The effect of deuteration on the stabilities of *cis*-polyacetylene and polystyrene

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Differential scanning calorimetry (d.s.c.) confirms the greater stability of deuterated polystyrene compared to normal polystyrene with respect to oxidation in air. However, the same technique shows that the stability of deuterated *cis*-polyacetylene with respect to oxidation in air is no better than that of normal *cis*-polyacetylene. Our d.s.c. results also suggest that there may be a weak isotope effect for the hydrogen migration reaction under nitrogen but not for the isomerization of deuterated *cis*-polyacetylene to the *trans* isomer.

(Keywords: polyacetylene; polystyrene; deuteration)

INTRODUCTION

A potential application of D_2O is the production of deuterated plastics, which may have desirable properties compared to the non-deuterated equivalents[1-3]. For example, the greater stability of deuterated polystyrene with respect to oxidation has been reported[1]. Another polymer that may have improved stability and other properties upon deuteration is polyacetylene. Doped *cis*-polyacetylene $(CH)_x$ is a potentially valuable organic conductor, with conductivities[4] of up to $10^5\,S\,cm^{-1}$. However, its usefulness is limited by poor stability with respect to *cis–trans* isomerization[5,6] (especially in the presence of oxygen[7,8]), crosslinking[9,10] and oxidation in air[11-14]. These processes can decrease the conductivity and increase the brittleness[11] of the polymer. It is the purpose of this study to determine whether or not deuteration will slow these undesirable processes, and thereby to gain insight into the mechanisms by which they occur.

Essentially the same mechanism has been proposed for the oxidative degradation of several polymers, including polystyrene[15,16] polypropylene[17] and polyacetylene[11,18]. In each case the oxygen-induced cleavage of C–H bonds is proposed to result in the formation of hydroperoxides, which decompose to form either hydroxyl or carbonyl groups[19,20]. Such a mechanism would lead to a kinetic isotope effect if the C–H bond cleavage step were rate-determining. Studies on the rates of oxidative degradation of deuterated *versus* non-deuterated polystyrene[1] and polypropylene[17] have shown just such an isotope effect. To our knowledge, there have been no reports on the effect of deuteration on the rate of oxidative degradation of *cis*-polyacetylene.

We report here, as a test case, data confirming that the favourable effect of deuteration on the stability of polystyrene is easily detected by differential scanning calorimetry (d.s.c.) as a significant difference in the oxidative induction time and the temperature of the onset of oxidation. Similar experiments using deuterated and non-deuterated *cis*-polyacetylene were performed in order to test for an isotope effect in the stability of that polymer.

EXPERIMENTAL

Materials

All reactions and tests were performed under inert-gas conditions unless otherwise stated. The reagents CaC_2 (Aldrich), $Ti(OBu)_4$ (Aldrich) and $AlEt_3$ (Ethyl Corp.) were used without further purification. Distilled water and D_2O (donated by Ontario Hydro, 99.92%) were degassed before use. Styrene-d_8 (Aldrich) was distilled before use. The solvent 1,4-dioxane (BDH, analytical grade) was purified by refluxing 500 ml with concentrated HCl (50 ml) for 10 h under nitrogen, neutralizing with KOH (40 g), and then separating from the aqueous layer. The solvent was then dried with $MgSO_4$, refluxed (3 h) and subsequently distilled over 4 Å molecular sieves. The free-radial initiator 2,2′-axobisisobutyronitrile (AIBN; Eastman Kodak) was recrystallized from methanol. The Ziegler–Natta catalyst was prepared in silicone oil by the method of Naarmann and Theophilou[21]. The oil (SWS-101, 1000 cS, polydimethylsiloxane) was manufactured by Wacker Silicones Corp. and donated by Henley Chemicals.

Polystyrene preparation and characterization

The polystyrenes were prepared by the AIBN-catalysed free-radical polymerization of distilled styrene or per-

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Table 1 Properties of the polystyrenes

Parameter	Poly(styrene)	Poly(perdeuterostyrene)
M_n	3.7×10^4	6.6×10^4
M_w	7.2×10^4	1.38×10^5
M_p	7.6×10^4	1.41×10^5
M_w/M_n	1.94	2.08
^1H n.m.r. H_α (ppm)	2.26[a]	–
^1H n.m.r. $H\beta$ (ppm)	1.75[a]	–
^{13}C n.m.r. C_α, C_β (ppm)	41.37[a]	40.1[b]
^{13}C n.m.r. C_1 (ppm)	146.38[a]	146[b]
Glass transition (°C)	104	104
Onset of oxidation (°C)	271	299
OIT at 240°C (min)	13	48
OIT at 270°C (min)	–	11

[a] In C_6D_6
[b] In $CDCl_3$

deuterated styrene in 1,4-dioxane at 65°C for 47 h. The solid was precipitated by addition of methanol, filtered under argon, and dried under vacuum overnight. The solid was then redissolved in benzene and freeze-dried. The molecular weights were determined by gel permeation chromatography with a Waters liquid chromatography system including a 30 cm stainless-steel DuPont PSM bimodal column pair and a Waters R410 differential refractometer. The eluent was BHT-stabilized tetrahydrofuran ($1.0\,ml\,min^{-1}$). The calibration curve of molecular weight *versus* elution volume was obtained by use of nine near-monodisperse polystyrene standards of molecular weight 1000 to $1.8 \times 10^6\,g\,mol^{-1}$. ^1H and $^{13}C\{^1H\}$ n.m.r. spectra of the polystyrenes at room temperature were acquired with a Varian XL-200 n.m.r. spectrometer externally referenced to tetramethylsilane (TMS) at 0 ppm.

Polyacetylene preparation and characterization

Acetylene and deuterated acetylene were synthesized by dropwise addition of H_2O or D_2O to calcium carbide under N_2. The gas thus generated was passed through Drierite and activated alumina and into a 500 ml flat-bottomed three-necked reaction flask, the bottom of this flask being covered by an even film of the catalyst (7 ml). After the desired reaction time (220 min each for samples 2 ($(CD)_x$) and 3 ((CH_x)) and 70 min for sample 1 ($(CH)_x$), the reaction flask was flushed with nitrogen. The polyacetylene was washed under nitrogen as described by Naarmann and Theophilou[21], and dried by a slow flow of nitrogen for 30 min, during which it turned from black to gold colour. The samples were stored under nitrogen at room temperature in amber glass (samples 1 and 2) or clear glass bottles (3) in a glove box. The gold colour faded slowly over months for the samples stored under amber glass. The sample stored under clear glass was exposed to room light and showed no fading.

The reflectance infra-red spectra of the shiny side of $3 \times 5.5\,cm^2$ rectangular sections of washed undoped polyacetylene films (samples 2 and 3) were obtained at room temperature in air with a Nicolet 20SXB FT-IR (He/Ne laser) adapted for reflectance measurements. The thickness was measured by use of a TMI Precision Micrometer model 49-61.

The conductivity measurements were made under argon on unstretched samples doped with iodine by the method of Naarmann and Theophilou[21], which resulted in a doping level of $(CHI_{0.2})_x$ or $(CDI_{0.2})_x$ (calculated from the weight increase). The standard four-probe technique was used for conductivity measurements; the constant current (0.25 to 1.87 mA) was applied by an EG&G Potentiostat model 273, while the voltage drop was measured with a fluke 8505A Digital Multimeter.

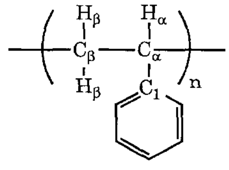
Differential scanning calorimetry

The d.s.c. experiments were carried out in an enclosed heating chamber, under $200\,cm^3\,min^{-1}$ of N_2 or O_2 in the dark using a DuPont instruments 920 AutoDSC with scan rates of 10°C min^{-1}. The polyacetylene samples were also scanned under N_2 at 60°C min^{-1} up to 480°C. At the higher scan rate, the observed transition temperatures are higher because of a temperature lag. Sample weights were 1 to 5 mg for polyacetylene and 5 to 9 mg for polystyrene.

RESULTS AND DISCUSSION

Polystyrene characterization

The molecular weights and other properties of the polystyrene and deuterated polystyrene samples are summarized in *Table 1*. The width of the $^{13}C\{^1H\}$ n.m.r. lines prevented the observation of coupling to the deuterium nuclei. The chemical shifts refer to the following structure:



The d.s.c. traces of both non-deuterated and deuterated polystyrene under nitrogen show a glass transition temperature of 104°C. The literature value of 100°C is known to vary with molecular weight and other factors[22].

Under oxygen, the polystyrenes underwent a strongly exothermic transition, attributed to oxidative degradation, with the onset 28.3°C higher for the deuterated polystyrene than for the non-deuterated sample (*Figure 1*). This represents a substantial isotope effect. At a

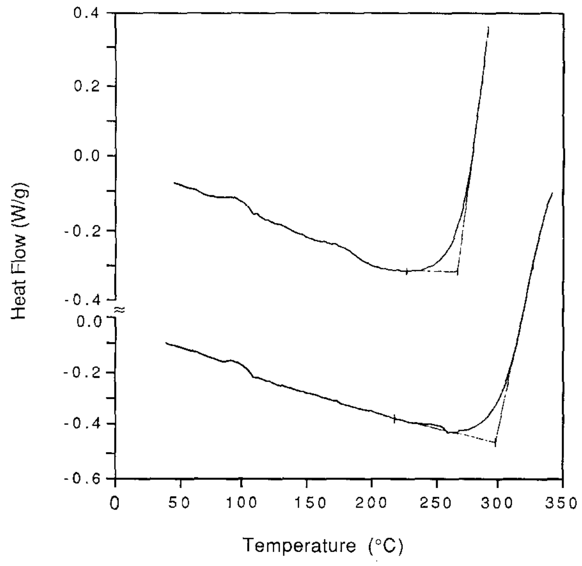


Figure 1 The d.s.c. thermograms of polystyrene (upper curve) and deuterated polystyrene (lower curve) under oxygen, showing the temperatures of the onset of oxidative degradation

Table 2 Preparation and properties of polyacetylene samples[a]

Sample	1	2	3
Formula	$(CH)_x$	$(CD)_x$	$(CH)_x$
Reaction time (min)	70	220	220
Mass (mg)	145	355	194
Thickness (mm)	0.0843	0.1592	0.1405
Grammage ($g\,m^{-2}$)	36.7	62.5	53.8
1st trans. onset, 10°C min^{-1} (°C)	103	110	–
1st trans. max., 10°C min^{-1} (°C)	168	168	–
1st trans. onset, 60°C min^{-1} (°C)	142	141	145
1st trans. max., 60°C min^{-1} (°C)	194	194	193
2nd trans. max., 60°C min^{-1} (°C)	373	376	372
OIT at 80°C under O_2 (min)	1.32	1.03	0.97
Onset of oxidation (°C)	96.4	95.2	–
Doping level	$(CHI_{0.24})_x$	$(CDI_{0.22})_x$	$(CHI_{0.15})_x$
Conductivity ($S\,cm^{-1}$)	200	200	200

[a] trans. = transition

constant temperature of 240°C and under 200 ml min^{-1} of O_2, the deuterated sample had an oxidative induction time (*OIT*) 3.6 times longer than that for non-deuterated polystyrene. The *OIT* of the deuterated polymer at 270°C was comparable to that of the non-deuterated polystyrene at 240°C. The results confirm the observation by Beachell and Nemphos[1] that deuteration of polystyrene slows the rate of oxidation and increases the oxidative induction time, presumably because the rate-determining step is C–H bond cleavage. Their work compared polymers of similar molecular weight, which rules out the possibility that the initiation time for oxidative degradation just depends on the number of reactive end-groups; this could have been an explanation for the lower reactivity of our deuterated sample, which has twice the molecular weight of the non-deuterated one.

Synthesis of polyacetylene

One $(CD)_x$ and two $(CH)_x$ gold-coloured films were synthesised by passing acetylene (from D_2O or H_2O and CaC_2) over a Naarmann-type Ziegler–Natta catalyst. The samples were stored in a glove box under nitrogen.

Polyacetylene characterization

Characterization of polyacetylene is difficult because it is not soluble in any solvent. The films are too thick for conventional transmittance i.r., so reflectance i.r. was used. The spectrum of sample 3 (non-deuterated) was acquired 59 days after synthesis. The corresponding spectrum of sample 2 could not be used because of interference fringes. The vibrations observed for sample 3 (assignments[23] in parentheses) were weak in-plane C–H deformations at 1292 (B_{1u}, *trans*) and 1249 (B_{3u}, *cis*), strong out-of-plane C–H deformations at 1015 (B_{2u}, *trans*) and 740 (B_{3h}, *cis*), and a strong C–C–C deformation at 446 cm^{-1} (B_{1u}, *cis*). The absence of bands at 1670 and 1730 cm^{-1} indicates the absence of ketone and diketone groups, respectively[11]. Therefore there has been no detectable oxidation.

The preparative method produces *cis*-rich polyacetylene[24]. Although the extent of isomerization of N-type $(CH)_x$ to the *trans* isomer is reported to be negligible over several months[21], the observation of i.r. bands for vibrations of the *trans* polymer indicates that some isomerization has taken place. The i.r. and d.s.c. results (see below) show that significant amounts of the *cis* isomer remain in the samples. It was not possible to stretch the samples more than 22% (for $(CD)_x$) or 7% (for (CH_x), which suggests that some crosslinking has also taken place.

Even after 7 months under N_2, the three samples of polyacetylene, when doped with iodine, had conductivities of $2.0 \times 10^2\,S\,cm^{-1}$ (*Table 2*). This value is somewhat lower than recently reported conductivities of three-month-old Naarman-type *cis*-polyacetylene (as high as $1.8 \times 10^3\,S\,cm^{-1}$) but higher than the conductivity of one-month-old Shirakawa-type polyacetylene $(1.5 \times 10^2\,S\,cm^{-1})$[21].

The differential scanning calorimetry of polyacetylene under nitrogen has been reported by Kleist and Byrd[5] and Ito *et al.*[25]. No glass transition temperature is observed[25]. An exothermic transition has a maximum at 145°C and corresponds to *cis–trans* isomerization. The onset of this is between 75 and 120°C (read from the figures of the reference)[25]. The isomerization is believed to take place via an excited state in which π electrons are no longer bonding (a biradical), thus allowing rotation about the single σ bond[26]. It is likely that the preferred initial isomerization pathway involves the simultaneous formation of two biradicals, which permits a low-energy 'crankshaft rotation'[6]. One would not expect an isotope effect for such a pathway. At 325°C, an exothermic transition is observed, which Kleist and Byrd attribute to a crystallization phenomenon and Ito *et al.* attribute, more believably, to hydrogen migration and possible main-chain scission. At approximately 420°C, decomposition to benzene and other products takes place; the temperature is higher for *cis*-polyacetylene.

The d.s.c. traces (at 10°C min^{-1}) of our samples of non-deuterated and deuterated *cis*-polyacetylene under nitrogen show an exothermic transition peaking at 168°C, corresponding to *cis–trans* isomerization. Although the peak temperature for the transition is independent of deuteration, a slight shift of the curve for the deuterated sample to higher temperature is evident in *Figure 2a* and in the 7°C higher onset temperature. These observations suggest a possible weak and unexpected isotope effect. However, at the higher scan rate of 60°C min^{-1} (*Figure 2b*), used for scans of up to 480°C, the isotope effect in the isomerization is not detected. The existence of an isotope effect was further tested by calculating the percentage *cis* content of the films from the ΔH ($J\,g^{-1}$ or $cal\,g^{-1}$) of isomerization by the method of Tober and Ferraris[27]. Samples 1 (non-deuterated) and 2 (deuterated), both stored under amber glass, had equal *cis* contents of 40% after 5 months and 30% after 10 months. These observations do not support a possible isotope effect in the isomerization rate. Sample 3, stored under clear glass, had a lower *cis* content of 22% after 9 months. The remaining *cis* content could have been lower in sample 3 because of light-assisted isomerization.

The second exothermic transition, which Ito *et al.* attribute to hydrogen migration and possible main-chain scission[25], had, in our experiments, a peak temperature of 372–373°C (at 60°C min^{-1}) for the non-deuterated polyacetylenes and 376°C for the deuterated sample. If the temperature difference is significant, this also constitutes a weak isotope effect; a result that is reasonable if the process is hydrogen migration. The products of chain scission

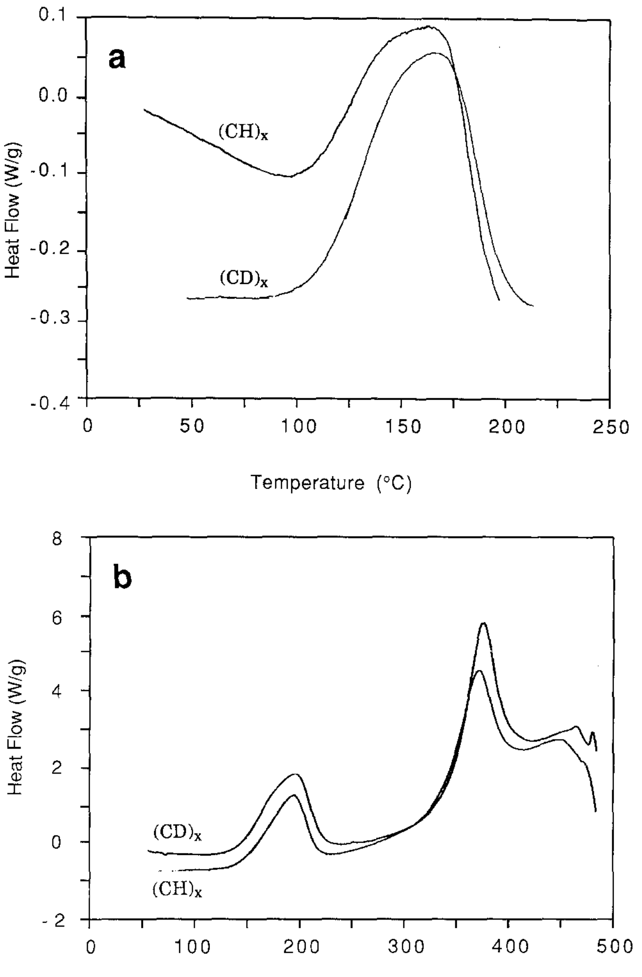


Figure 2 The d.s.c. thermograms of *cis*-$(CH)_x$ and *cis*-$(CD)_x$ under nitrogen at scan rates of (a) 10°C min^{-1} and (b) 60°C min^{-1}

induced by pyrolysis have been analysed previously[28,29].

The d.s.c. of polyacetylene under O_2 has not been previously reported, but the t.g.a. of a sample of *cis*-polyacetylene under air was described by Kleist and Byrd[5] as a weight gain (due to oxidation) up to 232°C, and a gradual weight loss thereafter. The near-coincidence of the peak of this weight gain (182–202°C) and the maximum rate of *cis–trans* isomerization (147–182°C) suggested to those authors that the C=C double bond is most susceptible to oxidation during the isomerization reaction. Yen *et al.*[11] reported that the half-life for the oxidation of polyacetylene in dry air at 80°C is 14.7 h, determined by i.r. spectroscopy, although they did not mention an induction period.

Under oxygen, the *cis*-polyacetylenes in the present study undergo a strongly exothermic transition, with onset temperatures of about 96°C for both $(CD)_x$ and $(CH)_x$ (*Figure 3*). At a constant temperature of 80°C and under 200 ml min^{-1} of O_2, the oxidative induction time (1 min) is also the same for $(CD)_x$ and $(CH)_x$. These results show that no advantage in resistance to oxidation is obtained upon deuteration of polyacetylene.

The lack of an isotope effect in the case of polyacetylene proves that the induction period does not involve rate-determining C–H bond cleavage. Therefore the mechanism of oxidation of polyacetylene is different from that of polystyrene, where C–H bond cleavage during the induction period, followed by hydroperoxide formation, results in an isotope effect. Instead, if the induction period represents a build-up of a charge-transfer complex between oxygen and polyacetylene, as suggested by Gibson and Pochan[19], then no isotope effect is expected. Another obvious alternative mechanism is direct addition of the O_2 molecule across the C=C double bond[18], which would not involve a primary isotope effect. Because the d.s.c. results do not give kinetic data for the reaction that occurs after the end of the induction period, that mechanism cannot be considered to be disproved. A truer test of the mechanism would be a complete kinetic study, like that of Yen *et al.*[11] applied to both deuterated and non-deuterated samples.

CONCLUSIONS

Differential scanning calorimetry confirms the greater stability of deuterated polystyrene compared to normal polystyrene with respect to oxidation in air. However, the same technique shows that the stability of *cis*-$(CD)_x$ with respect to oxidation in air is no better than that of *cis*-$(CH)_x$. Previous reports have also suggested that there is little advantage to using $(CD)_x$ rather than $(CH)_x$ for applications; Schlenoff and Chien[30] showed that the electrochemistry of $(CD)_x$ is the same as that of $(CH)_x$, while Kamiya and Tanaka[31] showed that the conductivity of doped $(CD)_x$ is 5–9 times lower than that of equally doped $(CH)_x$. Our d.s.c. results also suggest that there is no isotope effect for the isomerization of deuterated *cis*-polyacetylene to the *trans* isomer, but there may be a weak isotope effect for the hydrogen migration reaction under nitrogen. Future studies are needed to compare the d.s.c. thermograms of samples of *trans*-$(CH)_x$ and $(CD)_x$ in order to probe the relationship between the *cis–trans* isomerization reaction and oxidative degradation.

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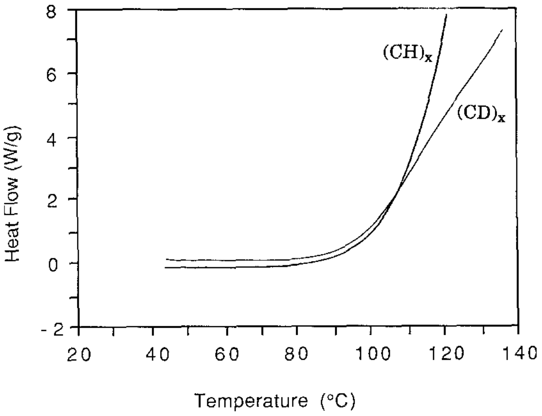

Figure 3 The d.s.c. thermograms of *cis*-$(CH)_x$ and *cis*-$(CD)_x$ under oxygen

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