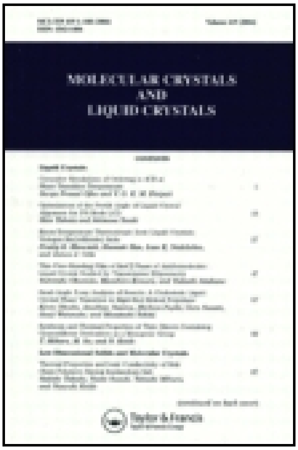

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Chemical Modification of Polyacetylene by Diels-Alder Reactions

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Chemical Modification of Polyacetylene by Diels-Alder Reactions

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Polyacetylene may be chemically modified by the Diels-Alder reaction. Standard reagents provide only modest conversions but the reaction with 4-methyl-1,2,4-triazoline-3,5-dione provides conversions up to 18 mole %, corresponding to the occupation of nearly $\frac{3}{4}$ of the carbon centres of polyacetylene. The insoluble adduct films were more brittle and had electrical conductivities (after doping with iodine) which were inferior to those of the starting films.

Some potential Diels-Alder dienophiles (quinones) acted merely as p-dopants, enhancing the conductivity of standard N—$(CH)_x$.

Spin label introduction into the polyacetylene was at best carried out by an indirect addition, the addition of 4-amino-TEMPO to maleic anhydride modified polyacetylene, leading to an incorporation of up to 1.4 mole %.

Keywords: polyacetylene, modification, nitroxyl, Diels-Alder, conductivity, doping

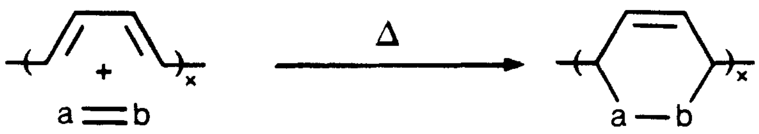
1. INTRODUCTION

The chemical modification of polyacetylene was investigated with a view to:

a) improvement of the physical and chemical characteristics of the polymer, e.g. electrical conductivity, solubility and resistance to air oxidation, and,

b) the incorporation of spin-labelled moieties and the study of the magnetic properties of the resultant modified polymer.

The Diels-Alder reaction (Scheme 1) of several dienophiles with polyacetylene was investigated. The success of such reactions of an insoluble polymer will, of course, be limited by the diffusion of the reagent into the porous structure, and high conversions would only be expected for highly reactive dienophiles. The conversion may also be subject to the influence of statistical effects,[1] since this cycloaddition reaction requires the participation of 4 adjacent carbon centres along the polyacetylene backbone. The maximum random occupation of the carbon centres for an irreversible reaction of this type has been calculated to be 80%.[2]



SCHEME 1

2. EXPERIMENTAL

a) Starting materials

Polyacetylene N—$(CH)_x$ was prepared by the literature method[3] except that the films were repeatedly washed with toluene only. A typical elemental analysis of this material was C: 84.2, H: 7.9, O: 4.5, Al: 0.4, Ti: 1.7 and Si: 1.3%.

The dienophiles employed, e.g. maleic anhydride, 4-phenyl-1,2,4-triazoline-3,5-dione, were all commercially available and used as received.

The spin labels 4-Amino-TEMPO, 4-Maleimido-TEMPO, etc. were obtained from Aldrich Chemicals. Solvents were dried and distilled before use.

b) Modification reactions

The modification reactions were carried out by heating under reflux a stirred mixture of unstretched standard polyacetylene film (N—$(CH)_x$—prepared by the BASF silicon oil method[3] 100–500 mg, ca. 20 μm thick and cut into small strips of approx. 7 × 3 cm) and the reagent in an appropriate solvent/usually toluene (50–100 ml)/under an argon atmosphere. At the conclusion of the reaction, the mixture was allowed to cool, the solvent was removed by decantation and the modified polyacetylene film strips were washed with pure solvent (3 × 100 ml) and dried under vacuum (0.1 Torr, 25°C) for 1 hour.

Manipulations performed before and after the modification reactions were carried out in a glove box under an anhydrous and oxygen-free (< 0.3 and < 0.8 ppm respectively) nitrogen atmosphere.

c) Product characterisation

The success and extent of the modification reactions were investigated by the techniques of infrared spectroscopy and elemental analysis. Infrared spectra (FT, negative extinction), measured on a Bruker IFS 85 instrument, showed the characteristic absorption bands of the adducts. Microanalysis (combustion analysis) was employed to determine the carbon, hydrogen, and, where appropriate, nitrogen content of the adduct films. The weight uptake of the $(CH)_x$ films upon modification provided another means for the calculation of the resultant conversion.

d) Doping and electrical conductivity

The doping of all polyacetylene films was performed with a saturated solution of iodine in carbon tetrachloride, as previously described.[3]

Electrical conductivity measurements were performed by the four-probe technique inside the glove box.[4]

3. RESULTS AND DISCUSSION

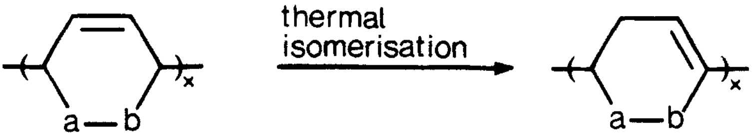
a) Scope of reaction

The applicability of the Diels-Alder reaction with polyacetylene was investigated by employing a wide range of potentially suitable dienophiles *1–11* (Figure 1), and the results are summarized in Table I.

The Diels-Alder cycloaddition reaction of a large excess of maleic acid derivatives, maleic anhydride *1*, maleimide *2* and *N*-phenylmaleimide *3* proceeded slowly during prolonged reflux in toluene (≈13 h). From the microanalytical data and the mass uptake of the reagent, it was shown that 1–4 mole % reagent had been added (Table I). The infrared spectra of all three adducts displayed the two typical frequencies of the succinic anhydride, succinimide groups, the lower frequency being always of greater intensity.[5,6]

The characteristic infrared bands of the adduct film were superimposed on the spectrum of *trans*-polyacetylene, due to simultaneous *cis-trans* isomerization, which had taken place during prolonged refluxing.[7]

Under the prevailing reaction conditions, migration of the double bond in the newly-formed six-membered ring may take place, as shown in Scheme 2.[8]



SCHEME 2

TABLE I

Reaction of polyacetylene film with various Diels-Alder reagents in refluxing toluene

Reagent	Reaction time (h)	Conversion (mole %)	Characteristic IR frequencies (cm^{-1}), assignment
1	13	3.5	1852, 177 (C=O)
2	14	4	1778, 1711 (C=O), 3270 (NH)
3	12.5	1.5	1778, 1712 (C=O)
4	1[a]	15	1778, 1721 (C=O)
5	2[a]	18	1776, 1718 (C=O)
6	7	2.5	1724 (C=O)
7	7	1	1729 (C=O)
8	5	1.5	–[b]
9	5	0.8	–[b]
10	5	0.3	–[b]
11	7	0.1	–[b]

[a] Reaction performed in toluene at 90–100°C

[b] No characteristic peaks observed due to either the low conversion and/or weakness of the relevant infrared bands.

If appreciable isomerization does occur, then the Diels-Alder addition to polyacetylene would be rendered essentially irreversible. Experimental evidence supports this postulate: A maleic anhydride modified acetylene film, formed from polyacetylene and maleic anhydride in refluxing toluene over 13 hours, lost only 14% of the incorporated maleic anhydride on further reflux for 13 hours in toluene alone. Similarly, a maleimide modified film lost only 10% of the incorporated maleimide upon further reflux for 10 hours.

The reaction of polyacetylene with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD, *4*, 0.30 equiv.), one of the most powerful dienophiles known,[9] in toluene or chloroform as solvent, proceeded much more rapidly (reaction time 1 hour) than those of the maleic acid derivatives and provided an adduct (infrared carbonyl frequencies 1778 and 1721 cm^{-1}) into which 15 mole % PTAD had been incorporated. Polyacetylene modified in this way was found to be particularly dull, dark, brittle and just as insoluble.

The reaction of polyacetylene with the methyl analogue of PTAD, 4-methyl-1,2,4-triazoline-3,5-dione *5*, proceeded even more favourably, with 18 mole % incorporation of the reagent. This figure corresponds to the occupation of 72% of the carbon centres of the polyacetylene, closely approaching the theoretical 80% maximum random occupation.[2]

The cycloaddition reaction of polyacetylene with an excess of the dienophiles, diethylazodicarboxylate *6* and diethylacetylenedicarboxylate *7* also proved to be successful, as evidenced by carbonyl stretching frequencies of 1724 and 1729 cm^{-1} respectively in the adduct and provided conversions similar to those obtained from maleic acid derivatives *1–3*.

The asymmetrical dienophile nitrosobenzene *8*[10] was also found to yield an adduct with polyacetylene. This adduct was particularly brittle.

Similar reactions were attempted with the relatively unreactive dienophile 1,4-benzoquinone *9*,[11] and the analogues 3,3′,5,5′-tetramethyl-4-4′-diphenoquinone *10* and the stable free radical galvinoxyl *11*. All were incorporated into polyacetylene to a small extent (Table I). However, these quinones may also act as π-acceptors in charge-transfer complexes,[12] and the available evidence indicated this to have been the case: firstly, the infrared spectra of the product films lacked the corresponding carbonyl stretch required for a Diels-Alder adduct and, secondly, the electrical conductivity of these product films was found to be much superior to that of normal undoped N—$(\mathrm{CH})_x$, as will be discussed in more detail in Section 3 (c).

In summary, the results of the modification reactions indicate that polyacetylene may be chemically modified via the Diels-Alder reaction. A broad range of dienophiles may be employed, but the use of commonly employed Diels-Alder reagents provides only modest conversions.

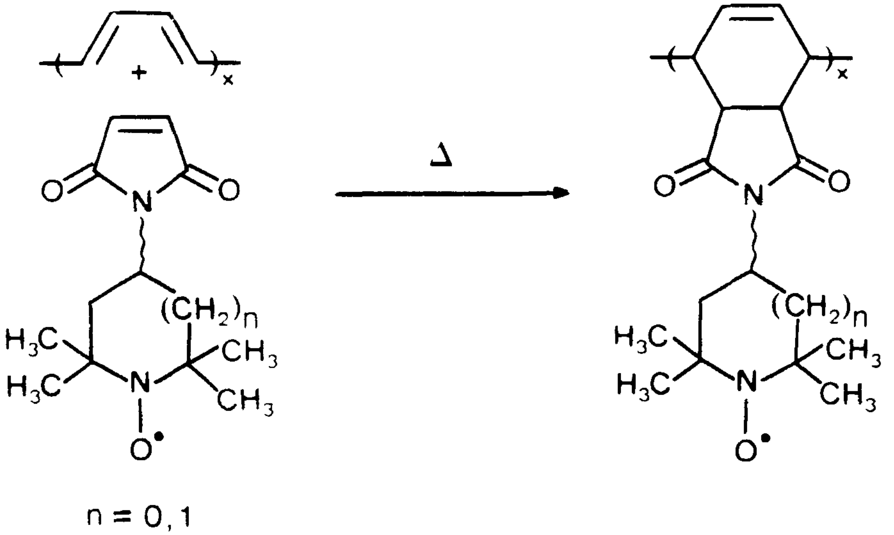
b) Application of modification procedures to the introduction of spin labels into polyacetylene

The technique of spin-labelling[13] of synthetic polymers is widely employed for the analysis the dynamics of polymer segments.

The methodology of the Diels-Alder modification of polyacetylene was extended to the introduction of spin-labelled moieties into the polyacetylene skeleton. Due to the only moderate degree of functionalization which could be achieved with normal Diels-Alder dienophiles, the possibility of incorporating a very large number of spin labels was immediately ruled out.

Three general methods of spin label incorporation were investigated, namely, (i) direct addition, (ii) diffusion and (iii) indirect addition.

The *direct addition* of commercially available spin labels such as *12–16* (Figure 1) to polyacetylene in a Diels-Alder reaction was carried out (Scheme 3). These spin labels are composed of a Diels-Alder active maleimide fragment which is attached to stable free nitroxyl radical[14] units such as 2,2′,5,5′-tetramethyl-pyrrolidine-1-oxyl (PROXYL) and 2,2′,6,6′-tetramethylpiperidine-1-oxyl (TEMPO) by various covalent linkages.



SCHEME 3

Owing to the expense of the nitroxyl spin labels *12–16*, only relatively small amounts (100 mg) were employed in Diels-Alder reactions. As expected, these attempts proved to be far less successful than in the examples of model reactions described in the previous section in which a large excess of dienophiles such as the analogous maleimide *2* and *N*-phenylmaleimide *3* were used. Combustion analysis of the adduct films from *12–16* showed the proportion of the newly-introduced heteroatom, nitrogen, to be less than the limit of detection (0.5% nitrogen, by mass). This result indicated that the spin label incorporation was less than 0.2 mole % (Table II).

The use of the cheaper but less potent dienophile *17* (Figure 1), which could be employed in greater amounts, led to the incorporation (Table II) of only 0.4 mole % spin label. However, in this case it is more likely that simple *diffusion* of the spin label into the porous polyacetylene film has taken place. This postulate is supported by the observation that the saturated equivalent of *17*, spin label *18* (Figure 1), was incorporated into polyacetylene to a similar degree (0.3 mole %). The spin labels TEMPO *19* and 4-amino-TEMPO *20* (Figure 1) were also shown

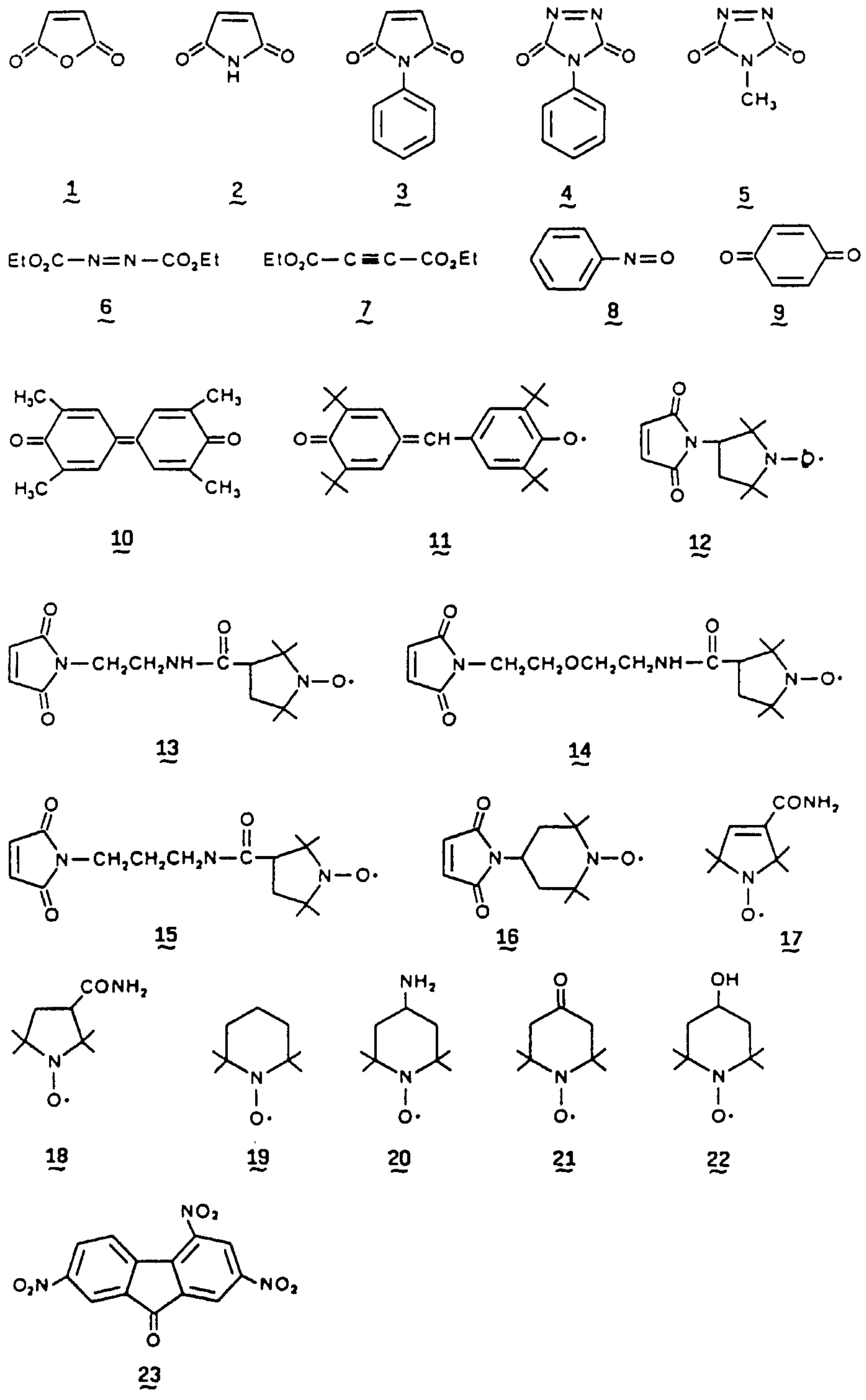

1
2
3
4
5
EtO₂C—N=N—CO₂Et
6
EtO₂C—C≡C—CO₂Et
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

FIGURE 1

TABLE II

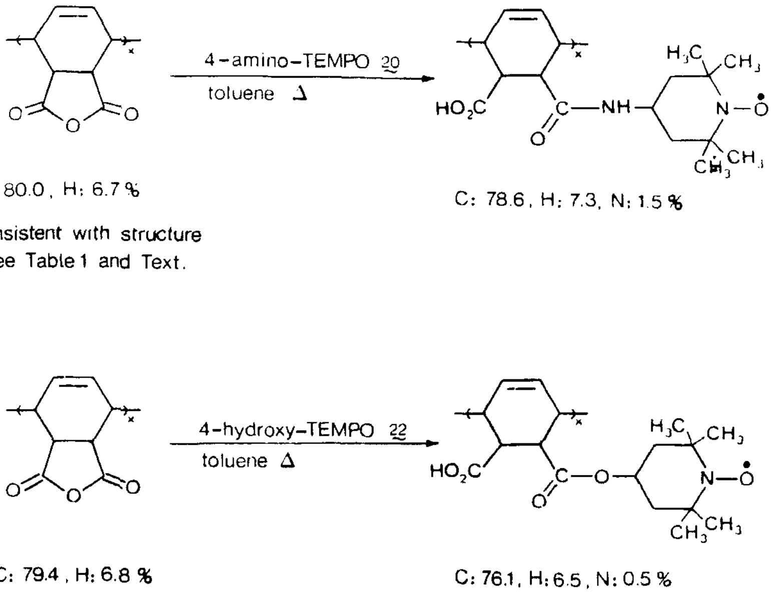
Reaction of polyacetylene film with various spin labels in refluxing toluene

Spin Label	Mass % N (analysis)	Incorporation (mole %)
12	<0.5	<0.2
13	<0.5	<0.2
14	<0.5	<0.2
15	<0.5	<0.2
16	<0.5	<0.2
17	0.8	0.4
18	0.7	0.3
19	0.7	0.8
20	0.5	0.2

to diffuse into polyacetylene film to a slight degree, the former up to 0.8 mole % (Table II). The incorporation of the spin label galvinoxyl *11* into polyacetylene, as described earlier, constitutes a special case.

It has previously been shown that the free nitroxyl radicals such as TEMPO *19* and 4-oxo-TEMPO *21* (Figure 1) can readily diffuse into various polymers, e.g. polyethylene, polyisobutylene and polystyrene, as investigated by ESR spectroscopy.[15]

The most successful approach for the introduction of spin labels into polyacetylene was that of *indirect addition*, in which an already modified polyacetylene film, e.g. a polyacetylene film modified with maleic anhydride, is treated with spin labels such as 4-amino-TEMPO *20* and 4-hydroxy-TEMPO *22* (Figure 1), the anhydride groups undergoing reaction[16] as depicted in Scheme 4.



SCHEME 4

The success of such an indirect addition will, of course, be limited by the degree to which the precursor film had previously been modified, that is, 3.5 mole % of spin label can be introduced into maleic anhydride modified polyacetylene when all anhydride groups undergo a reaction.

Treatment of maleic anhydride polyacetylene film with an excess of 4-amino-TEMPO *20* in refluxing toluene gave up to 1.4 mole % spin label incorporation, in comparison to only 0.2 mole % obtained by simple diffusion (Table II).

Treatment with the poorer nucleophile 4-hydroxy-TEMPO *22* gave a smaller degree of spin label incorporation (0.6 mole %), inferior to the incorporation of spin label TEMPO *19* by normal $(CH)_x$ through diffusion (0.8 mole %, Table II).

The reaction of 4-amino-TEMPO *20* with polyacetylene, which had been modified by the incorporation of epoxide groups through the reaction with 3-chloroperbenzoic acid,[17] proved to be a less effective means for introducing spin labels than the corresponding reaction with maleic anhydride modified film.

The study of the magnetic properties of the spin label-modified polyacetylene films will be reported elsewhere.[18]

In conclusion, it appears that only a relatively small number of spin-labelled moieties can be introduced into the polyacetylene skeleton through modification reactions.

c) Electrical conductivity of modified polyacetylene film

Pristine standard N—$(CH)_x$ has only a very small room-temperature electrical conductivity ($\sigma = 10^{-8}$ S cm^{-1}) which can be improved up to 2000 S·cm^{-1} upon p-doping with iodine.[3] It was of interest to compare the electrical properties of chemically modified polyacetylene with these results.

As noted in Section 2 (a), treatment of standard polyacetylene with π-acceptors of the quinone type, 1,4-benzoquinone *9*, 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone *10*, and galvinoxyl *11* led to incorporation through simple diffusion. The electrical conductivity of standard polyacetylene film was enhanced by some 4 orders of magnitude to around 10^{-4} S·cm^{-1} (Table III). These oxidants therefore act as effective p-dopants[19] for polyacetylene despite their only small incorporation into the film (< 1 mole %, Table I).

TABLE III

Electrical conductivity of standard N—$(CH)_x$ modified with various reagents

Reagent	Conductivity (S·cm^{-1})
9	3×10^{-4}
10	5×10^{-4}
11	1×10^{-4}
22[a]	1×10^{-4}
1	7×10^{-4}
3	4×10^{-4}

[a] 0.3 mole % incorporation

TABLE IV

Electrical conductivity of modified standard $N(CH)_x$ after doping with iodine/CCl_4[a]

Film	Conductivity ($S \cdot cm^{-1}$)
Unmodified $(CH)_x$	1400
trans $(CH)_x$	670
$(CH)_x$ + *8*	580
$(CH)_x$ + *4*[b]	190

[a] Mass fraction of iodine in the films after doping is approximately 65%.

[b] 2 mole % incorporation

Treatment of polyacetylene with the π-acceptor 2,4,7-trinitrofluourenone *23* (Figure 1) led to a similar improvement in the conductivity (Table III). The somewhat weaker π-acceptors, maleic anhydride *1* and *N*-phenylmaleimide *3*, also acted as p-dopants.

The conductivity values of these doped films remained essentially unchanged after a period of two months.

Polyacetylene which had been treated with spin-labelled compounds *12–20* showed no measurable conductivity.

In contrast, chemically modified polyacetylene films which were subjected to doping with iodine showed lower conductivities than the doped starting (predominantly-*cis*-)(3)polyacetylene film and the doped *trans*-polyacetylene (formed by isomerization of the *cis*-film in refluxing toluene) (Table IV). For example, a polyacetylene film that was modified with 2 mole % PTAD and subsequently doped with iodine showed a conductivity less than 15% of that of the doped starting film. The deterioration in the conductivity of the doped, chemically modified polyacetylene can be attributed to the interruption of conjugation along the carbon chains.

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