BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 22, pp. 4315–4326, 1995

0032-3861/95/$10.00+0.00

Formation of poly(1,4-phenylene sulfide) by solution polymerization of copper(I) 4-bromobenzenethiolate: experimental evidence for operation of single-electron transfer processes

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(Received 1 December 1994; revised 21 March 1995)

An investigation into the mechanism of formation of poly(1,4-phenylene sulfide) (PPS) by solution polymerization of copper (I) 4-bromobenzenethiolate (CBT) at 200°C in quinoline under nitrogen at atmospheric pressure is reported. The polymerization has been monitored as a function of reaction time by electron spin resonance (e.s.r.) spectroscopy and by evaluating the yield and molar mass of the PPS formed. The e.s.r. spectra show the existence of organic free radicals throughout the polymerization and also reveal the presence of Cu^{2+} ions during the period, up to about 2 h reaction time, when PPS yield and molar mass increase rapidly, suggesting initiation by single-electron transfer (SET) from Cu^+. Ultra-violet radiation and 1,3-dinitrobenzene are shown to have significant effects on the yield and molar mass of the PPS, lending further support to the argument for a mechanism involving free radicals. Confirmation that CBT is capable of undergoing irreversible reactions via both reductive and oxidative SET processes is provided by results from cyclic voltammetry of CBT solutions. The results from the study, therefore, provide strong evidence for operation of a SET mechanism in solution polymerization of CBT.

(Keywords: Cu(I) 4-bromobenzenethiolate; solution polymerization; poly(1,4-phenylene sulfide))

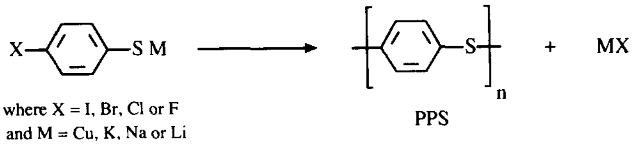
INTRODUCTION

Poly(1,4-phenylene sulfide) (PPS) quickly became established as an important engineering plastic following its commercialization by Phillips Petroleum in 1973 [1,2]. The route to PPS developed and used by Phillips involves the reaction of 1,4-dichlorobenzene with sodium sulfide in an aprotic solvent at about 250°C under pressure[3]. In recent years, interest in the preparation of PPS has been growing, with a wide range of new routes being published[4–14]. The present paper, however, is concerned with a convenient laboratory method for preparation of PPS[15,16] that is based upon a long-established, general route involving polymerization of metal(I) 4-halobenzenethiolates (*Scheme 1*) and was first reported by Lenz, Smith and Handlovits[17,18].

The following general observations have resulted from studies of this route to PPS:

(i) I.r. spectra of the PPS formed show evidence only of 1,4-phenylene sulfide repeat units.
(ii) Relatively high-molar-mass PPS is formed at low monomer conversions for a condensation polymerization (i.e. 70–90%).
(iii) The trends in monomer reactivity are for the halogen I > Br > Cl,F and for the metal ion $Cu^+ > Li^+ > Na^+ > K^+$.

An S_N2Ar mechanism via Meisenheimer complexes was invoked[18] to explain the first of these observations. Also, since the propagation step in this mechanism requires two electron-rich species to react with each other, and since charge separation in the intermediate increases with the degree of polymerization, it was suggested that this would lead to 'preferential polymer formation', thus explaining the second observation. However, the trend in halogen reactivity is opposite to that expected for reactions proceeding by an S_N2Ar mechanism and leads to doubt about the validity of this mechanistic interpretation. Nevertheless, at the time of the original work, the only accepted alternative mechanism for aromatic nucleophilic substitution was the S_N1Ar mechanism via benzyne intermediates. The absence of



where X = I, Br, Cl or F
and M = Cu, K, Na or Li

Scheme 1 Formation of poly(1,4-phenylene sulfide) (PPS) by polymerization of metal(I) 4-halobenzenethiolates

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1,3-phenylene sulfide repeat units showed clearly that the S_N1Ar mechanism was not operating.

During the 1970s, Bunnett and coworkers established that many reactions that produce simple diaryl sulfides proceed via an $S_{RN}1$ mechanism involving single-electron transfer processes with radical and radical-anion intermediates[19]. This mechanism has now become more widely recognized in organic chemistry[20]. The expected, and observed, order of reactivity for haloarenes in $S_{RN}1$ is $I > Br > Cl > F$, suggesting that this mechanism may be operating in the polymerization of metal(I) 4-halobenzenethiolates. An $S_{RN}1$ mechanism has already been proposed by Novi *et al.*[4] in order to explain the effect of diazonium salts in facilitating solution polymerization of sodium 4-bromobenzenethiolate at room temperature. Additionally, other single-electron transfer mechanisms have been proposed for reactions that produce PPS: Koch and Heitz[21] suggested that the formation of PPS by the Phillips method proceeds via a mechanism that involves radical and radical-cation intermediates; and Tsuchida *et al.*[5-9] have proposed a cationic oxidative mechanism to explain the formation of PPS when either thiophenol or diphenyl disulfide is subjected to oxidizing conditions. Furthermore, free-radical mechanisms have been proposed by Hay and Wang for the formation of PPS by thermolysis of bis(4-iodophenyl) disulfide[10-12], and by Rule *et al.*[13,14] for the related polymerization in which PPS is formed by melt-phase reaction of 1,4-diiodobenzene with sulfur.

The principal objective of the work described in this paper was to establish whether or not a mechanism involving single-electron transfer reactions and intermediates possessing unpaired electrons operates in solution polymerization of copper(I) 4-bromobenzenethiolate (CBT). To assist the mechanistic interpretation, a further important objective was to obtain accurate information on the development of PPS molar mass with reaction time. Some results from the work have already been reported in preliminary from[22-24] and give the first direct evidence for the existence of organic radical species in the solution polymerization of CBT. The present paper reports all the results from the research programme and provides further strong evidence for the operation of a single-electron transfer (SET) mechanism. Interpretation of the results in relation to the body of knowledge on polymerizations of metal(I) 4-halobenzenethiolates is considered in detail in the following paper[25].

EXPERIMENTAL

Materials

The procedures used to prepare and characterize CBT, and to purify toluene, 1-chloronaphthalene and methanol have been described previously[15,26].

Quinoline (Fluka, purum.) was stored over potassium hydroxide pellets upon receipt and, prior to use, was dried further at room temperature over powdered calcium hydride for 24 h before distillation under nitrogen through a lagged Hempel column at reduced pressure: b.p. 80°C/2.0 mmHg, $n_D^{20} = 1.6266$: lit. b.p. 80°C/3.1 mmHg[27], $n_D^{20} = 1.6268$[28]. Pyridine (Fluka, puriss.) was treated in a similar manner to quinoline except that it was distilled at atmospheric pressure: b.p. 116°C, $n_D^{20} = 1.5093$; lit.[28] b.p. 115.5°C, $n_D^{20} = 1.5095$. The water contents of the purified quinoline and pyridine were determined to an accuracy of ±0.01% by Karl-Fischer titrimetry, which gave values of $<0.01\%$ and 0.03% respectively.

1,3-Dinitrobenzene (BDH, AnalaR) was recrystallized from methylated spirit to give white crystals that were dried to constant weight at 40°C under vacuum: m.p. 89–90°C; lit.[28] m.p. 90°C. Copper(I) bromide (Aldrich, 99.99%), copper(I) benzenethiolate (Fluka, purum.), tetraethylammonium tetrafluoroborate (Aldrich, 99%), bromobenzene (Fluka, puriss.) and 1,4-dichlorobenzene (Fluka, purum.) were used as received.

Cyclic voltammetry

Cyclic voltammetry was carried out under a static argon atmosphere using a three-electrode cell comprising a platinum-foil working electrode, a platinum-gauze counter-electrode and a calomel reference electrode. All solutions were thoroughly purged with argon prior to analysis. Current was measured continuously on a galvanometer (2 mA current limit) during both cathodic and anodic voltage sweeps, which were performed over the voltage ranges 0 to -4 V and 0 to $+2$ V, respectively, employing a sweep rate of $20\,\mathrm{mV\,s^{-1}}$.

Polymerizations

CBT was polymerized at 200°C as a $1\,\mathrm{mol\,dm^{-3}}$ solution in quinoline using different procedures for long and short reaction times.

For reaction times from 2 to 24 h, the following procedure was used. Quinoline ($100\,\mathrm{cm^3}$) was added by pipette to a $100\,\mathrm{cm^3}$ three-necked round-bottomed flask equipped with a thermometer, drawn gas inlet tube and a condenser fitted with a calcium chloride guard tube. After establishing a flowing, dry nitrogen atmosphere, the flask was placed in an oil bath thermostatted at 200 ± 0.1°C. Upon temperature equilibration, CBT (25.0 g, 0.10 mol) was added and polymerization was allowed to proceed for 24 h before cooling the reaction mixture to room temperature. Two samples were removed at each of several intervals during polymerization for (i) isolation, fractionation and characterization of the PPS, and (ii) analysis by electron spin resonance (e.s.r.) spectroscopy. In each case the first sample ($\sim 20\,\mathrm{cm^3}$) was removed using a pipette pre-heated at ~ 220°C; the PPS was worked up and fractionated into cold-toluene-soluble (CTS), cold-toluene-insoluble (CTI) and 1-chloronaphthalene-soluble (CNS) material using established procedures[26] before drying each fraction overnight under vacuum at 110°C, grinding the fractions to powders and then drying them to constant weight at 110°C /0.2 mmHg. The second sample ($\sim 2\,\mathrm{cm^3}$) was removed using a small, pre-heated (~ 220°C) syringe and injected into a pre-heated (~ 220°C) silica-glass e.s.r. tube, which was immediately quench-cooled in liquid nitrogen, sealed and then stored in liquid nitrogen before e.s.r. analysis.

For reaction times up to 60 min, the polymerizations were performed individually in modified Stokes tubes using otherwise identical procedures to those for the longer reaction times. CBT (3.80 g, 0.015 mol) and quinoline ($15\,\mathrm{cm^3}$) were added to a modified Stokes tube that had been fitted with a capillary gas inlet tube and an air condenser. After establishing a flowing, dry nitrogen atmosphere, the Stokes tube was placed in an oil bath thermostatted at 200 ± 0.1°C and polymerization allowed to proceed for the required time. At the required reaction time, a sample was removed for analysis by e.s.r. using the procedure described above, and the remaining reaction mixture cooled to room temperature to stop the polymerization. The PPS from the cooled reaction mixture was then worked up and fractionated.

Polymerization of CBT (25.0 g, 0.10 mol) in quinoline (100 cm^3) also was carried out under nitrogen at 200°C simultaneously with exposure to u.v. radiation. For these experiments a specially designed, vertical-sided, 250 cm^3 flanged reaction vessel was used, which had the usual inlet and outlet ports around its side plus a flat quartz lid which acted as the window for u.v. radiation supplied from a high-intensity Hanovia lamp (wavelength range 185–254 nm) placed with its outlet about a centimetre above the quartz lid. At intervals during the reaction, samples were removed for e.s.r. analysis and for isolation of the PPS.

Control experiments and model reaction

A series of control experiments were performed on quinoline, and 1 mol dm^{-3} solutions of copper(I) bromide and copper(II) bromide in quinoline, to assist in the interpretation of e.s.r. spectra from the polymerizations. The experiments were carried out in exactly the same way as described for the polymerizations but were sampled only for e.s.r. analysis.

A model reaction of copper(I) benzenethiolate (2.591 g, 0.015 mol) with bromobenzene (2.355 g, 0.015 mol) in quinoline (15 cm^3) was carried out using the conditions and apparatus described for the shorter polymerizations. The reaction was allowed to proceed for 6 h, samples being removed at intervals for e.s.r. analysis in the way described for the polymerizations. The final reaction mixture was cooled to room temperature and the yield of diphenyl sulfide determined by gas–liquid chromatography using the internal standard method as follows. A sample (~ 4 g) of the cooled reaction solution and 1,4-dichlorobenzene (~ 1 g) (internal standard) were weighed accurately into a 10 cm^3 volumetric flask, which was then made up to the mark with toluene. The resulting solution (1 μl) was injected onto a glass column (length= 2 m, inside diameter= 2 mm) that was packed with 10% silicone SE-30 on Chromosorb W (80/100 mesh) and fitted in a Hewlett-Packard 5830A Gas Chromatograph equipped with a flame ionization detector. The components were separated using the following temperature programme: a temperature of 100°C was held for 5 min followed by heating at 5°C min^{-1} to 175°C and then at 10°C min^{-1} to 350°C, this temperature being held for a further 5 min. Retention times and the relative detector response factor determined from calibration solutions were used in analysis of the chromatograms of the reaction mixture to quantify the amount of diphenyl sulfide present.

E.s.r. spectroscopy

E.s.r. spectroscopy was carried out at −150°C on a Varian model E9 spectrometer operating with a microwave frequency of 9.5 GHz at 20 mW power and with a modulation frequency of 10 kHz. Spectra were recorded over the ranges 3200–3600 and 2400–4400 G using modulation amplitudes of 1 and 10 G respectively. Samples were mounted in one cavity with a pitch carbon standard (g-value, $g_s = 2.0028$) as a calibrant in the other. The g-values for e.s.r. signals from the samples were calculated from $g = g_s[2 - (H/H_s)]$ (ref. 29) where H and H_s are the values of the resonance field strengths for the signals from the sample and the standard respectively.

Polymer characterization

Combustion analyses were carried out by the Microanalysis Section of the Chemistry Department at UMIST to the following limits of accuracy: C ±0.3%, H ±0.2%, S ±0.5%, Br ±0.1% and N ±0.3%. I.r. spectra were recorded on a Grubb-Parsons GS8 spectrometer using 1% dispersions in potassium bromide. Dilute solution viscometry was performed at 209.0 ± 0.1°C using a specially designed viscometer and procedures previously reported[16]. Established procedures of d.s.c. analysis[26] were used to determine the glass transition temperature, cold crystallization temperature and melting temperature of samples shock-cooled from the melt by immersion in liquid nitrogen.

RESULTS AND DISCUSSION

General features of CBT polymerization

A previous study[15] focused on the development of molar mass with time in the preparation of poly(1,4-phenylene sulfide) (PPS) by solution polymerization of copper(I) 4-bromobenzenethiolate (CBT) at 1 mol dm^{-3} concentration in a quinoline/pyridine (91% v/v quinoline) mixture at reflux. However, the results were subject to a degree of uncertainty arising from loss of bromine end-groups during the reaction. In the present work it was important to obtain accurate information on the changes in molar mass with time to assist in the mechanistic interpretation of the e.s.r. observations. In this respect, advantage was taken of the findings from a more recent study[30], which showed that high-molar-mass PPS can be formed in high yield without significant debromination if the reaction temperature is held at 200°C. These observations are in agreement with the results from a model compound study[31], which indicated that debromination should only be significant when the temperature was around 220°C or above. Thus the polymerization temperature was maintained at 200°C in the studies reported here.

The fractionation procedure used in the work-up of the PPS yields cold-toluene-soluble (CTS) and cold-toluene-insoluble (CTI) PPS fractions, which are of relatively low molar mass, and a 1-chloronaphthalene-soluble (CNS) PPS fraction of much higher molar mass. The total yield of PPS, and the yields of the CTS, CTI and CNS PPS fractions are plotted in *Figure 1* as a function of reaction time. Both the total PPS yield and the yield of CNS PPS increase rapidly with reaction time, in accord with previous observations on solution polymerization of CBT[15]. The yields of CTS and CTI PPS pass through maxima at about 0.4 h and 0.6 h reaction time respectively. After about 1 h reaction time the yield of CTS PPS reaches a limiting value of ~ 6%, whereas the yield of CTI PPS has reduced to zero.

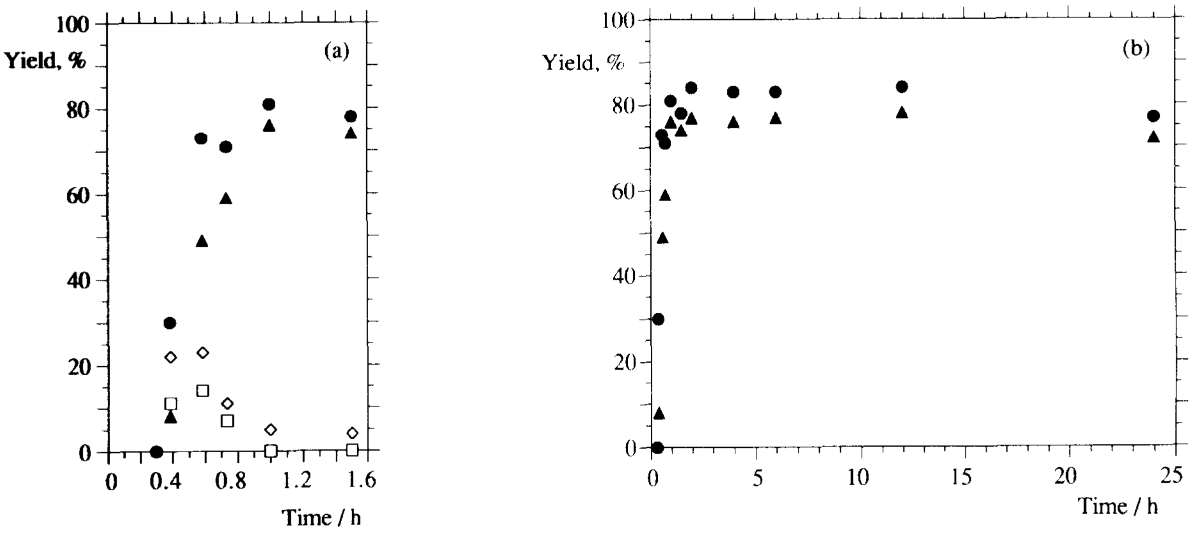

Figure 1 Plots showing the effect of reaction time upon the total yield of PPS (●), the yield of the CNS PPS fraction (▲), the yield of the CTI PPS fraction (□) and the sum of the yields of the CTS and CTI PPS fractions (◇): (a) 0–1.5 h reaction time; (b) 0–24 h reaction time

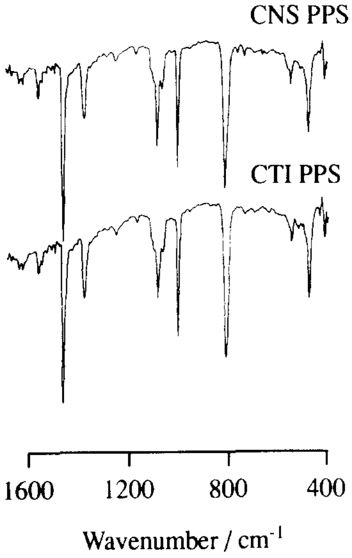

Figure 2 Typical i.r. spectra of the CTI and CNS PPS fractions. The single absorption, at 810 cm^{-1}, in the aromatic out-of-plane C–H bending region confirms 1,4-disubstitution. The triple absorption in the region 1040–1140 cm^{-1} is characteristic of linear PPS[16]. (Note that the higher-frequency absorption appears as a shoulder at the resolution shown)

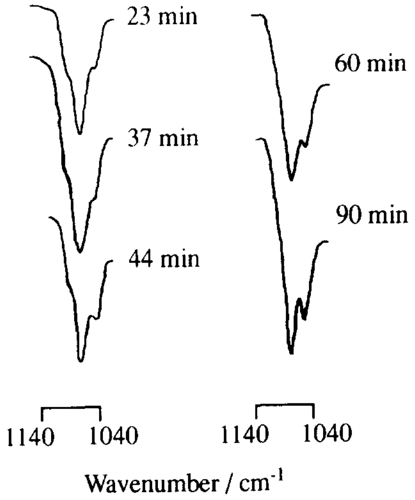

Figure 3 I.r. spectra (1040–1140 cm^{-1} region) of the CTS PPS fractions obtained during the first 1.5 h of reaction. The spectra of the CTS PPS fractions obtained at 60 and 90 min reaction times show only the two absorptions characteristic of cyclic PPS[16]. The spectra of the CTS PPS fractions obtained at 23, 37 and 44 min reaction times show an additional shoulder at higher wavenumber indicating that they are mixtures of linear and cyclic PPS[16]

The changes in the yields of CTS and CTI PPS take on greater significance when considered together with structural information from i.r. spectroscopy. Previous work[16] revealed that linear PPS gives three absorptions in the 1040–1140 cm^{-1} region whereas cyclic PPS shows only two absorptions. On this basis, the i.r. spectra of the CTI and CNS PPS fractions shown in *Figure 2* are consistent with their being linear PPS. Furthermore, they show evidence only for 1,4-phenylene sulfide repeat units, in accord with the previous observations described in the 'Introduction'. The i.r. spectra of the CTS PPS fractions given in *Figure 3* show that they are mixtures of cyclic and linear PPS oligomers at reaction times below 1 h, but comprise only cyclic oligomers at longer reaction times. The inference to be drawn from consideration of these observations in relation to the results presented in *Figure 1* is that the linear oligomeric PPS initially present in the CTS and CTI fractions is consumed in forming higher-molar-mass CNS PPS as the reaction progresses. Clearly, this important feature must be taken into account in the mechanistic interpretation of the polymerization.

A further important feature of the polymerization is revealed by the changes in molar mass of the CNS PPS fraction with reaction time. Several properties give measures of the molar mass of this fraction.

The measured percentage by weight of bromine, %Br, in the PPS can be used to calculate the number-average molar mass, M_{Br}, from the following equation assuming that debromination has not occurred and that the PPS chains have the structure Br–$(C_6H_4S)_n$–H:

$$M_{\mathrm{Br}} = \frac{7.991}{\%\mathrm{Br}}\ (\mathrm{kg\ mol^{-1}})$$

Viscosities of 40 mg cm^{-3} solutions of CNS PPS in 1-chloronaphthalene measured at 209°C gave reduced viscosities from which intrinsic viscosities were calculated using the single-concentration method of Soloman and Ciuta[32], a method that previously has been shown to be satisfactory for this polymer–solvent system[30]. The intrinsic viscosities were then converted into viscosity-average molar masses, M_η, using the Mark–Houwink equation[33,34] with the constants reported by Stacy[35].

The changes in M_{Br} and M_η of the CNS PPS fraction with reaction time are shown in *Figure 4*. Thus there is a relatively rapid increase in molar mass during the first 2–3 h of reaction, which is followed by a much slower increase in the period up to 24 h reaction time. As is to be expected, $M_\eta > M_{\mathrm{Br}}$. The polydispersity ratio M_η/M_{Br} does not alter significantly with reaction time and takes values in the range 2.7 to 3.9 with a mean of 3.2 and standard deviation of 0.4.

Glass transition temperatures, T_g, cold crystallization temperatures, T_{cc}, and melting temperatures, T_m, measured by d.s.c. give further indications of changes in CNS PPS molar mass with reaction time, though the latter two properties are insensitive to molar mass at the higher molar masses and so are useful only for revealing the initial rapid increase in molar mass. The use of these properties to monitor changes in molar mass is further restricted because quench-cooling of the CNS PPS fractions isolated at reaction times < 1 h gave samples that were not sufficiently amorphous to detect the glass transition and cold crystallization. Despite these limitations, the changes in T_g, T_{cc} and T_m with reaction time shown in *Figure 5* provide evidence in support of the observed changes in molar-mass averages with reaction time.

Careful comparison of the results presented in *Figure 1* with those shown in *Figure 4* reveals that, although the yield of CNS PPS increases rapidly to an approximately constant value of 78% after 1 h reaction time, the molar mass of this fraction increases continuously throughout the reaction. This is very clearly demonstrated in *Figure 6*, which shows how the molar-mass averages correlate with the yield of CNS PPS. Thus the molar mass of the CNS PPS fraction does not increase greatly until the yield of this fraction has reached its limiting value. This is yet another important feature of the polymerization that is of significance in terms of establishing an understanding of the reaction mechanism. *Figure 6* also shows that, contrary to predictions of the classical theory of condensation polymerization, relatively high-molar-mass PPS is formed at monomer conversions well below 100% in solution polymerization of CBT.

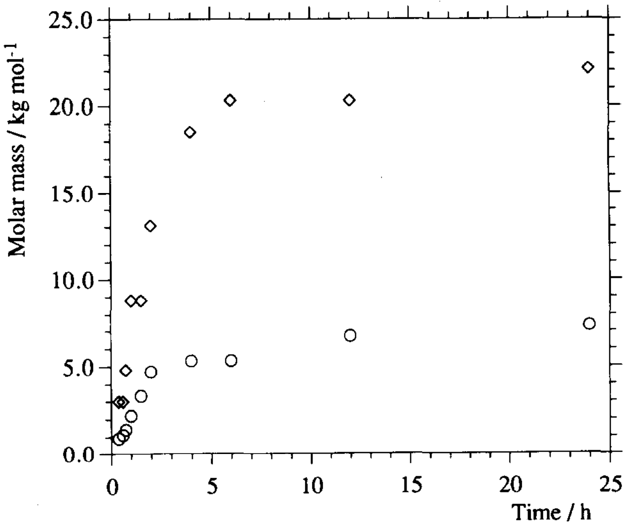

Figure 4 Variation of the number-average molar mass M_{Br} (○) and the viscosity-average molar mass M_η (◇) of the CNS PPS fraction with reaction time

Comparison with previous work on CBT polymerization

As stated at the beginning of the previous section, the conditions selected for CBT polymerization were expected to prevent debromination of the PPS chains. Strong evidence that debromination was negligible is provided by the data in *Table 1*, which show that the

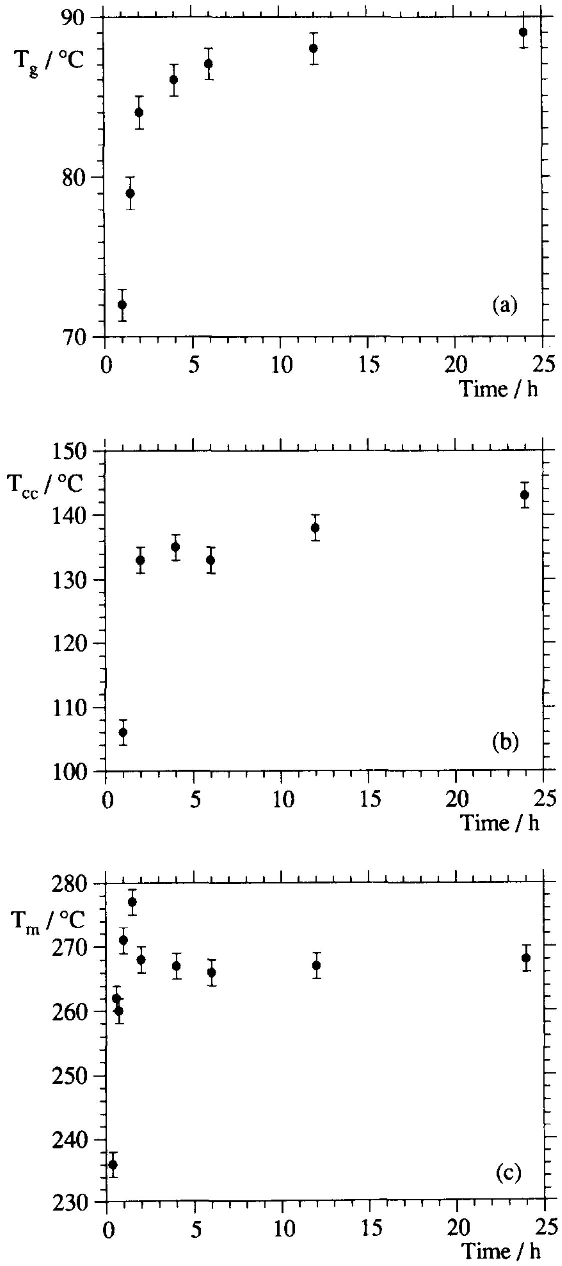

Figure 5 Variation of the transition temperatures of the CNS PPS fraction with reaction time: (a) glass transition temperature T_g; (b) cold-crystallization temperature T_{cc}; (c) melting temperature T_m

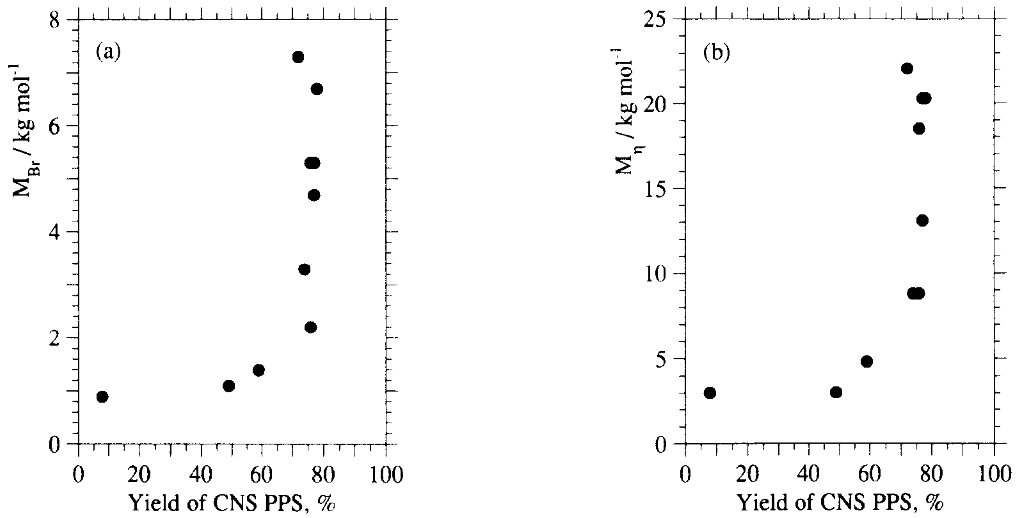

Figure 6 Correlation of molar-mass averages with yield for the CNS PPS fraction: (a) number-average molar mass M_{Br}; (b) viscosity-average molar mass M_η

Table 1 Elemental compositions of the CNS PPS fractions

CNS PPS isolated at reaction time	%C		%H		%S		%Br
	Expt	Theory[a]	Expt	Theory[a]	Expt	Theory[a]	Expt
23 min	61.0	60.7	3.2	3.4	26.5	26.9	9.0
35 min	62.3	61.7	3.2	3.4	27.4	27.4	7.5
44 min	63.3	62.9	3.2	3.5	27.6	27.9	5.7
60 min	64.7	64.3	3.5	3.6	28.0	28.5	3.6
90 min	64.9	65.0	3.3	3.6	29.2	29.0	2.4
2 h	65.3	65.5	3.5	3.7	29.4	29.1	1.7
4 h	65.6	65.6	3.4	3.7	29.5	29.2	1.5
6 h	65.6	65.6	3.6	3.7	29.5	29.2	1.5
12 h	65.7	65.8	3.5	3.7	29.2	29.3	1.2
24 h	65.7	65.9	3.6	3.7	29.5	29.3	1.1

[a] %C, %H and %S were calculated from the experimentally measured bromine contents, %Br, assuming that the CNS PPS has the structure $Br-(C_6H_4S)_n-H$

elemental compositions of the CNS PPS fractions determined by combustion analysis are in good agreement with the elemental compositions calculated from the measured values of %Br. Additionally, the observation that the M_{Br} and M_η data presented in *Figure 4* are self-consistent further supports the conclusions that in the present work debromination essentially has been eliminated and that the observed changes in molar mass with reaction time are real.

In *Figure 7* the change in M_{Br} of the CNS PPS fraction with reaction time from the present work is compared directly with the corresponding changes in M_{Br} and M_η calculated from the results of a previous study[15] of CBT polymerization carried out using boiling quinoline/pyridine (91% v/v quinoline) mixture as solvent. The data from the previous work show M_{Br} rising with reaction time at an ever-increasing rate, and it is of great significance that the M_{Br} data rapidly attain values in excess of the corresponding M_η data. These unrealistically high values of M_{Br} result from artificially low values of %Br, which arise as a direct consequence of loss of bromine end-groups in the polymerization, the extent of debromination increasing with reaction time

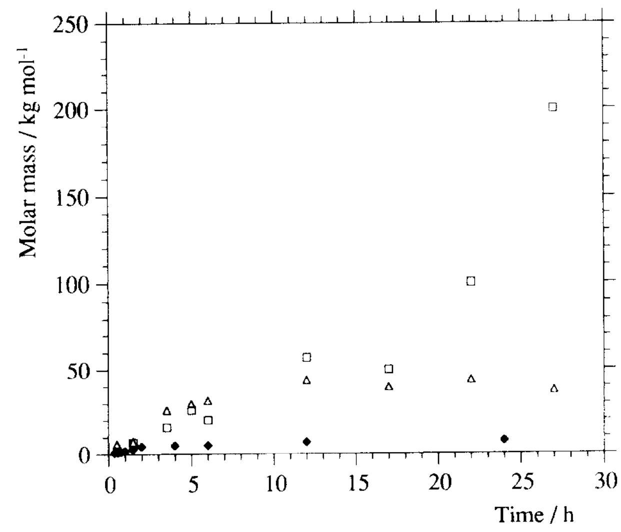

Figure 7 Comparison of the variation of the molar-mass averages of the CNS PPS fraction with reaction time for solution polymerizations of CBT: number-average molar mass M_{Br} (□) and viscosity-average molar mass M_η (△) data calculated from the results reported in a previous paper[15]; M_{Br} (◆) data from the current work (as presented in *Figure 4*)

due to the increasing reaction temperature as may be expected from the results of model compound studies[31]. In comparison to this previous study, therefore, the elimination of debromination through the control of temperature exercised in the present work results in observation of the correct trends for the changes in number-average molar mass with reaction time and monomer conversion.

Experimental evidence for operation of single-electron transfer processes in the polymerization

The results presented above are in accord with previous observations on CBT polymerization and confirm that the polymerizations reported herein are representative. Additionally, the elimination of debromination facilitated by control of the reaction conditions has enabled accurate information on the development of molar mass with time to be obtained. These observations, therefore, provide a firm foundation for interpretation of the results from experiments aimed at probing the possible operation of a single-electron transfer (SET) mechanism in the polymerization. Two techniques have been used for the latter purpose, namely cyclic voltammetry and e.s.r. spectroscopy.

Cyclic voltammetry of reaction mixtures has provided direct evidence of the SET processes associated with the $S_{RN}1$ mechanism in the formation of simple diaryl sulfides by the reaction of thiolate ions with non-activated aromatic halides[20,36–38]. In the present studies, however, it was not possible to perform cyclic voltammetry on polymerizing CBT solutions, primarily due to the high reaction temperature but also because of the relatively high conductivity of 1 mol dm^{-3} solutions of CBT. Instead, cyclic voltammetry has been used to establish whether or not CBT readily undergoes single-electron oxidation and/or reduction in solution at room temperature. For convenience, pyridine was used as the solvent. Trial experiments showed that satisfactory voltammograms could be obtained with a CBT concentration of 0.01 mol dm^{-3} using tetraethylammonium tetrafluoroborate as a supporting electrolyte at 0.1 mol dm^{-3} concentration. These conditions were used in all the cyclic voltammetry work. Additionally, the experiments were performed under an inert atmosphere in order to prevent aerial oxidation of CBT to bis(4-bromophenyl) disulfide, a reaction that is known to be rapid in dilute solutions of CBT in pyridine[39]. Two control experiments were performed on solutions in which the CBT was (i) replaced by an identical concentration of copper(I) bromide and (ii) omitted. They showed no evidence for oxidation or reduction events in the voltage ranges investigated. Thus SET activity in cyclic voltammetry of the CBT solution can only be ascribed to processes involving 4-bromobenzenethiolate.

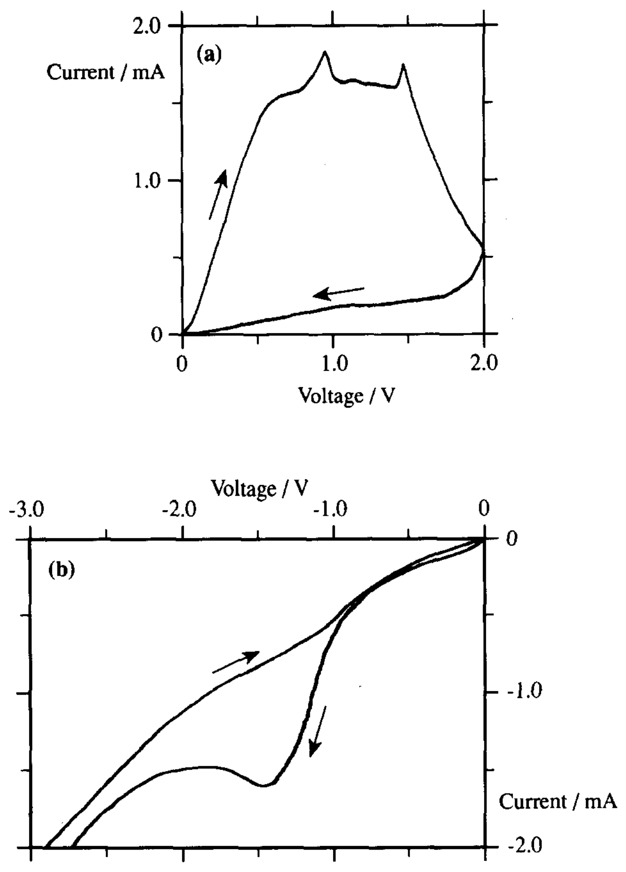

Figure 8 Cyclic voltammograms of 0.01 mol dm^{-3} solutions of CBT in pyridine obtained from: (a) an oxidative voltage sweep and (b) a reductive voltage sweep (during which the current exceeded the 2 mA limit of the galvanometer from about −2.7 V to −4 V and the complete cycle could not be recorded.) For each voltammogram the arrows indicate the direction of the cycle

Cyclic voltammograms from oxidative and reductive voltage sweeps of the CBT solution are shown in *Figure 8*. Both show evidence of SET events. During the cyclic sweep between 0 V and +2 V, two anodic oxidation events occur at +1.0 V and +1.5 V respectively, their irreversibility suggesting that the initial oxidation corresponds to a chemical reaction which produces species that undergo further oxidation in a second chemical reaction. The voltammogram is similar to that reported (but not interpreted) by Koch and Heitz[40] for a solution of bis(4-bromophenyl) sulfide in which consecutive, irreversible oxidation events occur at +1.1 V and +1.5 V. Tsuchida *et al.*[6] also observed two irreversible oxidation events (at +1.6 V and +1.8 V) by cyclic voltammetry during the electro-oxidative polymerization of benzenethiol in nitromethane containing 1.5 mol dm^{-3} trifluoroacetic acid. They assigned the first oxidation step to the formation of diphenyl disulfide and the second to generation of diphenyl disulfide radical-cations that act as reactive intermediates in the formation of PPS. Similar processes could explain the two oxidation steps observed for the CBT solution, with the first step corresponding to formation of bis(4-bromophenyl) disulfide (via coupling of 4-bromophenylthiyl radicals created by SET from the thiolate ion), and the second corresponding to the formation of radical-cations from bis(4-bromophenyl) disulfide. In the present work there was no visible evidence of PPS formation (PPS is insoluble in pyridine at room temperature, but no precipitate was formed). This also is in accord with the observations of Tsuchida *et al.*, who reported[6] that basic solvents inhibit the formation of PPS in the electro-oxidative polymerization of benzenethiol.

Cyclic voltammetry of the CBT solution in the range 0 V to −3 V showed a single cathodic reduction event at −2.8 V. The reduction was irreversible and coincided with the formation of a very small amount of a brown deposit on the cathode, observations which again suggest that electron transfer is followed by chemical reaction. Similar cyclic voltammograms have been reported[38,40] for other aromatic halides. Pinson and Saveant[38] established that the reduction corresponds to formation of a radical-anion from the aromatic halide and that the irreversibility results from formation of a highly reactive aryl radical through loss of halide ion from the radical-anion. Hence, the irreversible reduction observed for the CBT solution may be assigned to formation of a 4-bromobenzenethiolate radical-anion followed by loss of bromide ion to yield a benzenethiolate aryl radical, which could act as a reactive intermediate in the formation of PPS via an $S_{RN}1$-type mechanism. Although PPS formation may explain the brown deposit produced on the cathode, the hypothesis cannot be proven because attempts to isolate and characterize the deposit were unsuccessful.

The important inferences from the cyclic voltammetry experiments are that reductive and oxidative SET reactions of 4-bromobenzenethiolate readily occur and, therefore, that such SET processes are possible in solution polymerization of CBT.

E.s.r. spectroscopy was used with the objective of establishing whether or not species with unpaired electrons exist during solution polymerization of CBT. It was not possible to carry out polymerization in an e.s.r. tube for real-time e.s.r. analysis because the spectrometer would not operate at the temperature of polymerization. Thus samples had to be removed from polymerization mixtures for subsequent analysis by e.s.r. The sampling procedure described in the experimental section was developed in recognition of the fact that, owing to crystallization, PPS precipitates from solution at temperatures below about 180°C. The procedure was designed to enable samples to be transferred from the polymerization mixture to an e.s.r. tube without significant cooling before quenching in liquid nitrogen such that the reaction mixture was transformed into a solid solution with no air pockets and without precipitation of the PPS. An advantage afforded by this procedure was that the samples could be analysed at low temperature (−150°C), thereby increasing the sensitivity of the e.s.r. measurements.

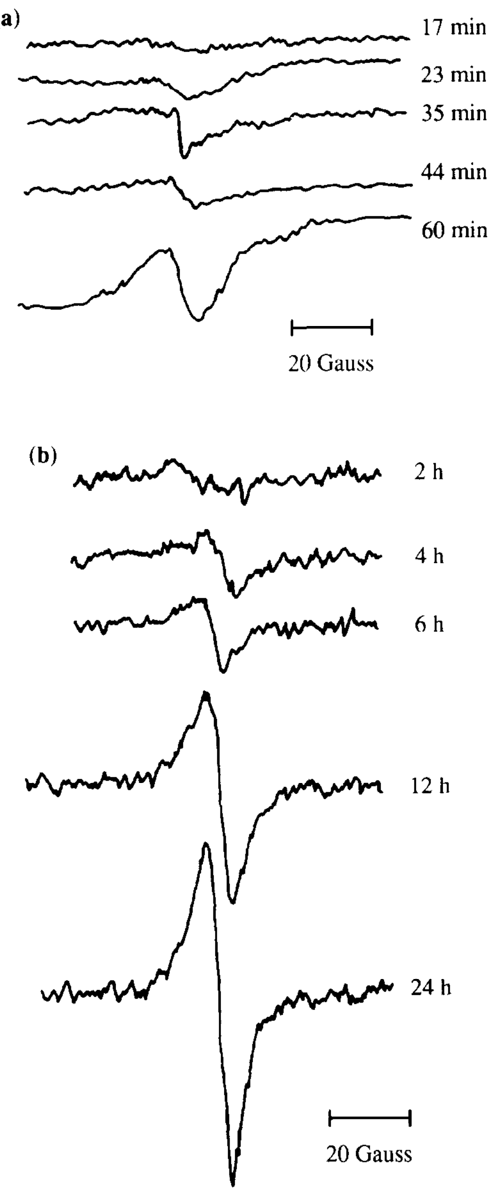

Figure 9 E.s.r. spectra of samples removed from CBT solution polymerizations. The spectra were recorded in the range 3200–3600 G: (a) for individual polymerizations at the specified reaction times in the range 0–60 min; (b) for samples removed at the specified times from a continuous 24 h polymerization. The scale bars show the respective displacements along the abscissa which correspond in each case to a magnetic field difference of 20 Gauss

The e.s.r. spectra shown in *Figure 9* are of samples removed at the same time and from the same polymerization mixtures as the samples used to isolate PPS for determination of the yields and properties presented in *Figures 1–6*. They give direct evidence for the operation of an SET mechanism, showing the presence of organic radical species at low concentrations in the polymerization mixtures. The signals have *g*-values in the range 2.003–2.004 and become stronger as reaction time increases, but the absence of hyperfine splitting prevents structural information from being obtained. The *g*-values and lack of splitting are consistent with signals associated with aryl radical-ions in e.s.r. spectra of PPS and of doped poly(1,4-phenylene)[41–44]. For the samples removed early in the polymerization, analysis over a wider range of field strengths revealed the presence of additional signals superimposed upon, and to the low-field side of, the signal from the organic radical species. These additional signals can be seen in *Figure 10* and are similar in form to the characteristic e.s.r. signal of Cu^{2+} ions (see *Figure 11*)[45], thus providing strong evidence for a mechanism involving SET from Cu^+ ions. As the reaction time increases beyond about 1 h, the intensity of the Cu^{2+} signal diminishes relative to that from the organic radical species.

Further polymerizations were performed specifically to evaluate the reproducibility of the observations made by e.s.r. spectroscopy. In each case the same observations resulted, the only differences being in the strength of the e.s.r. signals, which varied from one polymerization to another. One set of e.s.r. spectra obtained at reaction times up to 6 h are shown in *Figure 12* for comparison with those shown in *Figures 9* and *10*. It is significant that, with the stronger signals observed in samples from this polymerization, Cu^{2+} signals are still evident at 6 h reaction time. However, Cu^{2+} signals have not been detected in any samples removed at times greater than 6 h.

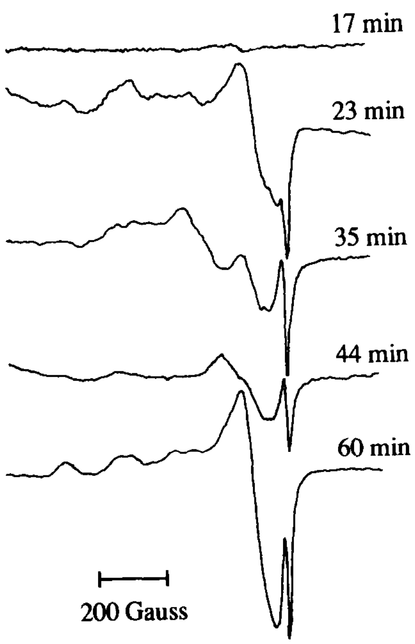

Figure 10 E.s.r. spectra of samples removed from CBT solution polymerizations at reaction times up to 60 min. The spectra were recorded in the range 2400–4400 G and are of the same samples that were used to obtain the spectra shown in *Figure 9a*. The scale bar shows the displacement along the abscissa which corresponds to a magnetic field difference of 200 Gauss

In order to establish that the two types of e.s.r. signals detected from polymerization mixtures arise from species associated with CBT polymerization, control experiments were performed with the following observations. First, the two individual components of the polymerization mixture were analysed independently. Solid CBT was analysed at room temperature and gave neither organic radical signals nor Cu^{2+} signals. Additionally, no e.s.r. signals were detected in samples taken at times up to 24 h from quinoline heated under nitrogen at 200°C. Thus the e.s.r. signals reported above must arise from the reaction(s) taking place during CBT polymerization. A further control experiment was performed by heating a 1 mol dm^{-3} solution of copper(I) bromide in quinoline under nitrogen at 200°C, and was designed to investigate the possibility that a reaction between Cu^{+} and quinoline was giving rise to the e.s.r. signals from the polymerization mixtures. Samples were removed from this reaction and analysed as for the polymerizations. The samples removed at times up to 1 h gave no e.s.r. signals; it was only after about 6 h reaction time that an e.s.r. signal was evident (see *Figure 13*). This signal, however, does not have a corresponding Cu^{2+} signal and is of much lower strength than those of samples taken from the polymerizations. Hence the results from the control experiments lead to the conclusion that the e.s.r. signals from the polymerization mixtures are due to species involved in the mechanism of polymerization of CBT.

The identification of organic radical species and Cu^{2+} in the polymerization of CBT gives direct evidence for the operation of an SET mechanism. By considering the evolution of the e.s.r. signals with reaction time in the early stages of the reaction, further important features are revealed. After 17 min reaction time the CBT had not completely dissolved in the quinoline, no PPS had formed and no e.s.r. signals were evident; whereas after 23 min reaction time the CBT appeared to have completely dissolved to give a characteristically deep red-brown solution, PPS was isolated in 30% yield and the e.s.r. signals from both the organic radical species and Cu^{2+} were evident. It may be inferred that the formation of Cu^{2+} is directly associated with initiation of the polymerization and that the formation of PPS proceeds rapidly after initiation. Quite clearly, these features are more in character with chain polymerization than with step polymerization.

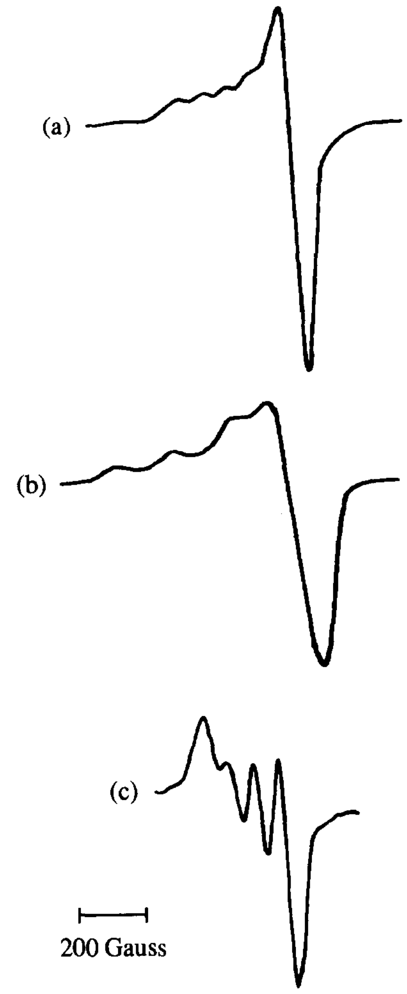

Figure 11 E.s.r. spectra of Cu^{2+} ions: (a) e.s.r. spectrum of a frozen solution of ceruloplasmin; (b) and (c) e.s.r. spectra of an aqueous solution of a Cu^{2+} complex with histidine in the frozen and liquid states respectively. The scale bar shows the displacement along the abscissa which corresponds to a magnetic field difference of 200 Gauss. Adapted from ref. 45

Comparison with observations on the model reaction

The reaction of copper(I) benzenethiolate with bromobenzene to form diphenyl sulfide closely relates to CBT polymerization and, on the basis of previous studies of similar reactions[19,20,38], is expected to proceed via an $S_{RN}1$ mechanism. Thus the reaction was studied as a simple model for the polymerization with a view to establishing whether or not it has features similar to those observed for CBT polymerization.

The model reaction was carried out for a period of 6 h

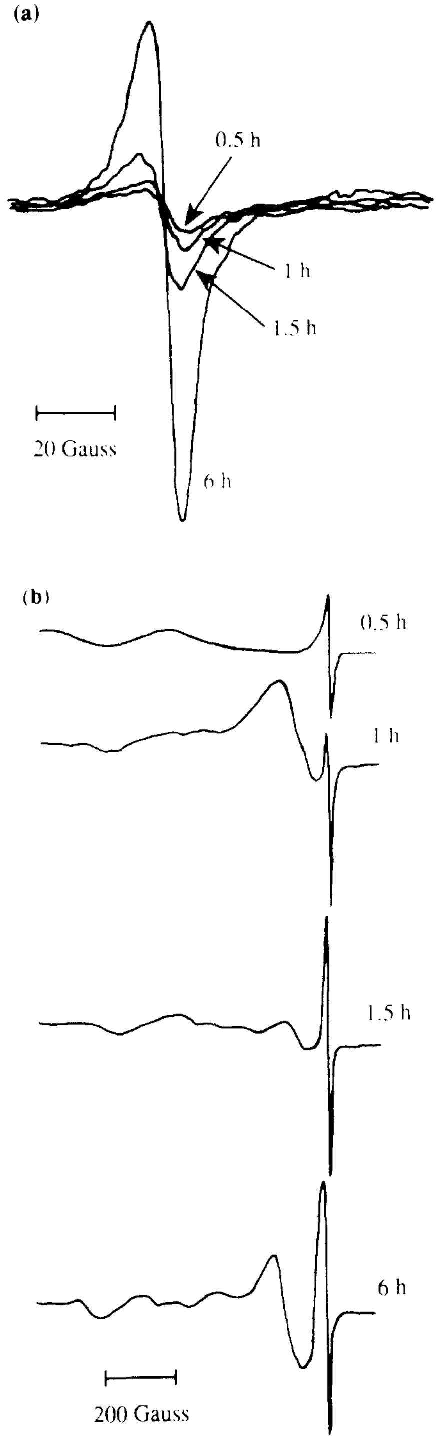

Figure 12 E.s.r. spectra of samples removed at the specified times from a 6 h CBT solution polymerization: (a) spectra recorded in the range 3200–3600 G; (b) spectra recorded in the range 2400–4400 G. The scale bars show the displacement along the abscissa which correspond to magnetic field differences of 20 and 200 Gauss, respectively

using conditions identical to those employed for CBT polymerization. Diphenyl sulfide was obtained in 87% yield, a value that is similar to the yields of PPS from the polymerizations. Furthermore, e.s.r. analysis of samples removed during the reaction showed the presence of organic radical species and Cu^{2+} in much the same way as for the polymerizations; during the first hour of the reaction a Cu^{2+} signal was superimposed upon a signal from organic radical species, whereas after 6 h

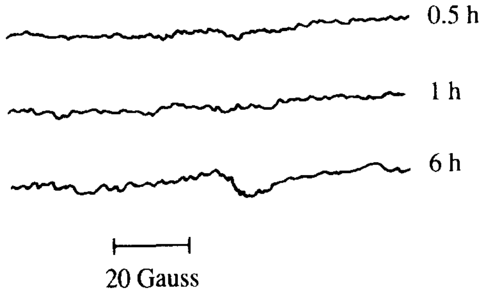

Figure 13 E.s.r. spectra of samples removed at the specified times from a 1 mol dm^{-3} solution of copper(I) bromide in quinoline heated at 200°C under nitrogen. The spectra were recorded in the range 3200–3600 G. The scale bar shows the displacement along the abscissa which corresponds to a magnetic field difference of 20 Gauss

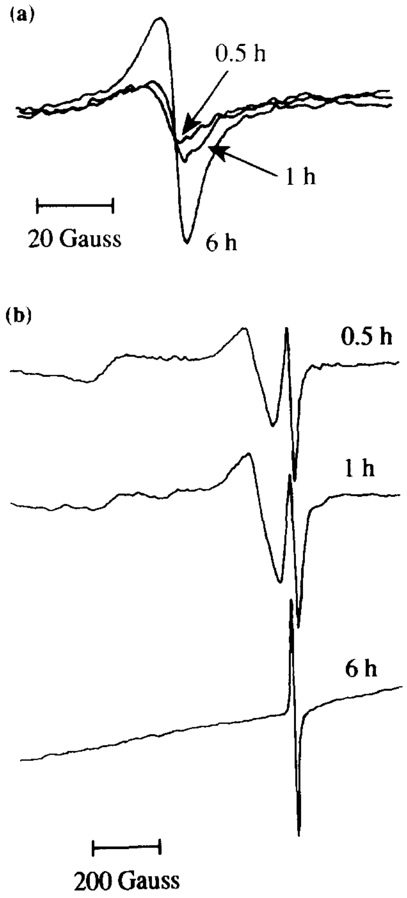

Figure 14 E.s.r. spectra of samples removed at the specified times from a 6 h reaction of copper(I) benzenethiolate with bromobenzene: (a) spectra recorded in the range 3200–3600 G; (b) spectra recorded in the range 2400–4400 G. The scale bars show the displacement along the abscissa which correspond to magnetic field differences of 20 and 200 Gauss, respectively

reaction only the signal from the latter was present (see *Figure 14*).

The similarities between the features of the model reaction and CBT polymerization, therefore, provide additional support to the hypothesis that CBT polymerization involves SET processes in which the formation of Cu^{2+} from Cu^{+} is associated with the early stages of reaction.

Effects of u.v. radiation

The effect of u.v. radiation is often used to establish whether or not the $S_{RN}1$ mechanism is operating in a

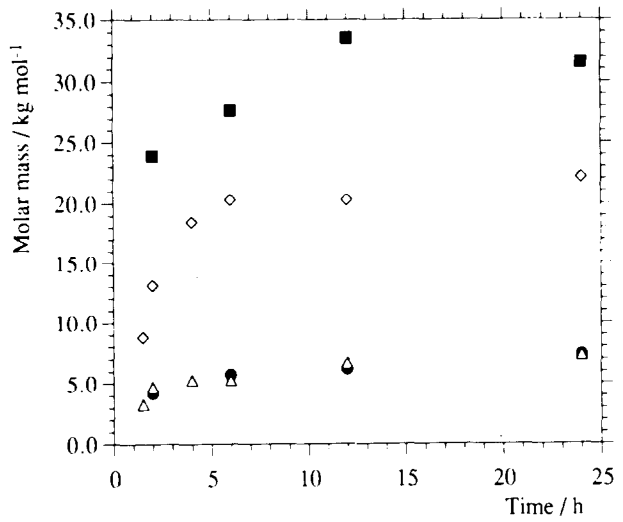

Figure 15 Variation of the number-average molar mass M_{Br} and the viscosity-average molar mass M_η of the CNS PPS fraction with reaction time. (a) Data for the CNS PPS fraction from a normal CBT polymerization: M_{Br} (△) and M_η (◇). (b) Data for the CNS PPS fraction from a CBT polymerization performed with exposure to u.v. radiation: M_{Br} (●) and M_η (■)

nucleophilic substitution reaction[19,20]. Since the $S_{RN}1$ mechanism is a chain reaction involving free-radical intermediates, it normally is promoted by u.v. radiation, whereas the S_N1Ar and S_N2Ar mechanisms are unaffected. Hence this is the reason for investigating the effects of u.v. radiation upon CBT polymerization.

The total yield of PPS was increased significantly by exposure of the polymerization mixture to u.v. radiation, attaining values of 94 ± 4% for reaction times of 2–24 h, which may be compared with 82 ± 2% over the same period of the normal polymerization. The relative proportions of the CNS and CTI+CTS fractions, however, remained the same within experimental error.

As can be seen from inspection of *Figure 15*, a further significant effect of u.v. radiation is to cause the viscosity-average molar mass, M_η, of the CNS PPS fraction to increase whereas the number-average molar mass, M_{Br}, remains essentially unchanged. This observation suggests that exposure to u.v. radiation leads to formation of branched molecules of PPS in which each branch has a single bromine end-group. The extent of branching required to give the observed increase in M_η is too low (about 0.3–0.5 branch points per 100 repeat units) to be detected by i.r. spectroscopy.

Table 2 Comparison of PPS yields from normal CBT polymerization and from CBT polymerization in the presence of 1,3-dinitrobenzene

Reaction time (h)	DNB[a] (mol%)	Overall yield (%)	Percentage of overall yield obtained as:[b] CNS	CTI	CTS
1.5	0	78	95	0	5
	20	58	93	0	7
6	0	83	93	0	7
	20	76	95	0	5

[a] Mole percentage of 1,3-dinitrobenzene with respect to CBT
[b] CNS, 1-chloronaphthalene-soluble fraction; CTI, cold-toluene-insoluble fraction; CTS, cold-toluene-soluble fraction

Table 3 Comparison of the properties of CNS PPS fractions from normal CBT polymerization and from CBT polymerization in the presence of 1,3-dinitrobenzene

Reaction time (h)	DNB[a] (mol%)	M_{Br} (kg mol⁻¹)[b]	M_η (kg mol⁻¹)[b]	T_g (°C)[b]	T_{cc} (°C)[b]	T_m (°C)[b]
1.5	0	3.3	8.8	79	–[c]	277
	20	3.5	8.8	79	–[c]	277
6	0	5.3	20.3	87	133	266
	20	13.3	18.5	84	127	275

[a] Mole percentage of 1,3-dinitrobenzene with respect to CBT
[b] M_{Br}, molar mass calculated from bromine end-group content; M_η, molar mass calculated from intrinsic viscosity; T_g, glass transition temperature; T_{cc}, cold-crystallization temperature; T_m, melting temperature of the shock-cooled material (see text for details)
[c] Very weak and broad cold-crystallization exotherm; T_{cc} could not be located with accuracy

Effects of 1,3-dinitrobenzene

In view of the evidence for a mechanism involving free radicals, further polymerizations were carried out using 1,3-dinitrobenzene as a free-radical trap[46] at a level of 20 mol% with respect to CBT. Two such polymerizations were performed using reaction times of 1.5 h and 6 h, which were chosen because they correspond respectively to periods during which the molar mass of the CNS PPS fraction is increasing rapidly and relatively slowly (see *Figure 4*).

The effects of 1,3-dinitrobenzene can be seen from the comparative data given in *Tables 2* and *3*. The most significant effect is to reduce the total yield of PPS from 78% to 58% at the 1.5 h reaction time. The difference in yield equates to the mole percentage of 1,3-dinitrobenzene to CBT, suggesting that 1,3-dinitrobenzene prevents the formation of PPS chains in a reaction with 1:1 stoichiometry. The PPS chains that do not react with 1,3-dinitrobenzene appear to grow in the normal manner since the relative proportions of the CTS and CNS PPS fractions, and the values of the molar-mass averages and transition temperatures of the latter, are not significantly affected.

At the 6 h reaction time, the total yield of PPS has recovered to 76% and is only slightly below the yield (83%) obtained at the same time in the normal CBT polymerization. The relative proportions of the CTS and CNS PPS fractions, and the CNS PPS transition temperatures, again are, within experimental error, the same as for a normal polymerization. However, although the value of M_η for the CNS PPS fraction is only slightly less than for the normal polymerization, the value of M_{Br} is much higher. Also, this CNS PPS fraction is unique in having a significant nitrogen content (0.7% by weight), suggesting that 1,3-dinitrobenzene has become incorporated into the structure of the PPS chains. One possible interpretation of these observations is that 1,3-dinitrobenzene reacts with intermediates in the polymerization to replace bromine end-groups.

CONCLUSIONS

The experiments described in this paper principally were designed to probe the mechanism of solution polymerization of copper(I) 4-bromobenzenethiolate (CBT). Cyclic voltammetry showed that CBT is capable of undergoing irreversible reactions via both reductive and oxidative single-electron transfer (SET) processes. Electron spin resonance spectra of the polymerization mixture gave clear evidence for the presence of organic free radicals throughout the polymerization and also revealed that Cu^{2+} ions are formed during the period, up to about 2 h reaction time, when PPS yield and molar mass increase rapidly, suggesting that SET from Cu^{+} is responsible for initiation. The observations that u.v. radiation and 1,3-dinitrobenzene have significant effects on the yield and molar mass of the PPS lend further support to the argument for a mechanism involving free radicals. The combination of results from the present studies, therefore, provides compelling evidence for operation of an SET mechanism in solution polymerization of CBT. Mechanistic interpretation of the results is the subject of the following paper[25] in which a mechanism is proposed that also seeks to account for all observations reported in the more general area of metal(I) 4-halobenzenethiolate polymerization.

ACKNOWLEDGEMENTS

The authors would like to thank Dr A. J. Parker and Mr M. M. J. McDonald of the Chemistry Department at UMIST for use of their e.s.r. spectrometer and for their assistance with the recording and interpretation of the spectra. They also wish to thank Dr R. Mayers of the Chemistry Department at UMIST for providing the facilities for cyclic voltammetry and for helping with the associated experimental procedures and analysis. One of us (ACA) wishes to thank the SERC for a research studentship.

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