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Stereoregular polyphenylacetylene

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Summary

Phenylacetylene (PA) has been polymerized using Rh(I) catalysts and the resulting polymers characterized by elemental analysis, GPC ^1H and ^{13}C nmr and infrared spectroscopy. Very well resolved spectra have been recorded indicating that these catalysts produce highly stereoregular polymers.

Introduction

Conjugated polymers attract attention at present, some substituted alkynes are used as monomers for the synthesis of such materials. Phenylacetylene gives polymers which are usually soluble and also reasonably air stable and consequently have been widely studied. It is clearly desirable to obtain a detailed knowledge of the polymer structure; and in pursuit of this knowledge, a very large number of investigations have been conducted; many spectra have been published and many interpretations produced (1,6,7). However, universal agreement about the correlation of observed spectra with sample microstructure has not been achieved.

Recently we have used a new series of Rh^I complexes as catalysts for the polymerization of PA and have obtained high field ^1H and ^{13}C nmr spectra on the polymers which are very well resolved and which we believe are characteristic of a highly stereoregular microstructure. This paper records these results in a preliminary form.

Experimental

Six different Rh based catalysts have been used namely: $[Rh(COD)bipy]PF_6$ (COD = cyclooctadiene; bipy = 2,2' bipyridine, Polymer obtained = PPA 1)
$[Rh(COD)bipyam]PF_6$ (bipyam = di(α-α' piridyl) amine; PPA 2),
$[Rh(NBD)bipy]PF_6$ (NBD = norbornadiene; PPA 3),
$[Rh(COD)Cl]_2$ PPA 4, [Rh(COD)EDA]Cl (EDA = N-N-N'-N' tetramethylethylendiamine; PPA 5) and [Rh(COD)TEDA]Cl (TEDA = triethylendiamine; PPA 6) (8).

In a typical experiment redistilled phenylacetylene (5 g) was dissolved in methanol (20 ml) at room temperature; the solution was stirred and the solid catalyst [Rh(NBD)bipy]-PF_6 was added in a monomer to catalyst molar ratio of 273:1. The mixture was refluxed for 3 hrs. and the polymer, a bright yellow powder, recovered by filtration, washed with methanol, and dried to give PPA (90%; found C: 94.12%; H: 5.48%; calc. for $(C_8H_6)_n$ 94.08; 5.92%). GPC measurements were performed using a Perkin Elmer 601 liquid chromatography apparatus containing 3 PL gel columns (10^5, 10^3 and 500 A) from Polymer Laboratories Ltd. and RI and UV detectors.

Results and Discussion

GPC analysis of THF solutions of PPA 4 and PPA 5 showed single broad peaks between the retention volumes of polystyrene standards of M_n 100.000 and 10.000; we can therefore conclude that the products are genuine polymers. All the IR spectra of PPA samples obtained were similar and showed bands at 740, 895, 920 cm^{-1} which have been repeatedly used as characteristic of cis-polyphenylacetylene (1,2, 6).

Both ^{13}C and ^{1}H nmr spectra of the PPA produced in this study seem to be somewhat better resolved than those reported previously, PPA 4 gave particularly well resolved spectra (Fig. 1 and 2). The spectra are consistent with the hypothesis that these catalysts give a high degree of stereoregularity. Fig. 1 shows an excellent signal to noise and resolution: the quality of resolution can be judged by reference to chloroform hydrogen signal at 7.25 p.p.m. The sharp singlet at 5.84 p.p.m. can be assigned to the backbone hydrogen resonance of the PPA chain; the system at 6.63, 6.64, 6.93, 6.95 p.p.m. can be assigned to a AA' MM' N system arising from the phenyl ring hydrogens as indicated; the integrated intensities are in required 3:2:1 ratio and the coupling constant between the ring hydrogens at b and c is 6.3 Hz. The low intensity peaks at low field are consistent with the presence of small amounts of triphenylbenzene. The spectrum shown in Fig. 2 also displays good signal to noise and resolution. The DEPT spectrum identifies the quaternary carbon resonances at 142.81 and 139.32 p.p.m., the signal at 131.71 p.p.m. is assigned to the vinylic carbon, carrying hydrogen: the aromatic ring carbons carrying hydrogen are seen at 127.67 and 127.49 (ortho and meta) and 126.59 (para) p.p.m. It is clear that we are dealing with a highly stereoregular polymer with an all head to tail structure, owing the presence of a singlet at 5.84 p.p.m. in the ^{1}H nmr spectrum. ^{1}H and ^{13}C NMR spectral data for PPA reported in the literature are collected in Table 1.

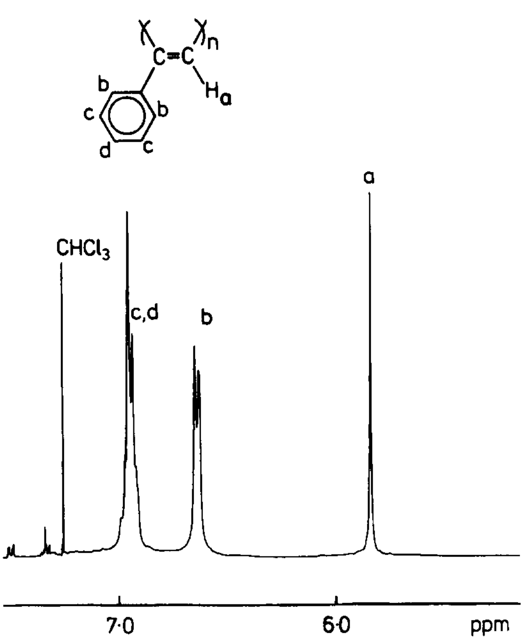

Figure 1. ^1H nmr spectrum of PPA 4 @ 360.4 MHz

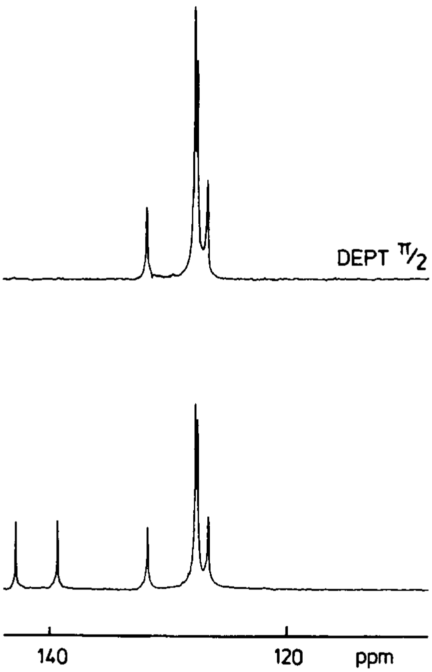

Figure 2. ^{13}C nmr spectrum of PPA 4 @ 90.56 MHz

Berlin et al. (9) reported ^1H nmr spectra for various PPA samples. On the basis of an examination of models for four types of PPA chain conformation they proposed that the signal for two of the benzene ring protons would be below 6.4 p.p.m. in the trans-transoidal structure (a helix with 12 monomer units per coil); no shift to strong field was expected for the trans-cisoidal conformation of the PPA chain (helix with three monomer units per coil). In the

TABLE 1. ^1H and ^{13}C nmr spectral data for PPA

^1H δ values[a,b]					proposed structure	Ref.
5.6	7.2 (two broad signals)				cis-transoidal	9
5.82(1)	6.7(1)	6.85(4)			"	2
5.83[β]	6.67[o]	6.99[m]	7.2[p]		cis-cisoidal	10
5.85	6.70		7.1		cis (E)	11
5.82		6.82			cis-transoidal and trans	7
5.84(1)	6.63-6.64(2)		6.93-6.95(3)			this work
^{13}C δ values						
142.6	139.2	131.5	127-128	126.6	cis-cisoidal	10,12
142.8	139.2	131.7	129.9-127.8	126.6	cis and trans	13
142.8	139.3	131.7	127.6 127.4	126.6		this work

a) intensities are given in parentheses; b) β proton of the polyenic chain o, m, p. protons of the benzene ring.

case of a cis-transoidal conformation two protons, one on the benzene ring and one on the polyene chain, were expected to be shifted to stronger field. They assigned trans-cisoidal (PPA-T) and cis-transoidal (PPA-C) on the basis of this analysis.

Simionescu et al. (2) reported similar spectra for PPA obtained with Ziegler-Natta type catalysts. Using Berlin's analysis they assigned their material a cis-transoidal structure. We have recorded similar ^{1}H nmr spectra for PPA samples exposed to some solvents or elevated temperatures, and observe that such treatments can result in a deterioration of the spectral resolution. For example, the spectrum of PPA 1 (Fig. 3) which was purified by precipitation from THF into hexane is considerably less well resolved than an untreated sample. In some cases, for example PPA 2, we observe extra spectral features on untreated (solvent or heating) samples and it seems likely that in these cases a polymer of lower stereoregularity is formed (see Fig. 4).

The intensity ratio of the signals of the ^{1}H nmr spectrum reported by Simionescu (see Table 1) is 1:1:4, but in the well resolved spectrum of Fig. 2 we observe a 1:2:3

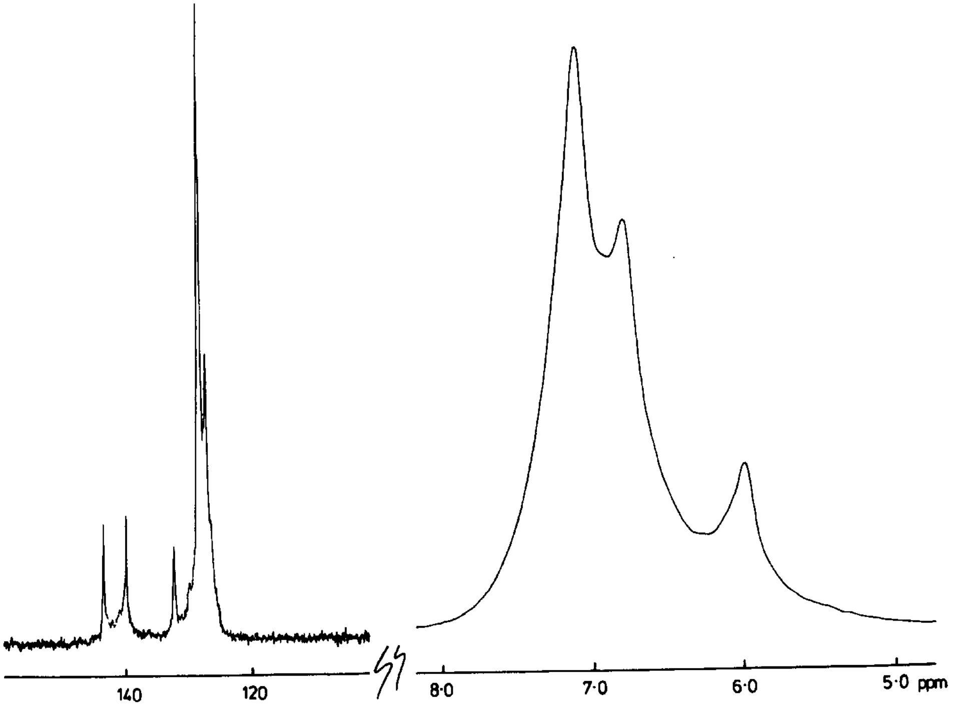

Figure 3. ^{13}C and ^{1}H nmr spectra for PPA 1

ratio, consistent with protons in a highly stereoregular PPA chain.

In a recent paper Katz (11) reported an analogous ^1H nmr spectrum for PPA-C for which he proposed a cis (E) structure, on the basis of the Simionescu's hypothesis. ^{13}C and ^1H nmr spectra of PPA-C have been reported by Sanford et al. (10,12). The ^1H nmr spectrum was similar to those reported previously, but the polymer was assigned a cis-cisoidal structure although Simionescu had predicted that for cis-cisoidal PPA only the resonance of one aromatic proton could be shifted to lower values of δ (2). The assignment rested on a comparison of ^{13}C nmr spectrum of the PPA sample with that of 1,3,5-triphenylbenzene (1,3,5 TPB), but re-examination of the data for the model compound suggests that Sanford's δ values for 1,3,5-triphenylbenzene are in error. The δ values for ^{13}C nmr spectra reported by Percec (3) are in agreement with those given by Sanford et al. and with this work (Table 1). However according to Percec, polymers of cis-cisoidal structure cannot be obtained with either WCl_6 or $MoCl_5$, which were the catalysts he used. He attributed the signal at 142.8 p.p.m. to the quaternary carbon atoms of polymeric chains both of cis-

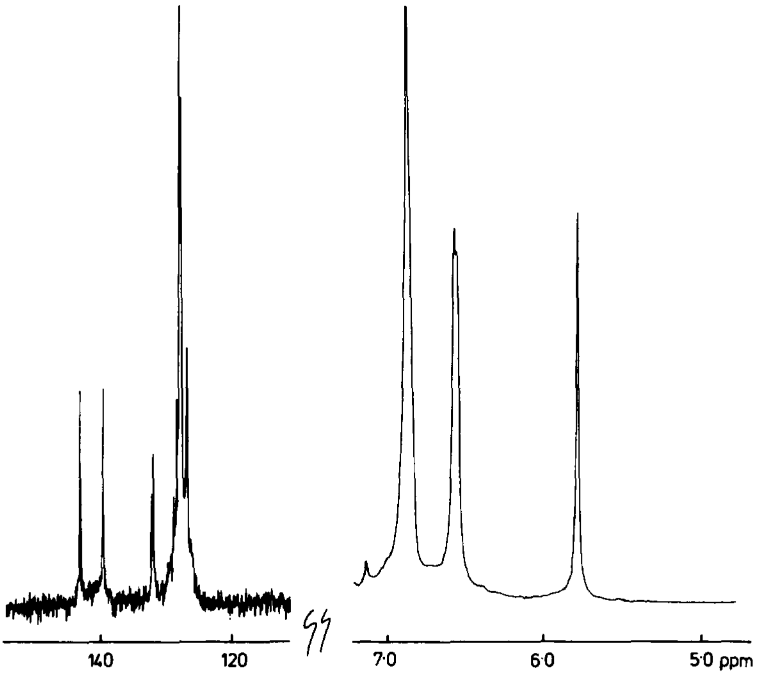

Figure 4. ^{13}C and ^1H nmr spectra for PPA 2.

transoidal or trans-cisoidal structure. The signal at 139.2 p.p.m. is attributed to quaternary carbon atoms of the benzene rings (also in cis or trans chain segments). A weak signal at 129.3 p.p.m. was assigned by Percec to cyclohexadienic structures in the chains. The signal at 126.6 p.p.m., which Percec assigned to CH group of trans vinylene units, was attributed by Sanford to vinylene segments of cis-cisoidal structure.

Clearly there is considerable uncertainty about the interpretations of the details of these ^{13}C and ^{1}H nmr spectra. As we have observed in a previous paper (14) it is evident that different catalysts give rise to polymer with similar structures, because of the similarity of the IR and nmr spectra reported in the literature. The Rh complexes that we have now used as catalysts give a product which appears to be highly stereoregular PPA. The stereoregularity of the polymeric chain is demonstrated by the well resolved ^{1}H and ^{13}C nmr spectra. Comparison of the spectroscopic data for the PPA produced in this study with those published previously suggests that either the initiators used by previous workers do not produce such highly regular materials or that the structural homogeneity of their initial products is degraded during recovery of product and/or by solvent treatment. The data given for the highly stereoregular PPA produced in this study is insufficient to unambiguously define the chain microstructure but can probably be correlated to a regular head-tail cis-transoidal structure. Further investigations to confirm this hypothesis are in progress.

Conclusion

Stereoregular polyphenylacetylene can be produced using Rh(I) based catalysts. The polymer structure and/or conformation is very sensitive to thermal and solvent induced isomerization.

Acknowledgements

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