

An approach to the preparation of conjugated polyradicals

C. Alexander and W. J. Feast*

Interdisciplinary Research Centre in Polymer Science, Department of Chemistry, Science Laboratories, South Road, Durham DH1 3LE, UK

SUMMARY

A new conjugated polymer, (poly(4-ethynylphenyl)diphenylmethyl) was prepared and characterized. The preparation involved the synthesis of a new acetylenic monomer, (4-ethynylphenyl)diphenylmethanol, which was polymerized by the well-defined catalysts $(t\text{-BuO})_2\text{Mo}(=\text{CH-}t\text{-Bu})(\text{NAr})$ and $[\text{Rh}(\text{COD})\text{Cl}]_2$. The resulting conjugated polymer was reacted with thionyl chloride and then reduced with silver to yield a material with pendant triphenylmethyl radicals attached to the conjugated polymer chain.

INTRODUCTION

In recent years there has been a considerable and growing interest in the field of organic and molecular ferromagnetism. There are several reports of systems exhibiting bulk ferromagnetic behaviour (1-9); however, there appears to be little correlation between the structures of these systems and those structures previously predicted to be good candidates for organic ferromagnets (10-13). This observation led us to attempt to test directly some of the theories formulated in this area. In particular, since certain conjugated polyradical species were predicted to exhibit ferromagnetic behaviour, the syntheses and characterization of such polymers were the main objectives of this work.

We decided to prepare a poly(acetylene) substituted with triphenylmethyl radicals. Although a number of studies of conjugated polyradicals as possible organic ferromagnets have been published (14-18), the preparation of poly(4-ethynylphenyl)diphenylmethyl is previously unreported. The synthetic sequence involved the preparation and polymerization of a suitably substituted acetylene, followed by functional group modification to generate the radical centres. This scheme is shown in Figure 1.

EXPERIMENTAL

Materials

All solvents were dried before use and stored under dry nitrogen. Benzene, toluene, tetrahydrofuran, and diethyl ether were distilled twice over sodium or potassium in the presence of benzophenone. Pyridine and triethylamine were distilled from fresh KOH pellets and stored over freshly activated 4A molecular sieves. Dichloromethane and carbon tetrachloride were distilled over P_2O_5 and stored over freshly activated 4A molecular sieves. All other reagents were used as received from Aldrich or Lancaster Synthesis.

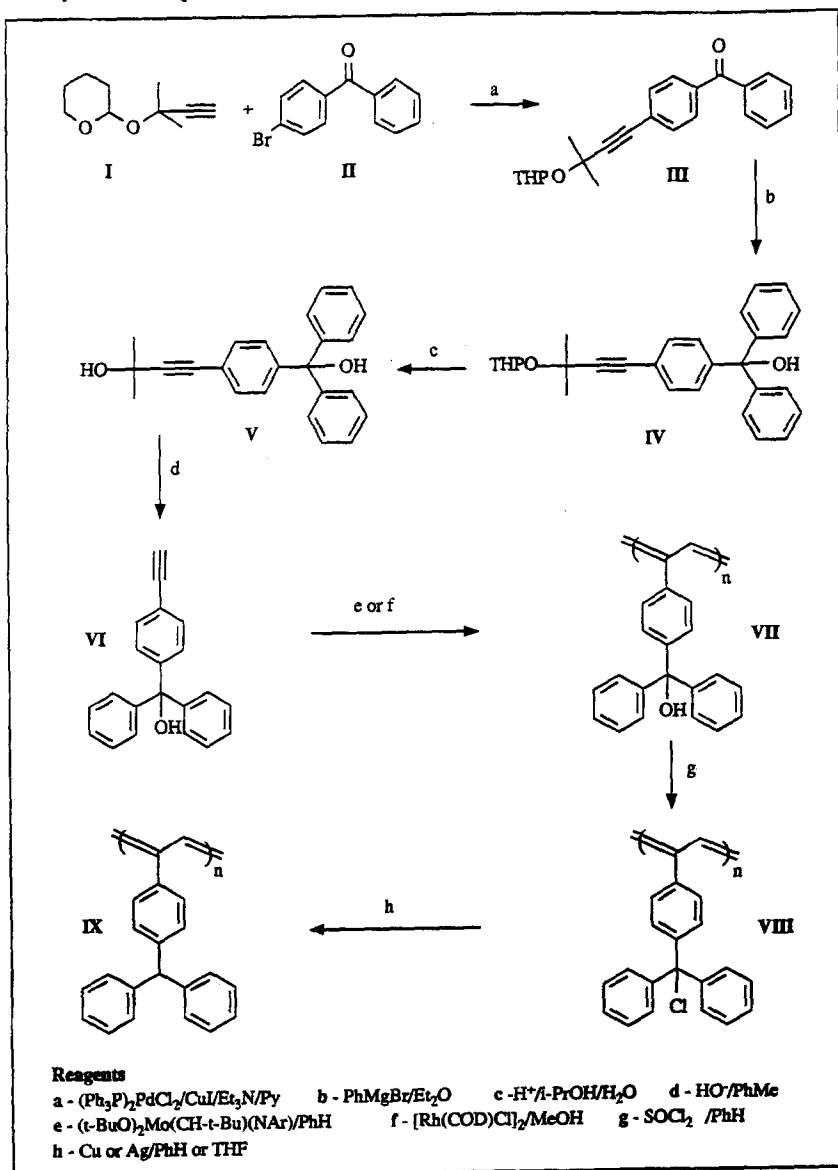
Instruments

Infra-red spectra were recorded on a Perkin-Elmer Model 577 Grating Spectrometer as thin films between KBr plates or as KBr discs. NMR spectra were recorded on a Varian VXR 400 spectrometer at 399.952 MHz (^1H) and 100.577 MHz (^{13}C) as solutions in

*To whom offprint requests should be sent

CDCl_3 or C_6D_6 . Elemental analyses were obtained from a Carlo-Erba Model 1105 Analyser. Mass spectra were recorded using a VG Analytical Model 7070E spectrometer. Gel permeation chromatography was carried out using a Waters Model 590 pump, Waters Model R401 Differential Refractometer detector, Polymer Laboratories PLgel cross-linked polystyrene columns, equipped with an SIC Chromacorder 12 computing integrator. Manipulations of air-sensitive materials were carried out under nitrogen in Faircrest MB41 or Miller-Howe P3131 Gloveboxes equipped with BASF copper alloy and molecular sieve deoxygenating or drying columns. Where the use of a Glovebox was not practicable, standard high vacuum line and Schlenk techniques were used.

Figure 1. Synthetic Sequence



Monomer synthesis

The method of Partridge (19) was used without modification for the preparation of 2-tetrahydropyran-yloxy-2-methyl-but-3-yne (I). 4-Bromobenzophenone was used as received from Aldrich. 4-(2-Tetrahydropyran-yloxy-2-methylbut-3-ynyl)benzophenone (II) was obtained via a modification of the standard palladium catalysed reaction of alkynes with aryl halides (20).

(4-(2-(Tetrahydropyran-yloxy)-2-methylbut-3-ynyl)phenyl)diphenylmethanol (IV) and (4-(2-methyl-2-hydroxyl)but-3-ynylphenyl)diphenylmethanol (V) were obtained by an adaptation of the method used by Manning (21) to prepare (4-bromophenyl)diphenylmethanol, followed by a new method of removing the tetrahydropyran-yl protecting group. This part of the reaction sequence can be carried out without isolation of (IV) i.e. as a "one pot" procedure to give (V) directly. The alkyne protecting group was removed by refluxing with sodium hydroxide in toluene to give the monomer (4-ethynylphenyl)diphenylmethanol (VI). The overall yield of VI from II was 46%, compounds III to VI inclusive are all new and the details of their synthesis and characterisation will be published elsewhere.

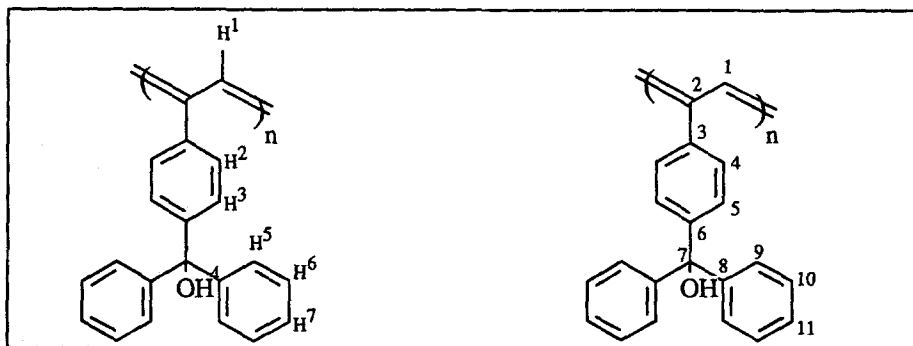
Polymerisation

The polymerisation catalysts $((t\text{-BuO})_2\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr}))$ where Ar = 2,6-di-*iso*-propylphenyl, and $[\text{Rh}(\text{COD})\text{Cl}]_2$ were prepared by literature methods (22,23). The polymer prepared using the molybdenum catalyst is referred to as (VII-Mo), and that using the rhodium catalyst as (VII-Rh).

Method A- Molybdenum catalysed polymerisation (VII-Mo)

A solution of (4-ethynylphenyl)diphenylmethanol (2.84g, 10mmol) in benzene (5ml) was added via cannula wire to $(t\text{-BuO})_2\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})$ catalyst (48.7mg, 0.1mmol) in benzene, with rapid stirring. The reaction was carried out for 24 hours at room temperature before addition to methanol (200ml). Repeated cycles of centrifugation (20,000rpm, 10 minutes), dissolving in benzene (15ml), and precipitation in methanol (200ml) gave *poly*((4-ethynylphenyl)diphenylmethanol) (VII-Mo) as an orange polymer (1.70g, 60%). Calculated for $\text{C}_{21}\text{H}_{16}\text{O}$: C, 88.70%; H, 5.67%; found C, 88.00%; H, 5.74%. Gel Permeation Chromatography (GPC): $M_w = 47,400$, $M_n = 21,000$; $M_w/M_n = 2.3$. ν (thin film)/ cm^{-1} : 3550, 3480 (OH), 3080, 3060, 3020 (aromatic CH), 1605 (C=C). ^1H NMR: The spectrum contained one broad, poorly resolved absorption. No hydroxyl protons were identified in the spectrum; δ/ppm (C_6D_6): 6.7-7.4 (H^{1-7}).

Figure 2 Numbering System for (VII-Mo) and (VII-Rh)



^{13}C NMR: δ/ppm (CDCl_3): 127.07, 127.16, 127.48, 127.87, 128.06, 128.22, 128.48, 128.66, 129.03, 131.71 ($\text{C}^{1,4,5,8-11}$), 146.44 ($\text{C}^{2,3,6,8}$).

The ^{13}C NMR CP/MAS spectra confirmed that the peaks at 81 and 146ppm were due to quaternary carbons. δ/ppm : 81.65 (C^7), 127.72 ($\text{C}^{1,4,5,8-11}$), 146.30 ($\text{C}^{2,3,6,8}$). QS: 127.78. NQS: 82.04, 127.85, 146.30.

Method B- Rhodium catalysed polymerisation (VII-Rh).

(4-Ethynylphenyl)diphenylmethanol (2.84g, 10mmol) was dissolved in dry, degassed methanol (20ml) at 50°C , and added to $[\text{Rh}(\text{COD})\text{Cl}]_2$ (24.9mg, 0.05mmol) in boiling methanol (30ml). The solution was stirred at 25°C for four hours and then centrifuged (20,000rpm, 10 minutes). The resultant brown solid was washed repeatedly with dry methanol to give: poly((4-ethynylphenyl)diphenylmethanol) (VII-Rh, 2.20g, 78%). Calculated for $\text{C}_{21}\text{H}_{16}\text{O}$: C, 88.70%; H, 5.67%; found C 88.30%, H, 5.54%. GPC: $M_w = 55,400$, $M_n = 6,500$; $M_w/M_n = 8.6$. ν (thin film)/ cm^{-1} : 3580, 3480 (OH), 3080, 3060, 3020 (aromatic CH), 2980 (w, aliphatic CH), 1605 (C=C); ^1H NMR: (integrals in parentheses). δ/ppm (C_6D_6): 2.7-3.1 (1, H^4), 6.2-7.1, 7.3-7.8 (10, $\text{H}^{1-3,5-7}$). ^{13}C NMR: δ/ppm (C_6D_6): 82.10 (C^7), 125.61, 127.47, 127.73, 127.98, 128.21, 128.49, 129.24, 131.85 ($\text{C}^{1,4,5,9-11}$), 147.37 ($\text{C}^{2,3,6,8}$).

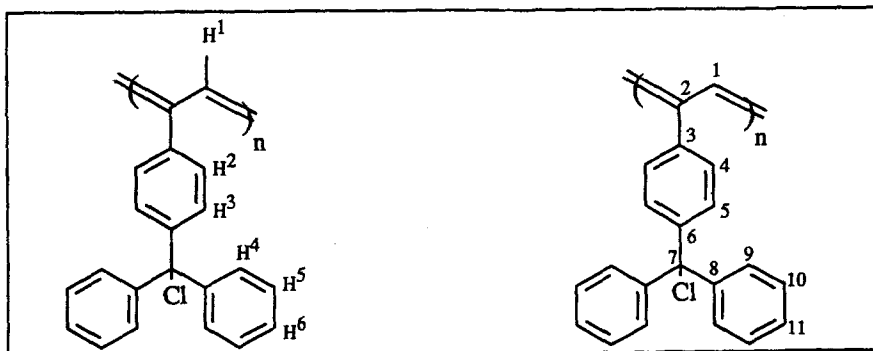
Polymer modification

Preparation of Poly(4-ethynylphenyl)diphenylchloromethane (VIII)

The same method of chlorination was used for both (VII-Mo) and (VII-Rh), giving polymers denoted as (VIII-Mo) and (VIII-Rh).

Poly(4-ethynylphenyl)diphenylmethanol (1.34g, 5mmol) was dissolved in benzene (20ml). The solution was stirred as freshly distilled thionyl chloride (2ml, ~20mmol) was added via cannula wire. The solution darkened almost immediately, and heat was evolved. Infra-red spectroscopy of films cast from solution indicated complete disappearance of hydroxyl groups after two hours. The solvent and unreacted thionyl chloride were then removed *in vacuo* (12hrs, 10^{-3} torr), leaving shiny red-brown flakes of poly(4-ethynylphenyl)diphenylchloromethane (VIII-Mo), (1.48g, 98%). Calculated for $\text{C}_{21}\text{H}_{15}\text{Cl}$: C, 83.29%; H, 5.00%; Cl, 11.71%; found C, 82.62%; H, 5.41%; Cl, 11.75%. GPC: $M_w = 22,900$, $M_n = 8700$; $M_w/M_n = 2.6$. ν (thin film)/ cm^{-1} : 3080, 3060, 3020 (aromatic CH), 1605 (C=C), 780 (C-Cl). ^1H NMR: broad unresolvable resonances were observed. δ/ppm (C_6D_6): 6.4-7.6 (H^{1-6}). Small peaks observed at 0.8-2.4 and 4.2ppm were assumed to be due to impurities. ^{13}C NMR: the polymer was not sufficiently soluble for solution state ^{13}C NMR spectra to be recorded. CP/MAS: δ/ppm : 81.29 (C^7), 128.50 ($\text{C}^{1,4,5,9-11}$), 144.82 ($\text{C}^{2,3,6,8}$). QS: 128.50. NQS: 144.69, 128.42, 81.88.

Figure 3 Numbering System for (VIII-Mo) and (VIII-Rh)



The yield for VIII-Rh, prepared in the same manner as VIII-Mo, was 1.24g (82%). Losses were incurred due to precipitation of some polymer on addition of thionyl chloride.

The recovered polymer was considerably less soluble in benzene and chloroform than the corresponding molybdenum prepared precursor.

For *poly(4-ethynylphenyl)diphenylchloromethane* (VIII-Rh); found C, 83.75%; H, 5.20%; Cl, 11.05%. GPC: $M_w = 3040$; $M_n = 1760$; $M_w/M_n = 1.7$. Note: the polymer was only slightly soluble in THF. ν (thin film)/ cm^{-1} : 3080, 3060, 3020 (aromatic CH), 1600 (C=C), 790 (C-Cl). ^1H NMR: broad poorly resolved absorptions: δ/ppm (CDCl_3): 5.6-5.7, 6.4-6.5, 6.6-7.4; (H^{1-6}). ^{13}C NMR: the polymer was not sufficiently soluble for solution state ^{13}C NMR spectra to be recorded. CP/MAS: δ/ppm : 80.73 (C^1), 127.60 ($\text{C}^{1,4,5,8-11}$), 144.70 ($\text{C}^{2,3,6,8}$). QS: 127.54. NQS: 144.60, 127.70, 80.79.

Preparation of Poly((4-ethynylphenyl)diphenylmethyl) (IX)

The removal of the tertiary chlorine atoms from the polymers was attempted with a range of metals and other reducing agents, under conditions found to be effective for the preparation of triphenylmethyl radicals. All manipulations were carried out in a GloveBox, or on a vacuum-line with glassware repeatedly dried, evacuated and purged with dry nitrogen.

A typical procedure is outlined below, with exact reagents and conditions recorded in Table 1. No major difference was observed between the reactivity of (VIII-Mo) and (VIII-Rh) samples.

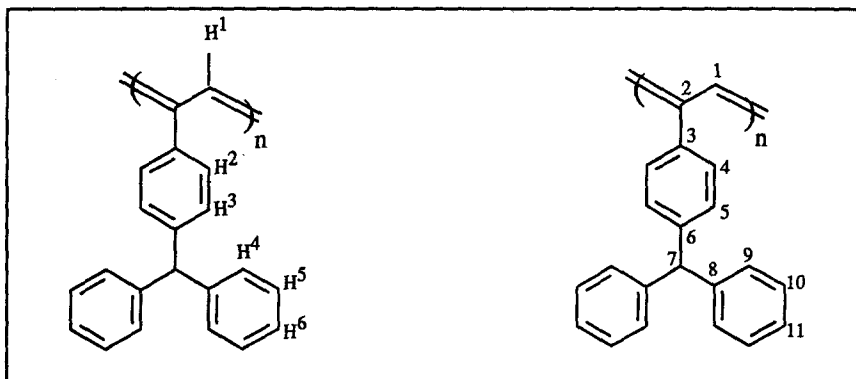
Table 1

<u>Reducing Agent</u>	<u>Solvent</u>	<u>Time</u>	<u>Temperature / Conditions</u>
Cu turnings	Benzene	2 hr	25 ⁰ C
Cu turnings	Benzene	3 hr	70 ⁰ C
Cu turnings	Benzene	6 hr	70 ⁰ C
Na/Hg(1%) amalgam	Benzene	14hr	reflux.30 fold xs Na/Hg.
Na/Hg(1%) amalgam	Benzene	14hr	reflux1hr: overnight 25 ⁰ C
Zn	Benzene	14hr	25 ⁰ C.20 fold xs Zn powder
Zn	Benzene	48hr	25 ⁰ C. High dilution: 6mM
Zn	Benzene	1hr	60 ⁰ C 100fold xs Zn
Zn	THF	2hr	60 ⁰ C Stirred 3 days 25 ⁰ C
Zn	Benzene	2hr	25 ⁰ C. Ultrasound at 40kHz
Ag	THF	2hr	Reflux
Ag	THF	30min	25 ⁰ C. Ultrasound at 40kHz
Ag	THF	2hr	25 ⁰ C. Ultrasound at 40kHz

A solution of the chlorinated precursor (151mg, 0.5mmol in C-Cl units) in dry, degassed solvent was stirred rapidly as the dechlorinating agent (5mmol) was added. After the reaction was adjudged to have reached completion, the mixture was filtered through a cannula wire fitted with glass and paper filters, and then passed twice through a sinter funnel (Porosity 3). Removal of solvent *in vacuo* left black shiny flakes of *poly(4-ethynylphenyl)diphenylmethyl* (IX); calculated for $(\text{C}_{21}\text{H}_{15})_n$: C, 94.34%; H, 5.66%. Found C, 91.41%; H, 5.17%, Cl, 1.21% (best figures): \bar{C} , 78.68%; H, 5.96%, Cl, 4.96% (typical and repeatable result); GPC: $M_w = 19,600$; $M_n = 8000$. $M_w/M_n = 2.4$.

ν (thin film)/ cm^{-1} : 3580 (weak OH), 3080,3060,3020 (aromatic CH), 1605 (C=C), 1270, 880 (w), 740. In several samples, a broad absorption was observed between 1000-1200 cm^{-1} , possibly due to aliphatic ether (see Discussion).

Figure 4. Numbering System for (IX)



^1H NMR: δ/ppm (CDCl_3); 5.2-7.8 (broad, unresolved resonance). Assignment of specific protons was not possible.

^{13}C NMR: solution state spectra were poorly resolved and thus yielded little useful information. CP/MAS: δ/ppm ; 67.37, 128.50 ($\text{C}^{1,4,5,9-11}$), 141.91 ($\text{C}^{2,3,6,8}$) Quaternary Suppressed (QS); 128.556. Non-Quaternary Suppressed (NQS); 142.28, 128.37. The peak at 67ppm was probably due to C^7 , but this could not be confirmed from the solution state spectra.

Characterization of "Polyradicals"

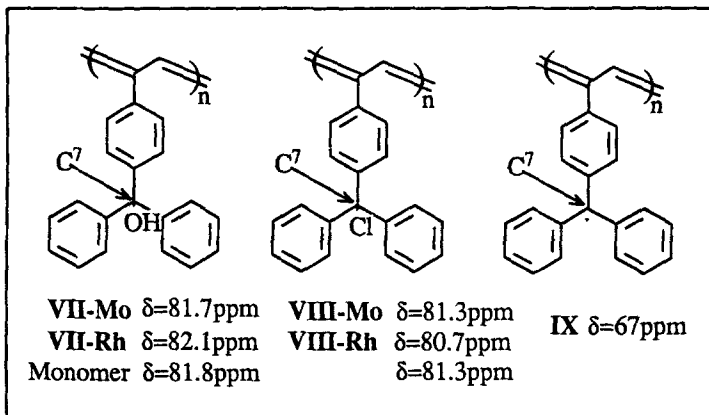
The dechlorination reactions were repeated many times, but consistent results proved extremely difficult to obtain. Initial characterization of the materials involved elemental analysis and IR spectroscopy: ^1H and ^{13}C NMR spectra displayed very broad and poorly resolved signals and thus were of little use in obtaining information about the polymers, which is consistent with reasonable expectation.

RESULTS AND DISCUSSION

The target polymer, poly((4-ethynylphenyl)diphenylmethyl) (IX), was incompletely characterized. Model reactions on triphenylchloromethane established reliable methods of generating the triphenylmethyl radical, and these were extended to reactions on the precursor polymer poly((4-ethynylphenyl)diphenylchloromethane) (VIII-Mo, VIII-Rh). Residual chlorine levels for the final polymers were 1-5%, and for materials produced by some protocols, the analyses were reproducibly "in error" by 10%. The silver content of these samples was never higher than 0.29%. Sulphur residues were less than 1%. The differences between observed and expected analytical results may be related to problems inherent to the analytical process, such as partial hydrolysis prior to combustion. Another factor may have been retention of, or reaction with, THF, used as the solvent for generation of these polyradicals. It has been shown (24), that in the reduction of Ph_3CCl in THF, an important step is the production of $(\text{Ph}_3\text{C}\cdot\text{THF}^+)\text{Cl}^-$ species, which encourages the belief that some THF might be trapped in the polymer. Some IR spectra showed a broad band between 1000-1100 cm^{-1} , in a region associated with -C-O- stretches of ethers. These spectra showed the removal of the C-Cl stretch at 790 cm^{-1} , but also the presence of a weak band at 3550 cm^{-1} , indicating that some hydrolysis had occurred. As Figure 5 shows, ^{13}C NMR spectra could be used to follow the course of these reactions

owing to the difference in shift of the quaternary aliphatic carbons from hydroxyl, chlorine and "radical" substituents.

Figure 5 - ^{13}C NMR Shift Positions for Quaternary Carbon C^7



The small change in shift from hydroxyl to chlorine substituents was also observed in the monomer spectra. Spectra of newly prepared "polyradicals" exhibited a resonance at 67ppm, which did not appear in the QS or NQS spectra. If these samples were exposed to the atmosphere for only 1 minute, resonances at 81.1ppm were seen, in combination with emerging IR bands at 3550cm^{-1} . These results indicate the production of quaternary C-OH or C-OOH sites. Exposure of the chlorinated polymers VIII-Mo and VIII-Rh to the atmosphere also resulted in the emergence of IR bands at 3550cm^{-1} , but this process was slower than for IX samples. Exposure of IX to the air for several hours solubilized the polymers to the extent that solution state NMR was possible, and the spectra obtained were very similar to those of VII-Mo.

The evidence presented above suggests strongly that (poly(4-ethynyl-phenyl)diphenylmethyl) radicals were synthesized in part, but that the polymer was extremely sensitive to air and moisture. Since the dechlorination of triphenylchloromethane was carried out successfully under the same reaction conditions, it is clear that access to the C-Cl sites in the polymer must have been impeded to account for the difference between monomer and polymer reactivity. The reaction of a heterogeneous metal surface with a hindered polymer site is unlikely to be a highly favourable process, as even in dilute solution, these polymers are probably highly coiled. The C-Cl bond might be hindered not only by the triphenylmethyl substituents, but also by the polymer chain itself. The probable occurrence of a variety of HT, HH, and TT sequences, combined with a range of cis/trans environments would decrease access to the chlorine atom, and thus even with sonication, reaction with the metal surface might not occur at all the sites.

Further evidence for the preparation of triphenylmethyl radical sites was provided by Electron Spin Resonance and Magnetic Susceptibility studies, the full details of which will be published elsewhere. In summary it was established that the polyradical concentrations were of the order of 10^{16} - 10^{17} spins.g $^{-1}$ at room temperature. This is at best only 10^{-3} of the theoretical spin concentration, assuming each repeat unit contains one unpaired electron. Magnetic susceptibility measurements suggested that the unpaired spin concentration was 0.5-1% of the expected value. These methods clearly show that the free radical centres were either never produced, or were subsequently spin-paired. The best analysis indicated a residual chlorine concentration of 1.2%, which corresponds to roughly nine out of every ten repeat units bearing a triphenyl methyl radical. For residual chlorine contents of 5%, every second unit should have contained a free radical site. It appears,

therefore, that spin pairing must have taken place subsequent to dechlorination. The results of variable temperature ESR studies showed a reversible increase in spins by a factor of 10^1 - 10^2 for the polyradical sample IX between -50 and 100°C. The ESR results were borne out by the magnetic susceptibility measurements, which showed an increase in the molar ratio of unpaired spins between 200-340K. In view of the known equilibrium between the triphenylmethyl radical and its dimer, the implication is that dimerization of triphenylmethyl radical moieties was taking place within the polymer. On heating, the radicals might be regenerated, giving rise to the observed changes in the ESR and magnetic susceptibility data.

Acknowledgements

We wish to thank Professor L.H. Sutcliffe (Royal Holloway and Bedford New College, University of London) for ESR measurements, and Dr. R.H. Friend (Cavendish Laboratory) for magnetic susceptibility measurements. One of us (C.A.) thanks the S.E.R.C. for a studentship.

REFERENCES

1. J.S. Miller, J.C. Calabrese, A.J. Epstein, R.W. Bigelow, J.H. Zhang, W.M. Reiff. *J. Chem. Soc. Chem. Commun.* 1026, (1986).
2. J.S. Miller, J.C. Calabrese, H. Rommelmann, A.J. Epstein, S.R. Chittapeddi, J.H. Zhang, R.W.Reiff. *J. Am. Chem. Soc.* **109**, 769, (1987).
3. S.R. Chittapeddi, K. Cromack, J.S. Miller, A.J. Epstein. *Phys. Rev. Lett.* **58**, 2695, (1987).
4. J.S. Miller, D.M. O'Hare, A. Chakraborty, A.J. Epstein. *J. Am. Chem. Soc.* **111**, 7853, (1989).
5. J.S. Miller, J.C. Calabrese, R.L. Harlow, D.A. Dixon, J.H. Zhang, R.W.Reiff, S.R. Chittapeddi, M.A. Selover, A.J. Epstein. *J. Am. Chem. Soc.* **112**, 5497, (1990).
6. Yu. V. Korshak, T.V. Medvedeva, A.A. Ovchinnikov, V.N. Spector. *Nature*, **326**, 370, (1987).
7. J.B. Torrance, S. Oostra, A. Nazzal, *Synth. Met.* **19**, 708, (1987).
8. M. Ota, S. Otani. *Chem. Lett.* 1179, (1989).
9. M. Ota, S. Otani, M. Igarashi, *Chem. Lett.* 1183, (1989).
10. H.M. McConnell. *J. Chem. Phys.* **39**, 1910, (1963).
11. N. Mataga. *Theor. Chim. Acta.* **10**, 372, (1968).
12. A.A. Ovchinnikov. *Theor. Chim. Acta.* **47**, 297, (1978).
13. N. Tyutyulkov, O.E. Polansky, P. Schuster, S.Karabunarliev, C.I. Ivanov. *Theor. Chim. Acta.* **67**, 211, (1985).
14. H. Iwamura. *Pure. Appl. Chem.* **58**, 187, (1986).
15. H. Nishide, N. Yoshioka, K. Inagaki, E. Tsuchida. *Macromolecules.* **21**, 3119, (1988).
16. H. Nishide, N. Yoshioka, T. Kaneko, E. Tsuchida. *Macromolecules.* **23**, 4487, (1990).
17. I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, F. Miko, Y. Sawaki, H. Iwamura, A. Izuoka, T. Sugawara. *J. Am. Chem. Soc.* **112**, 4075, (1990).
18. A. Rajca. *J. Am. Chem. Soc.* **112**, 5889, (1990); *ibid.* **112**, 5890, (1990).
19. J.J. Partridge, S. Faber, M.R. Uskokovic. *Helv. Chim. Acta.* **57**, 764 (1974).
20. D.E Ames, D. Bull, C. Takundwa. *Synthesis*, 1981, 364.
21. C. Manning, M.R. McClory, J.J. McCulloch. *J. Org. Chem.* **46**, 919 (1981).
22. R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M. O'Regan. *J. Am. Chem. Soc.* **112**, 3875, (1990).
23. G. Zassinovich, G. Mestroni, A. Camus. *J. Organometal. Chem.* **91**, 379, (1975).
24. M. Newcomb, T.R. Varick, S.W. Goh. *J. Am. Chem. Soc.* **112**, 5187, (1990).