cyclohexadiene units (sp^3 carbons) as shown in Scheme 1. The ratio of the signals at 142.8 ppm (Cαc, Cαt) and 139.2 ppm (C1c, C1t) changed in comparison with that in PPA-MT. This is

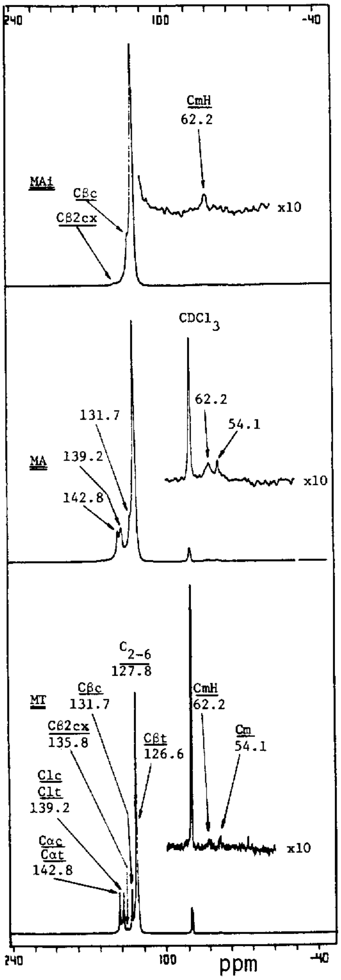


Figure 1: ^{13}C-NMR spectra of: PPA-MT (MT); PPA-MA (MA) and PPA-MA-INEPT (MAi)

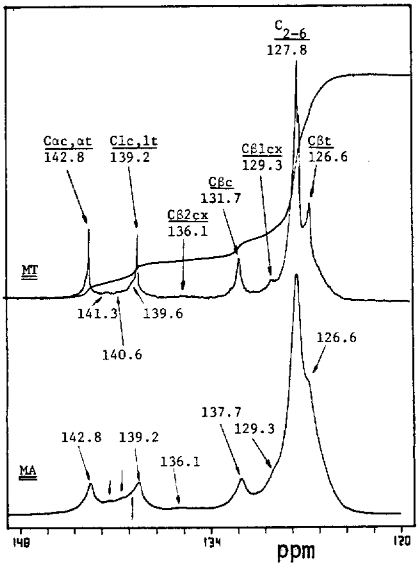


Figure 2: ^{13}C-NMR spectra of: PPA-MA (MA) and PPA-MT (MT)

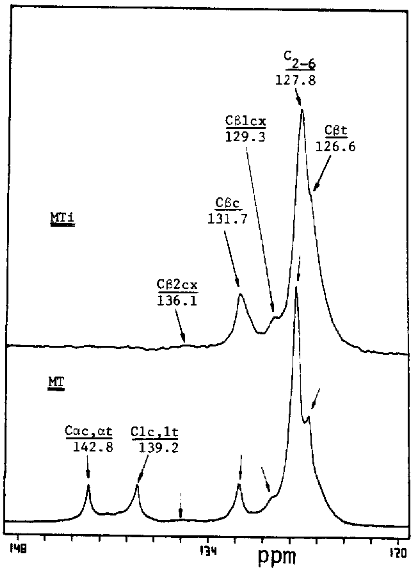


Figure 3: ^{13}C-NMR spectra of: PPA-MT (MT) and PPA-MT-INEPT (MTi)

expected as the decrease in cis content would decrease the number of Cαc carbons as a consequence of both double bond isomerization and formation of cyclohexadiene sequences. Cyclization will not significantly affect the ^{13}C resonance position of two of the three C1c carbons, but will result in an upfield shift for the resonances of all three Cαc carbons which form the cyclohexadiene unit; one Cαc becomes an sp^3 carbon (Cm) while the other two are part of a conjugated diene unit (Cα1cx and Cα2cx) instead of the conjugated polyene backbone. This difference can be better observed in Figure 2 which shows expansions of the aromatic region of the PPA-MA and MT spectra. At least three new resonances are observed at 141.3, 140.6 and 139.6 ppm which are due to Cα1cx, Cα2cx and C1cx (2 carbons). Additional experiments are necessary to completely assign these resonances. The signal due to C1m should appear at a lower field, and it can be observed in PPA samples having a higher concentration in cyclohexadiene sequences (Figure 5). The signal of Cβ1cx appears at 129.3 ppm.

Figure 3 presents expansions of the aromatic region of the spectra of PPA-MT and MTi (MT INEPT). The spectrum of PPA-MTi demonstrates that the signals at 129.3 and 136.1 ppm are due to protonated carbons and consequently supports our assignments.

Qualitative inspection of the spectra in Figures 1 and 2 shows that the quantitative analyses made by ^1H-NMR (Table 1) are reasonable. The decrease in PPA cis content in MA polymer is mainly due to the increase in cyclohexadiene sequences as was previously concluded (7).

The spectra of PPA-WT, WA and WD are presented in Figure 4. According to this figure and the data in Table 1, the cyclohexadiene content decreases in the following order: WA>WT>WD. PPA-WD still exhibits signals at 142.8 and 139.2 ppm. The other two polymers present only a resonance at 140.1 ppm. Expansions of the aromatic region of these spectra are shown in Figure 5. They all contain the signals diagnostic of cyclohexadiene sequences at 136.1 and 129.9, and 146.1 ppm. PPA-WT and WA have a broad signal centered at 140.1 ppm which contains the resonances of C1cx, Cα1cx and Cα2cx. No signals due to Cαc, Cαt (at 142.8 ppm) and C1c, C1t (at 139.2 ppm) appear in their spectra. This leads to the conclusions that PPA-WT and WA do not contain cis sequences, and that their trans content is not high. PPA-WD clearly contains a high concentration of trans sequences (126.5 ppm, Cβt) and low concentrations of cis (131.7 ppm, Cβc) and cyclohexadiene (129.3 ppm, Cβ1cx) sequences. In addition, the signals at 142.8 ppm (Cαc, Cαt) and 139.2 ppm (C1c, C1t) are present in PPA-WD spectrum. The quantitative determination of PPA-WD's cis content (Table 1, $f_c = 0$) is not accurate since the ^1H signals of cis sequences are not clearly resolved when there is very low cis content. The ^{13}C spectrum of PPA-WD indicates that there is still a small number of cis sequences in this polymer. An unidentified signal appears at 132 ppm in the spectrum of this polymer (Figure 5).

As we previously have assumed, the molecular weight of the PPA is controlled by the termination reaction involving the intramolecular cyclization of the cis-polymer chain ends (7). A cyclohexadienyl radical is sterically hindered and can be considered as a dead polymer chain end. This termination mechanism also explains the copolymerization behavior of PA with vinylic monomers (19, 20). Consequently, the PPA having a high concentration of trans sequences formed by isomerization prior to double bond formation should have a high molecular weight since intramolecular cyclization of its chain end is not probable. High molecular weight cis-PPA can be obtained when the termally induced reactions are avoided.

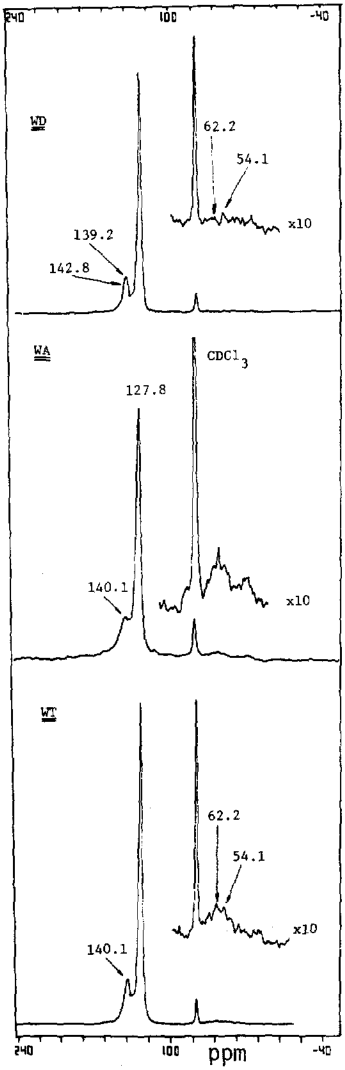


Figure 4: ^{13}C-NMR spectra of: PPA-WT (WT); PPA-WA (WA) and PPA-WD (WD)

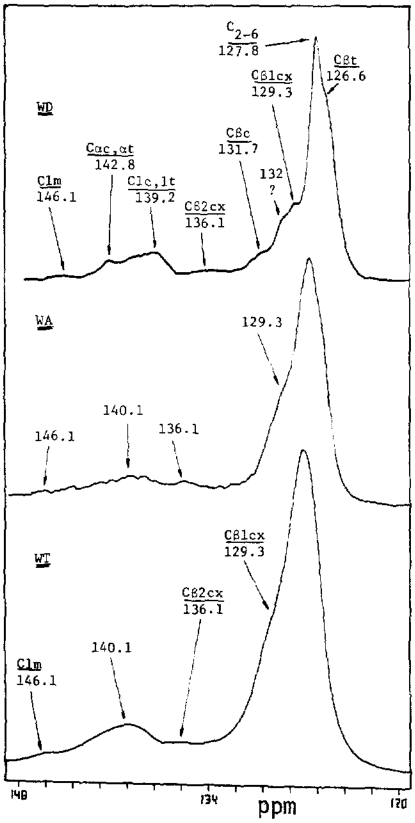


Figure 5: ^{13}C-NMR spectra of: PPA-WT (WT); PPA-WA (WA) and PPA-WD (WD)

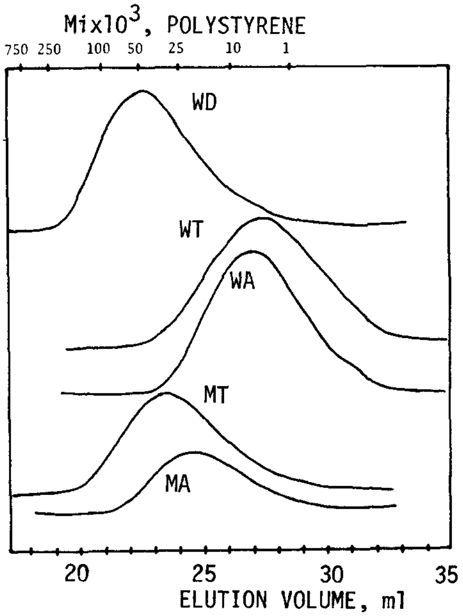


Figure 6: Gel Permeation Chromatograms of: PPA-WD(WD); PPA-WT(WT); PPA-WA(WA); PPA-MT(MT) and PPA-MA(MA)

The GPC curves of the polymers studied are presented in Figure 6 and demonstrate the validity of these conclusions. PPA-WD has the highest molecular weight. The second highest molecular weight is possessed by PPA-MT. All the other polymers contain high concentrations of cyclohexadiene sequences and have lower molecular weights.

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