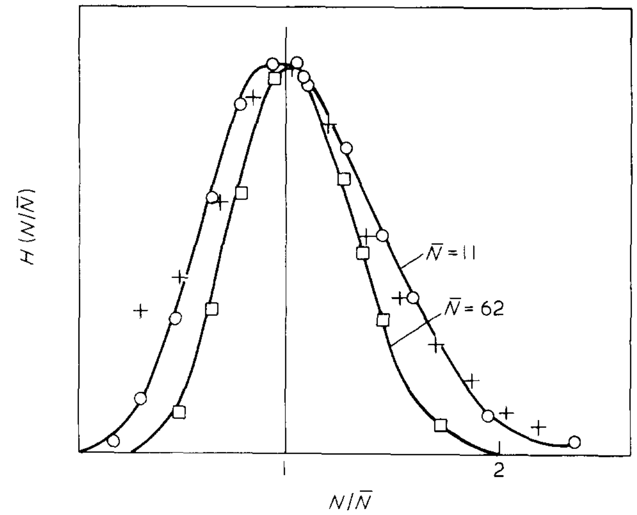

Figure 5 Theoretically calculated frequency distribution $H(N/\bar{N})$ of microparacrystals in equilibrium for two values of $\bar{N}$ (○○, □□), approximation by Maxwellian functions (——) and the size distribution of the microparacrystals of PPT-fibres with $\bar{N}_{110} = 12$ (+ + +)

Acknowledgement

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E.p.r. studies on poly(paraphenylene)s synthesized by two different routes

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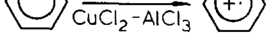
Polyphenylene has been prepared using two different polymerization procedures. We show that, if the two materials are very similar from a structural point of view, their magnetic properties as seen by e.p.r. are very different. We show that the existence of unpaired spins in one of these polymers is correlated with structural defects which are probably created during the polymerization process.

Keywords Polyphenylene; electron paramagnetic resonance; structural defects; magnetic behaviour

Much of the work performed on conducting and semiconducting organic polymers has been focused on polyacetylene in the last few years[1]. Only a small amount of work has been concentrated on the polyphenylene (PPP) system[2]. Shacklette *et al.* have made some structural determinations[3] on a PPP polymer prepared by the Kovacic method[4] (see below). Ivory *et al.* observed that the conductivity of this material could be raised by more than twelve orders of magnitude upon doping with the electron acceptor AsF_5[5]. While it was recognized that the d.c. conductivity of the undoped system was very sensitive to any thermal or chemical treatment[6], investigations of the magnetic properties have shown the presence in these materials very stable radicals yielding singlet e.p.r. spectra with a g-value close to 2.0023 and linewidths of the order of 5 Gauss[7]. It has been suggested that these radicals could be associated with structural defects due to an imperfect polymerization[8,9]. In this communication we want to show that the same PPP polymer synthesized, using two different techniques, yields two very different types of magnetic behaviour.

The polyphenylenes were synthesized using the methods described by Kovacic *et al.*[4] and by Yamamoto *et al.*[10].

The Kovacic method involves an oxidative cationic polymerization of benzene in the presence of $CuCl_2$ and $AlCl_3$. In this reaction, the initiation step would be the loss of an electron from the π cloud of benzene *via* $CuCl_2$ or a $CuCl_2$–$AlCl_3$ complex, leading to



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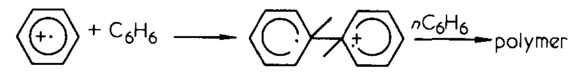
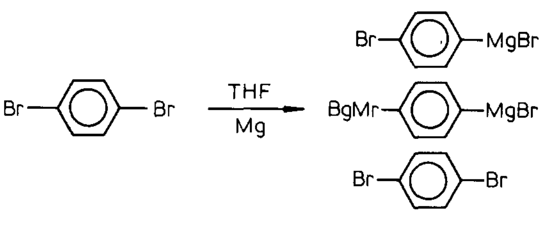
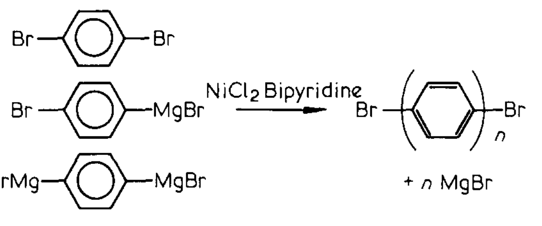
This radical cation would promote the propagation step through equation



The more recent method described by Yamamoto *et al.* would involve a step with the formation of a Grignard reagent when starting from a dihalobenzene.



The subsequent polycondensation of the Grignard reagent would be catalysed by Nickel complexes, such as $NiCl_2$(2,2′-bipyridine)[11] to give the polymer through the reaction:



The characteristics of the brown powder product of the Kovacic method have been published previously[6]. One main characteristic is that the insoluble polymer has a degree of polymerization of the order of 12.

The Yamamoto method gives a yellow powder which is only poorly soluble in *o*-dichlorobenzene. The chemical analysis of the insoluble part is presented in *Table 1*.

From these results and assuming there is at least one Br atom per chain we find a degree of polymerization of the order of 8, which is comparable with the above value of 12 for the Kovacic polymer.

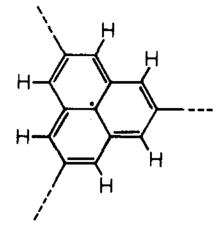
I.r. spectroscopy gives very similar spectra for both polymers leading to the conclusion that the molecular weights are comparable.

In order to investigate the magnetic properties of the two polymers, e.s.r. spectroscopy has been performed using a classical X-band spectrometer.

The Kovacic polymer shows, at room temperature, a singlet e.s.r. line, centred near $g = 2.0023$, which is roughly symmetric with a width of the order of 5 Gauss depending on the sample. The spin density also depends on the sample but is generally close to 10^{20} spins/gram, which corresponds to 1 spin for roughly 100 (C_6H_4) units. It should be noted that these characteristics are very stable even when the samples are submitted to dry or wet air.

With exactly the same experimental conditions as above, the Yamamoto polymer exhibits a much lower e.s.r. signal, with an upper limit of 10^{18} for the spin concentration per gram. This value is two orders of magnitude smaller than for the Kovacic polymer.

Such an enormous difference between the two polymers cannot be attributed to secondary effects occurring after the polymerization process. On the contrary we have noted that the two polymerization procedures are very different: while with the Kovacic method, linkages in the *ortho* or *meta* positions cannot be excluded, the Yamamoto method only involves polymerization in the *para* position. Defects such as the following:



suggested many years ago by Nechtschein[8], are then highly likely in the first case but not in the second. This type of macrocycle bears one unpaired electron which is delocalized on a few carbon atoms leading to an e.s.r. spectrum without hyperfine structure. The limited area of resonance type delocalization of the electron is consistent with the experimental observation of:

(i) a large e.s.r. linewidth (~ 5 Gauss) in contrast with the case of systems with strongly delocalized electrons, such as *trans*-$(CH)_x$[12].

(ii) a temperature independent e.s.r. linewidth down to 1K, which indicates that the electron mobility is not thermally activated, also in contrast with *trans*-$(CH)_x$[13].

Finally we note that n.m.r. T_1 measurements performed on protons at 16 MHz and room temperature show that the relaxation is much more rapid in the brown powder ($T_1 \sim 120$ ms) than in the yellow powder ($T_1 \sim 230$ ms). This result is also consistent with the existence, in the first case, of unpaired electrons whose interaction with the protons is an efficient relaxation mechanism.

We therefore conclude that the two polyphenylenes prepared using the Kovacic and Yamamoto methods show very different magnetic behaviour. In the first case the observed unpaired electrons are probably associated with structural defects which are created during the polymerization. In the second case the absence of unpaired electrons is consistent with a polymerization process involving only linkages in the *para* position.

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Table 1 Elemental analysis of the polymer prepared from *p*-dibromobenzene

Element	C	H	N	Ni	Mg	Br	O
Weight percent	82.46	5.27	⩽0.05	<0.05	<0.05	10.61	1.58

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Block copolymerization by a cation to anion transformation process: 2. Polymerization of styrene by polyTHF possessing terminal secondary nitranions

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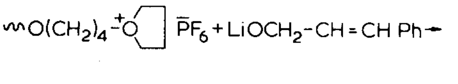
A route for preparing block copolymers by a cation to anion transformation is examined. PolyTHF possessing a terminal secondary amine group is prepared by reacting living polymer with excess of the primary amine, then metallated with potassium to create a terminal nitranion. This is then used to initiate the anionic polymerization of styrene, but initiation is relatively slow and, although all the styrene is consumed, only about 30% of polyTHF chains form a block copolymer.

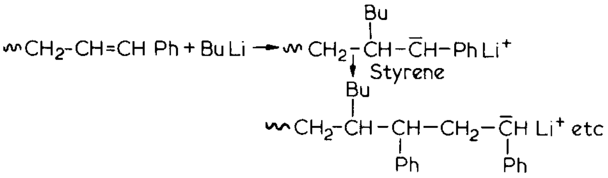
Keywords Copolymerization; cation; anion; transformation; polytetrahydrofuran; polystyrene; polymer amine

Introduction

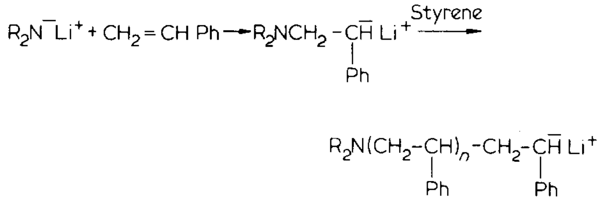
For a number of years we have been examining methods of synthesizing novel block copolymers by developing so called transformation reactions in which the mode of propagation of the first monomer is transformed *via* a 3 stage process into a different mode suited for the polymerization of the second. These processes have been recently reviewed[1], and it is evident that certain transformations may be achieved with greater efficiencies than others. Thus the anion to cation process has been carried out with overall efficiencies in excess of 90%[2-4], whereas the reverse reaction, cation to anion, has to date achieved an efficiency of only about 20%[5]. Alternative, more efficient transformation reactions are therefore still being sought, and one such approach to the cation to anion transformation forms the subject of this communication.

The method reported previously[5] used tetrahydrofuran (THF) as the cationically polymerizable monomer, and required a quantitative reaction of the living polyTHF with lithium cinnamate to form a polymer with a terminal styryl unsaturation (equation (1)). This was achieved, but the subsequent process which involved reacting the polymer with n-butyl lithium to form a terminal carbanion and then using this species to initiate the polymerization of a monomer such as styrene (equation (2)), yielded only small amounts of block copolymer. The reasons for this low efficiency were not fully elucidated, and it seemed desirable to seek an alternative method of effecting this transformation.


(1)


$$\sim CH_2{-}CH{=}CH\,Ph + BuLi \rightarrow \sim CH_2{-}\underset{}{\overset{Bu}{\overset{|}{C}H}}{-}\bar{C}H{-}Ph\,Li^+ \xrightarrow{Styrene} \sim CH_2{-}\overset{Bu}{\overset{|}{C}H}{-}\underset{Ph}{\underset{|}{C}H}{-}CH_2{-}\underset{Ph}{\underset{|}{\bar{C}H}}\,Li^+ \text{ etc} \quad (2)$$

Elsewhere, studies had been carried out on anionic initiation by alkali metal salts of amines[6-8], and these had shown the species to be active in the polymerization of monomers such as styrene or butadiene (equation (3)), although the initiation process was found to be slow relative to propagation. It seemed possible, however, that this approach could be adapted to carry out the cation to anion transformation required.


$$R_2\bar{N}\,Li^+ + CH_2{=}CH\,Ph \rightarrow R_2NCH_2{-}\underset{Ph}{\underset{|}{\bar{C}H}}\,Li^+ \xrightarrow{Styrene} R_2N(CH_2{-}\underset{Ph}{\underset{|}{C}H})_n{-}CH_2{-}\underset{Ph}{\underset{|}{\bar{C}H}}\,Li^+ \quad (3)$$

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