Polymer Bulletin 9, 582-587 (1983)

Polymer Bulletin

^{13}C-NMR Studies of Thermally Isomerized Polyphenylacetylenes Prepared with $MoCl_5$ and WCl_6 Catalysts

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SUMMARY

^{13}C-NMR studies of thermally treated polyphenylacetylenes (PPA) prepared with $MoCl_5$ and WCl_6 catalysts provide evidence for intramolecular cyclization and chain scission of both cis and trans polymers. The microstructures of thermally treated cis and trans PPA are different from the microstructure of trans PPA obtained by thermal isomerization during propagation.

INTRODUCTION

A kinetic study of solution and solid state cis-trans thermal isomerization of cis polyphenylacetylenes (PPA) demonstrated that at higher temperature (>120°C) the reaction is accompanied by cyclization, aromatization, and scission of the polymer chain (1). A similar study carried out on poly(pentadeuterophenylacetylene) showed that even below 120°C intramolecular cyclization takes place (2). Subsequent work showed that coordinative and thermal polymerization both occur with cis addition to the triple bond and that thermally induced reactions are responsible for the observed polymer microstructure (2-4).

Poly(pentadeuterophenylacetylene) obtained by thermal polymerization contains a microstructure which does not differ from that obtained by thermal isomerization of a cis polymer (3). This indicates that a study of thermally induced reactions of cis polymer can contribute to an understanding of the thermal polymerization of acetylenic monomers. This reaction is used extensively for the development of matrix resins for lightweight composite materials (5,6), and its mechanism is not understood.

Recent 200-MHz ^{1}H-NMR (7) and ^{13}C-NMR studies from our laboratory provided new evidence for a PPA microstructure containing cis, trans, and cyclohexadiene sequences. These results also demonstrated that in the case of polymerizations with metathesis type catalysts (i.e., $MoCl_5$ and WCl_6) at least two mechanisms are responsible for the polymer microstructure: isomerization prior to double bond formation (leading to trans sequences) and thermal isomerization after double bond formation (leading to cyclohexadiene and trans sequences). Intramolecular cyclization of the polymer chain end is responsible for the first order termination in the polymerization of acetylenic derivatives. Consequently, when the trans polymer sequences are obtained mainly by isomerization prior to double bond formation, very high molecular weight polymers should be obtained. This was demonstrated by changing the nature of the polymerization solvent (7,8).

These acetylenic polymers were thought to have high thermal stability. It was shown that this high thermal stability of cis-polyacetylenes is illusory and that the products resulting from the thermal degradation (e.g. triphenylbenzene derivatives) have a low volatility (3). Consequently, for the cases studied, the evaluation of the polymer thermal stability by thermogravimetric measurements gave misleading results (9).

The present paper presents preliminary data from a ^{13}C-NMR study of thermally isomerized PPA samples prepared with $MoCl_5$ and with WCl_6 catalysts.

EXPERIMENTAL

The syntheses and characterizations of PPA-WD, PPA-MT and PPA-MA were presented in the previous paper (8) and their characteristics are shown in Table 1.

Thermal isomerizations were carried out in dimethylsulfoxide (DMSO) and hexachlorobutadiene (HCB) solutions or in the solid state (S), at 160°C under nitrogen for 6 hours. The isomerized polymers were purified by precipitation from tetrahydrofuran solution with methanol. Previously, it was shown that after this purification process the cyclic trimers obtained during isomerization are removed (1). NMR and GPC analyses were carried out as previously reported (8).

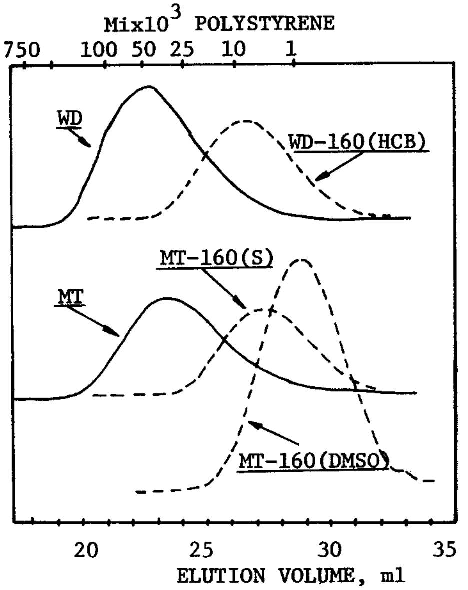
TABLE 1: Microstructure of PPA Obtained by $MoCl_5$ and WCl_6 Catalysts

Polymer sample	Catalyst	Polymerization solvent	Reaction time, hr	Polymer colour	Polymer composition		
					fcx	fc	ft
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
WD	WCl_6	D	19.0	brick-red	0.15	0	0.85

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

RESULTS AND DISCUSSION

Figure 1 presents the GPC curves of the following samples: PPA-WD, PPA-WD heated for 6 hours at 160°C in hexachlorobutadiene [WD-160(HCB)], PPA-MT heated for 6 hours at 160°C in solid state [MT-160(S)] and PPA-MT heated for 6 hours in DMSO [MT-160(DMSO)]. The most surprising behaviour is exhibited by sample WD-160(HCB). Despite the indication that fc=0 (for PPA-WD by ^{1}H-NMR Table 1), ^{13}C-NMR analyses (8) demonstrated the presence of a small concentration of cis sequences. This small concentration of cis sequences can not account for the more than 5 fold decrease of the polymer molecular weight. The low molecular weight was previously thought to arise from intramolecular Diels-Alder cyclization of cis polymeric units followed by chain scission (1-4). At least three consecutive cis-units are required for this reaction. Recent studies showed that Diels-Alder reaction can also occur for trans dienes (10) although the reaction rate is about 100 times slower. Consequently, at high temperatures the intramolecular cyclization reaction should also be considered for trans polyenes. The large decrease in the molecular weight of the PPA-MT upon thermal isomerization both in solid state [MT-160(S)] as well as in solution [MT-160(DMSO)] is expected (Figure 1). PPA-MT contains a high concentration of cis sequences and consequently the intramolecular cyclization followed by chain scission takes place.



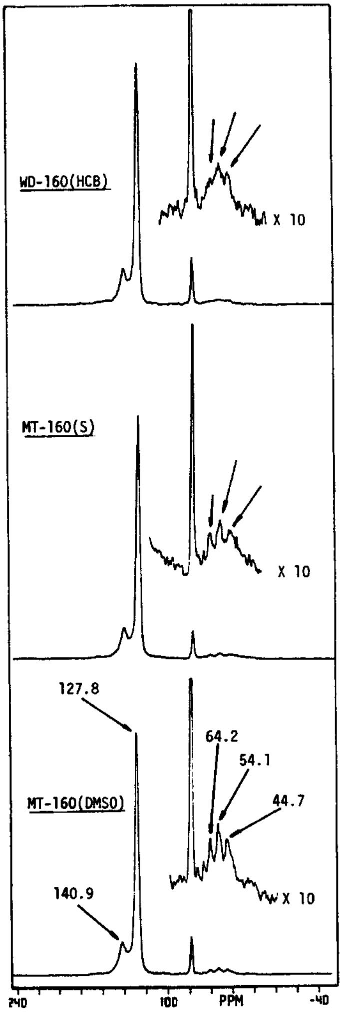


Figure 1: Gel Permeation Chromatograms of: PPA-WD (WD); PPA-WD heated at 160°C in HCB for 6 hr [WD-160(HCB)]; PPA-MT (MT); PPA-MT heated at 160°C in solid state for 6 hr [MT-160(S)] and PPA-MT heated at 160°C in DMSO for 6 hr [MT-160(DMSO)]

Figure 2: ^{13}C-NMR spectra of the following polyphenylacetylenes: WD-160(HCB); MT-160(S) and MT-160(DMSO)

Figure 2 presents the ^{13}C-NMR spectra of the thermally isomerized samples. It is interesting that the aliphatic region of all spectra are identical, exhibiting three signals at 44.7, 54.1, and 62.2 ppm. The signals at 54.1 and 62.2 ppm are present in the unisomerized samples and were previously assigned to the sp^3 carbons from cyclohexadiene units (i.e. methine and quaternary carbons, respectively) (8). The aromatic region of these spectra resemble that of the PPA containing a high concentration of cyclohexadiene sequences (8). The ^{13}C{^{1}H} INEPT spectrum of the sample MT-160-(DMSO) is presented in Figure 3. It demonstrates that the signals at 140.9 and 44.7 ppm are due to nonprotonated carbon atoms. In addition, the INEPT spectrum shows a decrease in the intensity of the signal at 54.1 ppm. Expansions of the aliphatic region of the PPA-MT spectra obtained before and after isomerization, are presented in Figure 4. It is clear from comparison of these spectra that the signal at 54.1 ppm represents a super-

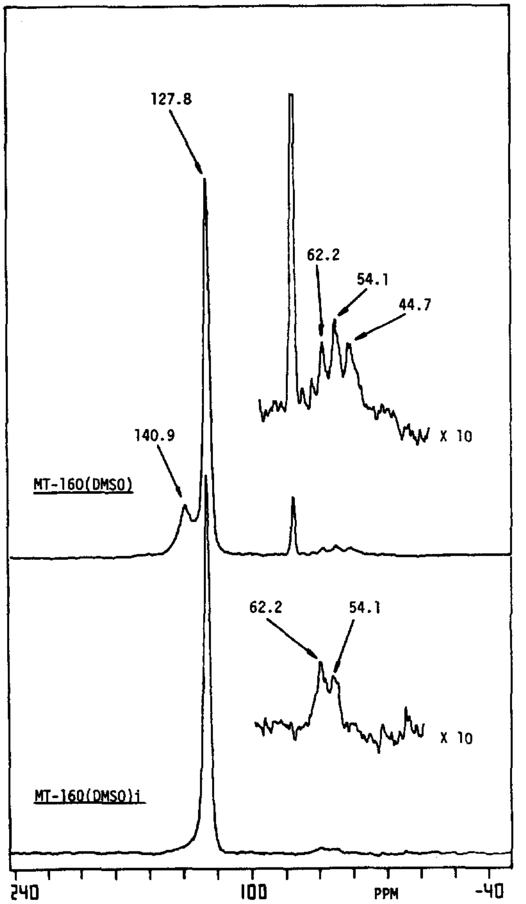


Figure 3: ^{13}C-NMR spectra of the following polyphenylacetylenes: MT-160(DMSO) and MT-160(DMSO)i (i=INEPT)

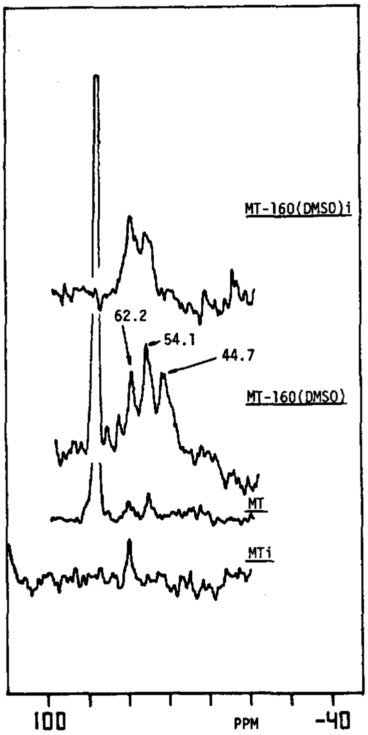


Figure 4: ^{13}C-NMR spectra of the following polyphenylacetylenes: MT-160(DMSO)i (i=INEPT); MT-160(DMSO); MT and MTi (i=INEPT)

position of two different resonances. One of this signals is due to a protonated carbon, and the other is due to a nonprotonated carbon. Consequently, during the thermal isomerization of both cis and trans PPA an increase in the 1,3-cyclohexadiene sequences (based on the increase of the signals at 62.2 and 54.1 ppm) occurs. This is accompanied by an additional reaction which gives rise to the other two signals at 54.1 ppm (protonated) and 44.7 ppm (nonprotonated). We are not yet able to assign these last two signals.

Expansions of the aromatic region of these spectra are shown in Figure 5. According to our previous assignements we can not find any evidence for the presence of cis or trans sequences in these spectra (8). The INEPT spectrum in Figure 3 also supports the fact that the signal at 140.9 ppm does not contain protonated carbons. In comparison with the spectra of the PPA containing high cyclohexadiene sequences obtained by isomerization during propagation, the thermally isomerized samples exhibit a shift of the downfield aromatic signal from 140.1 ppm to 140.9 ppm. This might result from

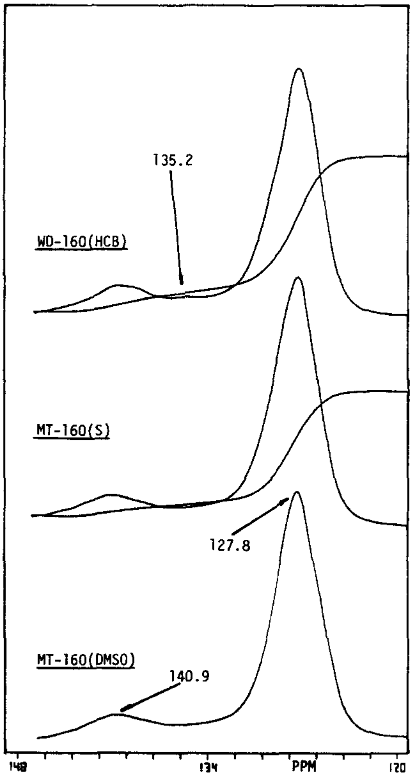


Figure 5: ^{13}C-NMR spectra of the following polyphenylacetylenes: WD-160(HCB); MT-160(S) and MT-160(DMSO)

the aromatization of the cyclohexadiene units.

The thermal intramolecular cyclization of both cis and trans PPA is a conceivable reaction; there is precedent for this reaction in the literature. The thermal cyclization of cis-1,3,5-hexatriene (11) and of 1,8-diphenyl-trans-1, cis-3,cis-3,cis-5,trans-7-octatetraene (12,13) to give cyclohexadienes are well known reactions. Other examples of intramolecular Diels-Alder reactions are presented in a recent review (14). The intramolecular cyclization of polyenes (undoubtedly trans) obtained by dehydrochlorination of polyvinylchloride are also well documented in literature (15-20). The simplest question which arises is: what is the influence of the size of a pendant group attached to a polyene chain on the intramolecular cyclization reaction ? Our experience has shown that steric hindrance induced by a bulky pendant group tends to decrease the probability of intramolecular cyclization (4). If this is so, then what is the probability for the intramolecular cyclization reaction coincident with the thermal cis-trans isomerization of polyacetylene? Can trans polyacetylene be prepared by using metathesis type catalysts ? Further research to answer these questions is in progress.

In conclusion, it was demonstrated that "thermal isomerization" of both cis and trans polyphenylacetylenes gives rise to intramolecular cyclization followed by chain scission. The intramolecular cyclization of the trans polymer was an unexpected reaction. The microstructure of the thermally isomerized cis and trans PPA are different from the microstructures of polymers whose cis structural units undergo thermally induced reactions during the propagation step. A new reaction leading to two additional sp^3 carbons occurs during polymer thermal isomerization.

ACKNOWLEDGEMENTS

Financial support from the Center for Applied Polymer Research and the National Science Foundation (grant ISI 81-16103) is acknowledged. We also thank the National Science Foundation (CHE-80-24633) and the sponsors of the Major Analytical Instruments Facilities at CWRU for funds used to purchase the VARIAN XL-200 NMR spectrometer.

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Accepted February 26, 1983 *C*