Synthesis of soluble polyphenylacetylenes containing a strong donor function

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Copolymers of substituted phenylacetylenes containing the *N*,*N*-dimethylamino group have been produced with a rhodium catalyst, (bicyclo[2,2,1]hepta-2,5-diene)-rhodium(I)chloride dimer, from substituted phenylacetylenes (PA) monomers. These include 4-(*N*,*N*-dimethylamino)PA, PA, 4-chloroPA, 3-chloroPA and 4-nitroPA. The copolymers generally have 'better' properties in terms of solubility and molecular weight distribution than the corresponding homopolymer of 4-(*N*,*N*-dimethylamino)PA. Electron spin resonance, ^{1}H nuclear magnetic resonance, infrared and ultraviolet/visual spectroscopy, elemental analysis and gel permeation chromatography revealed that the structure of the copolymers resembles that of polyphenylacetylene. Doping with electron acceptors, such as iodine or chloranil, in solution, gives rise to bands in the optical absorption spectra near 700 nm, probably due to a cation involving the dimethylamine function. This indicates the possibility of doping a polyacetylene chain via a functional group on a substituent.

(Keywords: polyphenylacetylene; *N*,*N*-dimethylamino group; synthesis; copolymerization; rhodium catalyst; donor function)

INTRODUCTION

Among polymers with a conjugated main chain, polyacetylene has attracted most attention because of its high conductivity upon doping (see, for example, Reference 1). Polyphenylacetylene (PA) has structural, conformational and magnetic properties similar to those of polyacetylene[2–11]. The conductivity is, however, relatively low[12–16], owing to the bulky substituent which gives rise to structural and conformational restrictions.

The chemically intuitive way to design conjugated polymers with 'useful' optical, electric and magnetic properties is to introduce donor and/or acceptor groups. The extended conjugated systems in this class of materials enable the entire system to act collectively via the large number of polarizable π-electrons. Referring to 'usefulness' also means that other properties normally encountered in polymeric systems are retained, such as solubility and high molecular weight.

In this report we show how the dimethylamine function can be introduced in the polyphenylacetylene system by copolymerization of 4-(*N*,*N*-dimethylamino)phenylacetylene with phenylacetylene (PA), 4-chloro-PA, 3-chloro-PA and 4-nitro-PA. The structures are characterized with ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy, elemental analysis and gel permeation chromatography (g.p.c.). These results together with electron spin resonance (e.s.r.) measurements on heat treated samples show that the copolymers have structural and physical similarities to polyphenylacetylene itself. Interestingly, the electronic behaviour is markedly different, as manifested by charge transfer bands near 700 nm in the optical absorption spectra of acceptor doped samples. They originate from oxidation of the dimethylamine function in the copolymer, and thus, an alternative way to introduce positive charge density to a polyacetylene chain is shown. This was also supported by preliminary e.s.r. results of copolymers doped in solution.

EXPERIMENTAL

Monomers

Phenylacetylene was obtained commercially (Merck) and distilled twice before use. 4-Chloro-, 3-chloro- and 4-nitro-phenylacetylenes were synthesized from their corresponding cinnamic acid or styrene analogues. 4-(*N*,*N*-dimethylamino)phenylacetylene was synthesized from 4-(*N*,*N*-dimethylamino)-1-iodobenzene by Pd catalysed coupling of trimethyl-silylacetylene and subsequent treatment in alkali. Details will appear elsewhere, together with a comprehensive presentation of the synthesis of substituted phenylacetylene using rhodium catalysts[17].

Polymerization

Polymerization solvents (triethylamine, benzene, THF and ethanol) were dried and purified according to standard methods. The catalyst, (bicyclo[2,2,1]hepta-2,5-diene)rhodium(I) dimer was obtained commercially (Aldrich) and used without further purification. The polymerization reaction took place in home-made H-type ampoules under mild vacuum or dried nitrogen atmosphere; [monomer] = 0.3–0.6 M, [catalyst] = 2.5–5.0 mM, temperature = 30°C, time = 2–24 h. The polymerizations were terminated by adding a large amount of methanol to the reaction solvent. The precipitates were washed carefully with hot methanol and dried under vacuum for 24–48 h. The resulting yield was obtained

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from gravimetry. Elemental analyses were made by the Analysis Centre at the Department of Pharmacy, Hokkaido University, Japan.

E.s.r.

E.s.r. spectra were recorded on a JEOL-FX-1XG spectrometer operating at 9.2 GHz with a 100 kHz field modulation. Relative spin concentrations were determined by integration of experimental spectra under identical spectroscopic settings (except for linear gain). Solid e.s.r. samples were pumped (0.05 torr $\approx$ 7 Pa) for at least 24 h and thereafter sealed under vacuum. The heat treatment consisted of keeping the sample tubes in an oil bath for at least 24 h at each temperature. The e.s.r. spectra were recorded at room temperature.

^{1}H n.m.r.

Spectra were measured with a HITACHI R-90FT spectrometer. $CDCl_3$ was used as solvent and TMS as reference. Sample concentration was 2.5 mg ml^{-1}.

U.v./vis.

Optical absorption spectra were recorded on a JASCO 660 photospectrometer. Samples were made by dissolving polymer and dopant (I_2 or chloranil) in THF and then mixed to desired molar ratios. The samples were kept for $\approx$1 h to allow for the dopants to react.

G.p.c.

Molecular weight distributions were determined by using a gel permeation liquid chromatograph (Toyo Soda HPLC-803A, column; TSK gel). Samples were made by dissolving $\approx$0.5 mg polymer in 1 ml solvent (THF). Molecular weight was calibrated against polystyrene standards ranging between 600 and 900 000.

RESULTS AND DISCUSSION

Polymerization and structural characterization

The homopolymer of 4-(*N*,*N*-dimethylamino)phenylacetylene was difficult to produce with high yields and molecular weight. Using benzene, THF, ethanol or triethylamine as polymerization solvents under reaction and reactant conditions as specified for the copolymerizations in *Table 1*, the yields were always found to be between 30 and 60%. The g.p.c. traces showed a large contribution from oligomer products in addition to a polymer fraction at $M_w \approx 10\,000$. On the other hand, copolymers were formed in high yield and with high molecular weight. Results on copolymerization reactions are summarized in *Table 1*. The materials were found to be soluble in conventional solvents such as THF, benzene and $CHCl_3$. The g.p.c. traces were sharp and without contributions from low molecular fractions. The colours of the copolymers were yellow to red, whereas the homopolymer was green to green–yellow. The copolymer with 4-nitrophenylacetylene was brown and only partially soluble in solvents such as THF, benzene or $CDCl_3$. The g.p.c. results as well as the optical absorption spectra of this copolymer refer to the fraction soluble in THF.

The results of the elemental analysis (e.a.) are presented in *Table 1*. The calculated values were obtained under the assumption that the polymer compositions are proportional to that of the molar ratio of monomers in the initial feed. This was justified by the ^{1}H n.m.r. results, to be explained below. Also, the experimental e.a. values were found to fit reasonably well according to this assumption. However, there was a tendency for the 'monomer' containing the dimethylamino group to contribute less to the composition of the final products. This is seen readily by comparing e.a. ratios of nitrogen and chlorine in *Table 1*.

A representative ^{1}H n.m.r. spectrum is shown in *Figure 1*. Solvent signals have been eradicated. The polymer here is poly(4-(*N*,*N*-dimethylamino)PA-co-3-chlorophenylacetylene). The peak at 5.8 ppm is due to the main chain proton[18] and the peak at 2.75 ppm can be assigned to the methyl groups.

The intensity ratio of these peaks was used to check the polymer composition. The peaks between 6.1 and 7.0

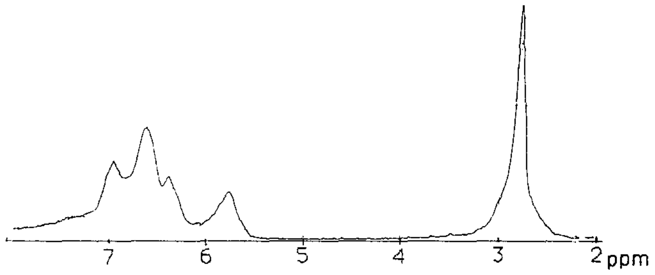

Figure 1 ^{1}H n.m.r. spectrum of poly(4-*N*,*N*-dimethylaminophenylacetylene-co-3-chlorophenylacetylene). $CDCl_3$ was used as solvent with TMS as internal standard

Table 1 Representative results of copolymerization of 4-(*N*,*N*-dimethylamino)phenylacetylene (4-DMA) with phenylacetylene (PA), 4-chlorophenylacetylene (4-Cl), 3-chlorophenylacetylene (3-Cl) and 4-nitrophenylacetylene (4-N) using (bicyclo[2,2,1]-hepta-2,5-diene)rhodium(I) chloride dimer as catalyst[a]

			Elemental analysis (obs./calc.)			
	Yield (%)	$10^{-3}M_w$	C	H	N	Cl
4-DMA/PA[a]	74	30	87.0/87.4	6.60/6.93	5.48/5.66	–
4-DMA/4-Cl[a]	87	80	75.8/76.7	5.47/5.72	4.67/4.97	13.2/12.6
4-DMA/3-Cl[a]	82	80	75.6/76.7	5.50/5.72	4.75/4.97	12.8/12.6
4-DMA/3-Cl[b]	82	80	75.6/76.7	5.50/5.72	4.75/4.97	12.8/12.6
4-DMA/3-N[c]	63	15	69.2/73.4	4.50/5.52	9.22/9.58	–

[a] In trimethylamine; [catalyst] = 2.5 mM, [monomer] = 0.32 M, time = 2 h; temperature = 30°C; ratio of feed monomers = 1:1
[b] In ethanol; [catalyst] = 5 mM, [monomer] = 0.5 M, time = 1 h, ratio of feed monomers = 1:1
[c] In THF; [catalyst] = 5 mM, [monomer] = 0.5 M, time = 24 h, ratio of feed monomers = 1:1

are all due to ring hydrogens. Note that no peaks can be discerned which are ascribable to monomers or oligomer compounds. If such species were present, they would give rise to sharp lines, easily distinguished among the broad peaks of the polymer, even in low concentrations.

Thus, ^1H n.m.r., g.p.c. and e.a. data clearly indicate that we are dealing with polymeric structures resembling polyphenylacetylene.

Magnetic and electronic properties

Previous e.s.r. studies on polyPA[2,3,5-7] can be summarized as follows. Heat treatment up to $\approx 120°C$ results in an increase of the spin concentration. At this point a phase transition occurs and on annealing above this temperature the number of radicals steadily decreases. This has been interpreted as a conformational change in the polymer backbone, where *cis* double bonds are twisted to a *trans* structure under the formation of two π radicals. We will not discuss the details further here. In a parallel report new e.s.r. data on various heat-treated substituted polyphenylacetylenes are presented[19]. (Our observations are similar to previous studies, but we can relate the increase of radical concentration to a decrease in molecular weight. Thus, the origin of radical formation might also be due to chain scission with chain end radicals as stable products.) The relative intensities (spin concentration) for selected homo- and copolymers are shown in *Figure 2*. All curves follow a similar trend, with a pronounced maximum in radical concentration at the annealing temperature near 120°C. Thus, the e.s.r. behaviour of the copolymers of phenylacetylene containing the dimethylamino group resembles that of polyphenylacetylene with respect to e.s.r. of annealed samples also. Consequently, we may expect a similar structure of the polymer backbone.

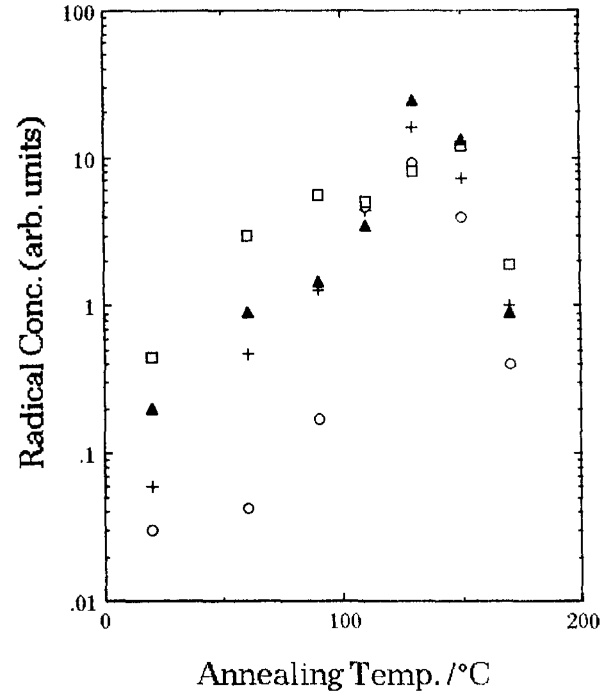

Figure 2 Relative radical concentration as a function of annealing temperature of selected copolymers and homopolymers: +, PA; ○, poly(3-chloroPA); □, poly(4-(*N*,*N*-dimethylamino)PA); ▲, poly(3-chloroPA-co-4-(*N*,*N*-dimethylamino)PA)

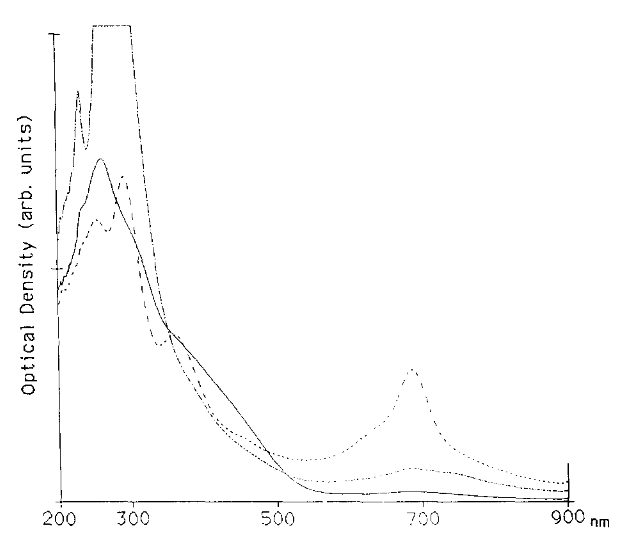

Figure 3 The optical absorption spectrum of poly(4-*N*,*N*-dimethylaminophenylacetylene-co-4-chlorophenylacetylene) (——), doped with I_2 2/1 molar ratio (- - -) and with chloranil 4/1 molar ratio (-·-·-). The molar ratios refer to a 'dimer' unit of the polymer chain

Conductivity, photoconductivity and optical absorption of doped polyphenylacetylene have been reported previously[12-16]. Doped PAs have very weak and broad charge transfer bands at 800-900 nm, which can be related to the photoconductivity[13,14]. Details of the mechanism and structures of charge transfer complexes are not known.

The d.c. conductivity has been reported to be low at all doping levels. The optical absorption spectra of all doped polymers containing the dimethylamine function are entirely different from those reported previously. Doping with I_2 or chloranil in solution (THF) results in a clearly detected band near 700 nm. The solution changes in colour from being yellow-red to green. The optical absorption spectra of poly(3-chloroPA-co-4-(*N*,*N*-dimethylamino)PA) undoped and doped with I_2 and chloranil in THF, are shown in *Figure 3*. The low energy peak originates from an oxidation of the dimethylamine function. With chloranil, two peaks are clearly discerned with an additional absorption towards the low energy side. Peaks in the same region have been observed for the Wurster cations or dications (see, for example, Reference 20), which also contain the dimethylamino group. This class of cations is usually stable, also as radicals. If more than one dimethylamine function is attached to a conjugated molecule dications can also be stabilized.

Preliminary e.s.r. results

In an attempt to relate the oxidation of the copolymers containing the dimethylamino group with a radical cation, e.s.r. signals of degassed copolymer/chloranil solutions (THF) were recorded. A large number of doping levels were examined in that the molar ratio, (polymer unit):chloranil, was varied from 100:1 to 1:3. The total concentration, which here means the sum of polymer dimer units and chloranil molecules per unit volume, was varied between 10^{-3} and 10^{-5} M. Samples containing copolymer and chloranil showed a single unresolved line centred on $g = 2.0059$. The line width (peak to peak of 1st der.) varied between 0.5 and 1.0 depending on chloranil concentration. This species is ascribable to the chloranil anion radical[21], and hence, cations must also be present in the system. In consistency with the optical data described above these can be related to an oxidation of the dimethylamino group. Thus, we may speak in terms of an acceptor doped conjugated polymer in solution. The detailed nature of the polymer cation is, however, still obscure. No evidence of radical cations was found in the e.s.r. spectra.

SUMMARY

It has been shown how a strong donor function *N*,*N*-dimethylamine, can be introduced into the polyphenylacetylene system by copolymerization of 4-(*N*,*N*-dimethylamino)phenylacetylene and phenylacetylene with various substituents, using a rhodium catalyst. The copolymers are soluble and have reasonably high molecular weight. From e.s.r. and optical data, doping with organic acceptors in solution results in cationic species. This shows an alternative way to introduce positive charge density to a polyacetylene main chain. Furthermore, the colour changes which follow the doping may point to a possible application in relation to photoelectronics. Further details of the optical, electronic and magnetic properties are yet to be examined.

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