

Formation of poly(1,4-phenylene sulfide) by solution polymerization of copper(I) 4-bromobenzenethiolate: mechanistic interpretation of experimental observations

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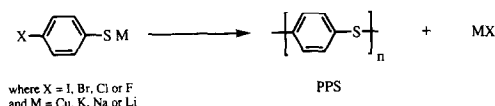
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The important results from the substantial body of experimental data on the formation of poly(1,4-phenylene sulfide) by polymerization of copper(I) 4-bromobenzenethiolate (CBT) have been documented. Single-electron transfer (SET) mechanisms are proposed that are capable of explaining all the experimental observations in a self-consistent manner. An $S_{RN}1$ -type mechanism is thought to be dominant, with a possible contribution from a free-radical mechanism as the polymerization progresses. Both mechanisms have the characteristics of chain polymerization in the initial stages, but as the monomer concentration reduces due to polymerization the same chemistry leads to a change in the nature of the polymerization to step-wise growth, in accord with the observed two-stage variation of molar mass with reaction time. The published experimental data in the more general area of polymerization of metal(I) 4-halobenzenethiolates (MHTs) also are most satisfactorily explained in terms of the proposed SET mechanisms. However, possible contributions from an S_N2Ar mechanism cannot be eliminated, especially for polymerizations of MHTs of alkali-metal ions with Cl or F as the halogen. It is clear, however, that SET mechanisms are dominant in polymerization of CBT.

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

INTRODUCTION

Experiments designed to probe the mechanism of formation of poly(1,4-phenylene sulfide) (PPS) in solution polymerization of copper(I) 4-bromobenzenethiolate (CBT) (Scheme 1 with $M = Cu$ and $X = Br$) were



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

described in the preceding paper¹ and provided strong evidence for operation of a single-electron transfer (SET) mechanism. In particular, radical species were detected in the polymerization mixture by electron spin resonance (e.s.r.) spectroscopy. The S_N2Ar mechanism originally proposed^{2,3} to explain the formation of PPS from metal(I) 4-halobenzenethiolates is inadequate in two

important respects: first, as recognized when it was proposed, the order of monomer reactivity with respect to the halogen in such polymerizations ($I > Br > Cl, F$)^{2,3} is opposite to that expected for an S_N2Ar mechanism; and secondly, it cannot explain the existence of radical species. These observations are, however, in accord with SET mechanisms^{4,5} that now are recognized to be important in many nucleophilic substitution reactions of simple organic compounds. Clearly an alternative to the S_N2Ar mechanism is required that is consistent with the body of information on metal(I) 4-halobenzenethiolate polymerizations. In this respect, the experimental observations that need to be accounted for are those summarized below.

General observations on metal(I) 4-halobenzenethiolate polymerizations:

- (i) I.r. and n.m.r. spectra of the PPS formed show evidence only of 1,4-phenylene sulfide repeat units^{1-3,6-8}.
- (ii) Relatively high-molar-mass PPS is formed at low monomer conversions for a condensation polymerization (i.e. 70–90%)^{1-3,6-8}, a feature that has been termed 'preferential polymer formation'².
- (iii) The order of monomer reactivity with respect to the halogen is $I > Br > Cl, F$ and for the metal ion is $Cu^+ > Li^+ > Na^+ > K^+$ (refs 2, 3).

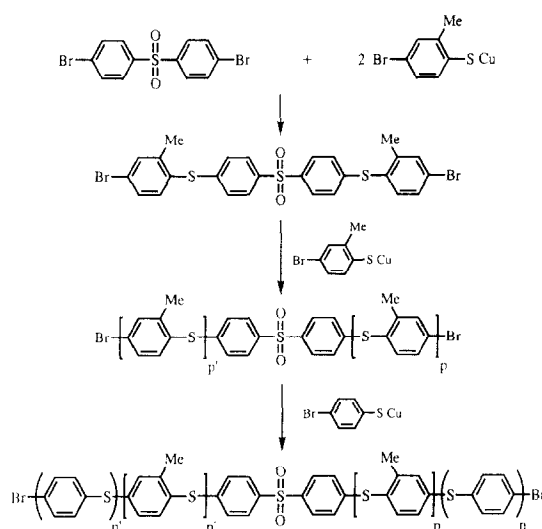
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Observations on copper(I) 4-bromobenzenethiolate (CBT) polymerizations:

- (iv) Cyclic voltammetry shows that CBT is capable of undergoing irreversible reactions via both reductive and oxidative SET processes¹.
- (v) Organic radical species are present during polymerization and give e.s.r. signals that have *g*-values characteristic of aryl radical-ions. The species first appear at the onset of polymerization and increase in concentration with reaction time^{1,9}.
- (vi) Cu²⁺ ions exist during the initial period of the polymerization when PPS yield and molar mass increase rapidly. The reaction time at which formation of Cu²⁺ ions is first evident coincides with the time at which formation of PPS begins. As reaction time increases, the concentration of Cu²⁺ ions passes through a maximum, which is attained at the time when the yield of PPS has reached its limiting value, and eventually decreases to a level undetectable by e.s.r.^{1,9}.
- (vii) Low-molar-mass linear PPS is produced early in the polymerization but is quickly consumed in producing higher-molar-mass PPS as the reaction progresses^{1,9}.
- (viii) The molar mass of the PPS formed increases rapidly with time in the early period of the reaction followed by a more steady increase. In relation to monomer conversion, however, the molar mass of the PPS increases most significantly only after the yield of PPS has reached its limiting value of approximately 83%^{1,9}.
- (ix) Inclusion of 1,3-dinitrobenzene at a level of 20 mol% with respect to CBT leads, at short reaction times, to a 20% reduction in the yield of PPS (58% compared to 78% in the absence of 1,3-dinitrobenzene) but no significant change in properties of the PPS that is formed. The yield of PPS recovers with time to normal values and the PPS produced has normal properties, though the PPS chains have lost bromine end-groups and have a significant nitrogen content¹.
- (x) U.v. irradiation of CBT polymerization produces an overall increase in PPS yield and also an increase in molar mass that is due to a low level of branching of the PPS molecules, the branches having bromine end-groups¹.
- (xi) PPS undergoes debromination (i.e. loss of bromine end-groups) during preparation at polymerization temperatures above 220°C^{1,10,11}.
- (xii) Block copolymers of PPS and poly(2-methyl-1,4-phenylene sulfide) (PMPS) have been prepared^{12,13} by the route shown in *Scheme 2* in which sequential additions of a series of aliquots of monomer are made to bis(4-bromophenyl) sulfone, the first series of additions being of copper(I) 4-bromo-2-methylbenzenethiolate and the second of CBT.

The present paper puts forward a mechanistic interpretation of metal(I) 4-halobenzenethiolate (MHT) polymerizations that is based upon SET processes and is consistent with the experimental observations cited above. The mechanism is described first in relation to normal solution polymerization of copper(I) 4-bromobenzenethiolate, for which the most substantial body of experimental evidence is available. The mechanism then



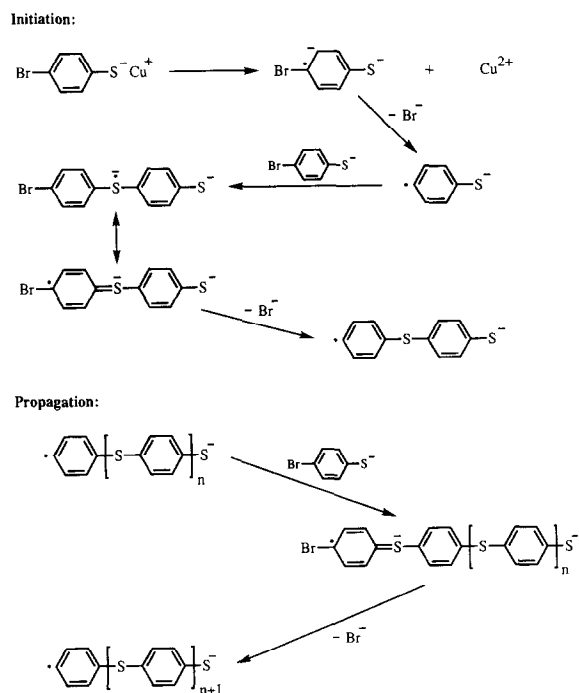
Scheme 2 Reaction scheme for the formation of PPS(A)/PMPS(B) ABA triblock copolymers

is used to account for the observed effects of 1,3-dinitrobenzene and u.v. radiation on polymerization of copper(I) 4-bromobenzenethiolate, and also to explain debromination and the formation of block copolymers. Finally, experimental observations in the more general area of metal(I) 4-halobenzenethiolate polymerizations are considered and shown to be consistent with the proposed mechanism.

THE MECHANISM PROPOSED FOR POLYMERIZATION OF COPPER(I) 4-BROMOBENZENETHIOLATE (CBT)

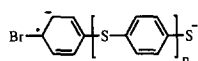
Observations (i) and (ii) were the basis for the original proposal^{2,3} that polymerizations of metal(I) 4-halobenzenethiolates proceed via an S_N2Ar mechanism. The absence of 1,3-phenylene sulfide repeat units clearly ruled out an S_N1Ar mechanism, and 'preferential polymer formation' could be explained on the basis that the propagation step in the S_N2Ar mechanism requires two electron-rich species to react with each other, charge separation in the intermediate (and hence the rate constant for addition) increasing with the degree of polymerization. The trend in halogen reactivity (i.e. observation (iii)), however, remained an anomaly.

During the 1970s, Bunnett and coworkers established that many reactions which produce simple diaryl sulfides by direct substitution without isomerization proceed via an S_{RN}1 mechanism involving single-electron transfer (SET) processes with radical and radical-anion intermediates⁴. This mechanism has now become more widely recognized in organic chemistry⁵. 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. Indeed an S_{RN}1 mechanism has already been proposed by Novi *et al.*¹⁴ in order to explain the effect of diazonium salts in facilitating solution polymerization of sodium 4-bromobenzenethiolate at room temperature. Bearing in mind observations (iii)–(vi) inclusive, it is not unreasonable to postulate that an S_{RN}1 mechanism is operating in polymerization of copper(I) 4-bromobenzenethiolate (CBT).



Scheme 3 Initiation and propagation steps in the $S_{RN}1$ -type mechanism for polymerization of CBT ($n = 0, 1, 2, 3, \dots$)

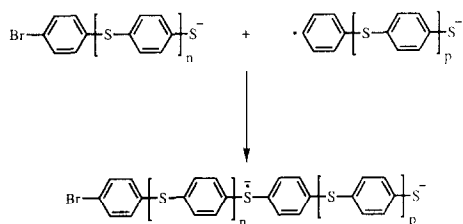
An $S_{RN}1$ -type mechanism that is consistent with the experimental observations on solution polymerization of CBT is shown in *Scheme 3*. In view of observation (vi), the initiation step is taken to involve formation of a Cu^{2+} ion by SET from a Cu^+ ion; the specific reaction proposed is SET from a Cu^+ ion to the aromatic ring of a 4-bromobenzenethiolate ion, leading to the formation of an aryl radical-anion and a Cu^{2+} ion. In keeping with the standard $S_{RN}1$ mechanism, the aryl radical-anion then loses a bromide ion to yield an aryl radical, which rapidly couples to the sulfur atom in another 4-bromobenzenethiolate ion. The latter step leads to formation of a dimeric radical-anion, which also loses a bromide ion to create a terminal aryl radical. Propagation proceeds by sequential coupling of monomeric thiolate sulfur atoms to terminal aryl radicals of growing chains, each coupling step being followed by loss of bromide ion in order to regenerate the chain carrier. In each of these reactions the polymer chain can grow only by formation of 1,4-phenylene sulfide repeat units because of the requirement for loss of a bromide ion from the site of substitution, thereby satisfying observation (i). In accordance with $S_{RN}1$ reactions, the loss of a bromide ion can be expected to be the rate-determining step, leading to the inference that the organic radical species detected by e.s.r. are the aryl radical-anions of general structure:



Since the mechanism proposed in *Scheme 3* is a chain reaction, it satisfies the general observation that relatively high-molar-mass PPS is formed at low monomer

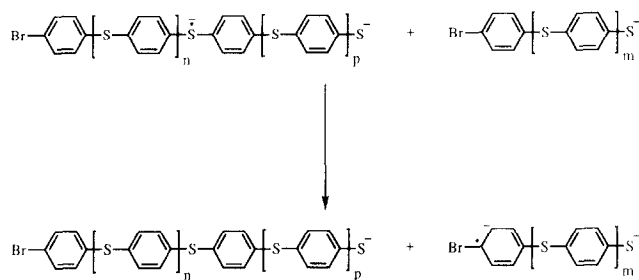
conversions. However, the manner in which the molar mass of the PPS increases with the yield of PPS warrants deeper consideration since it provides further insights into the reaction mechanism that again can be accounted for in terms of the reactions presented in *Scheme 3*. During the first 0.5 h of reaction, the overall yield of PPS reaches a value of $\sim 45\%$ and the PPS formed has a molar mass of $\sim 1000 \text{ g mol}^{-1}$, which corresponds to ~ 9 repeat units. The yield of the lower-molar-mass linear PPS fraction passes through a maximum of $\sim 15\%$ at 0.5 h reaction time. From 0.5–1 h reaction time the yield of this fraction diminishes to zero whilst the yield of the higher-molar-mass linear PPS fraction increases from $\sim 30\%$ to its limiting value of $\sim 83\%$. In this period of the reaction, the number-average molar mass of the PPS begins to increase, rising to a value of $\sim 2000 \text{ g mol}^{-1}$. Thereafter, the yield of PPS remains static at $\sim 83\%$ whilst the number-average molar mass of the PPS continues to increase (up to $\sim 8000 \text{ g mol}^{-1}$), but at a rate that steadily reduces with time. It is clear from these observations that in the initial stages of the reaction relatively short PPS chains are formed that subsequently chain-extend, and that chain extension is the dominant process leading to increase in molar mass when the yield of PPS has reached its limiting value.

The principal questions to be answered are: Why do relatively low-molar-mass PPS chains form in the early stages of the reaction, and how do these chains extend in the later stages? A possible explanation of the first point may be put forward in terms of the effects of charge separation on the loss of the bromide ion from the intermediate aryl radical-anions. The initiation step requires introduction of a second negative charge to the 4-bromobenzenethiolate ion; the resulting radical-anion has two negative charges in close proximity and so loss of a bromide ion can be expected to be facile. As the chains increase in length, so does the separation of the two charges in the intermediate radical-anions that result from coupling of monomeric thiolate sulfur atoms with terminal aryl radicals of growing chains. With each increment in chain length, charge separation in the intermediate radical-anion reduces, and so the effect of close charge proximity in assisting the loss of a bromide ion from the radical-anion can be expected to diminish as chain length increases. Thus the effect will be most significant for the first few propagation steps in the growth of a single PPS chain and can be expected to become much smaller, and essentially constant, as the chain length increases. The natural consequence of this is that the propagation step proceeds at a reducing rate for each of the first series of monomer addition steps (because loss of a bromide ion is the rate-determining step in propagation) and thereafter at a lower, but constant, rate. Each chain will quickly become oligomeric but will then grow at a much lower rate whilst other new chains are initiated and similarly become oligomeric. The first phase of the reaction in which relatively low-molar-mass PPS forms is, therefore, explained. As the conversion of monomer increases, there is an increasing probability for coupling of terminal aryl radicals of growing chains with thiolate sulfur atoms at the ends of other (already formed) PPS chains. This chain extension reaction is shown in *Scheme 4* and has two significant consequences: (i) the chain length increases in increments of multiples of repeat units, and



Scheme 4 Coupling of chain species involved in the $S_{RN}1$ -type mechanism for polymerization of CBT ($n = 1, 2, 3, \dots$ and $p = 0, 1, 2, 3, \dots$)

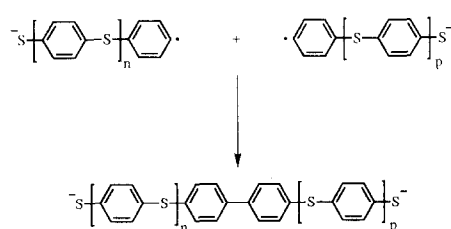
(ii) the product radical-anion is temporarily deactivated because the loss of the bromide ion required for a continuation of propagation is only possible when the unpaired electron is located in the terminal benzene ring which bears the bromine atom. With regard to the latter point, in order for the electron to delocalize to the end unit, the intervening aromatic rings must be coplanar, a requirement that is unlikely to be satisfied. Instead, the unpaired electron may be donated to the terminal unit of another chain in a transfer reaction which reactivates a temporarily inactive PPS chain and fully deactivates the donor chain (*Scheme 5*). The reactions shown in *Schemes 4* and *5* clearly will become more probable as the monomer concentration diminishes and can be expected



Scheme 5 Chain transfer reaction between chain species involved in the $S_{RN}1$ -type mechanism for polymerization of CBT ($n = 1, 2, 3, \dots$ and $p, m = 0, 1, 2, 3, \dots$)

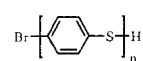
to become dominant when the monomer is fully converted. The observed continuous increase in PPS molar mass with reaction time beyond the time at which the PPS yield reaches its limiting value is, therefore, explained. This interpretation also is consistent with the observed continuous reduction in the rate of increase of molar mass with time, since the further increase in chain length results in a reduction of the concentration of chain ends once the limiting yield of PPS is attained.

The mechanism proposed so far is consistent with the observed continuous increase in the concentration of free-radical species since none of the proposed reactions involve loss of unpaired electrons from the reaction system. Coupling of the terminal aryl radicals of two separate chains is, of course, possible (*Scheme 6*) but generates a PPS chain with two thiolate sulfur end-groups which can undergo coupling to the terminal aryl radicals of growing PPS chains, thereby chain-extending and effectively remaining active. Thus, although the reaction shown in *Scheme 6* leads to loss of two unpaired electrons from the reaction system, it is not a 'true' termination step. Furthermore, since the reaction involves combination of two transient species of low



Scheme 6 Coupling of the terminal aryl radicals of transient species in the $S_{RN}1$ -type mechanism for polymerization of CBT ($n = 1, 2, 3, \dots$ and $p = 0, 1, 2, 3, \dots$)

concentration, it can be expected to be relatively infrequent. Additionally, the experimental data^{1,9} are for polymerizations that yield PPS for which the C, H, S and Br contents are self-consistent with the structure:



showing that PPS molecules formed by the coupling of terminal aryl radicals do not constitute a significant proportion of the total number of PPS molecules formed.

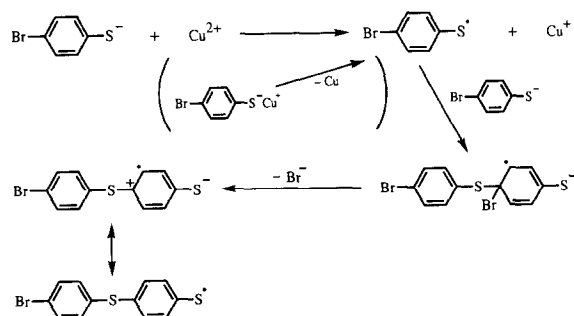
Whilst it has been possible to explain qualitatively most of the features of the polymerization of CBT on the basis of the $S_{RN}1$ -type mechanism presented in *Schemes 3–5*, the ultimate decrease in the intensity of the e.s.r. signal from Cu^{2+} ions and the corresponding, continued increase in that from organic radical species have still to be considered.

The most likely process leading to loss of a Cu^{2+} ion is the formation of a Cu^+ ion via donation of an electron from one of the species present in the polymerization mixture. This may simply be a process akin to the reverse of initiation in which a propagating radical-anion loses its activity by donating an electron to a Cu^{2+} ion, though this must be unlikely if the proposed initiation step in *Scheme 3* is favourable. A further point that argues against such a reaction making a significant contribution is that the reaction would reduce the concentration of organic radical species, i.e. in contrast to the observed trend. A more acceptable process is the donation of an electron from thiolate sulfur to a Cu^{2+} ion, which would also lead to formation of an aryl sulfenyl radical that would give an e.s.r. signal with a g -value close to that of the aryl radical-anion intermediates in the $S_{RN}1$ -type mechanism. This reaction would reduce the concentration of Cu^{2+} ions and increase the concentration of organic radical species, in accord with observations (v) and (vi). It would also lead to a contribution from the free-radical mechanism for the formation of PPS outlined in *Scheme 7*. As indicated in the scheme, the mechanism also could be initiated early in polymerization by SET from thiolate sulfur to a Cu^+ ion, since this yields a monomeric 4-bromobenzenesulfenyl radical. The mechanism of propagation proposed in *Scheme 7* involves addition of a terminal sulfenyl radical to the carbon atom bonded to the bromine atom in the aromatic ring of a molecule of monomer. This is followed by loss of bromide ion to generate a new terminal sulfenyl radical chain carrier. In this way only 1,4-phenylene sulfide repeat units are formed and, since

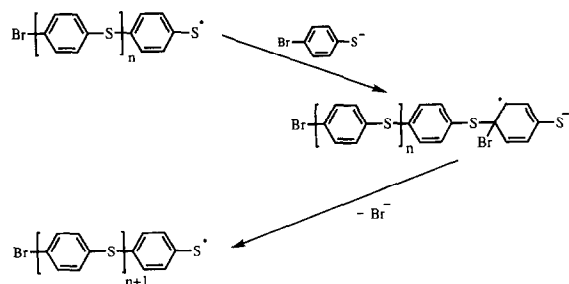
the loss of a bromide ion is again the rate-determining step, the mechanism is consistent with the order of halogen reactivity (observation (iii)). Although free-radical substitution at the *ortho* and *meta* positions is possible, it requires the unfavourable abstraction of a hydrogen atom and, in view of observation (i), cannot be significant.

In common with the $S_{RN}1$ -type mechanism, the free-radical mechanism initially has the characteristics of a chain polymerization, but switches to the step-wise

Initiation:



Propagation:

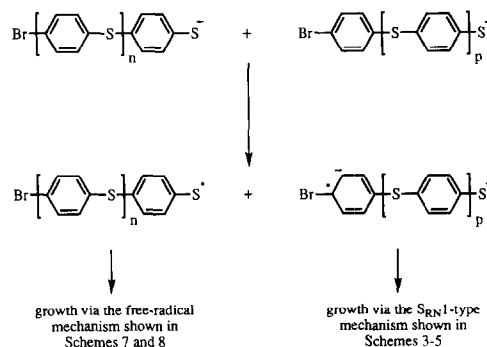


Scheme 7 Initiation and propagation steps in the free-radical mechanism for polymerization of CBT ($n = 0, 1, 2, 3, \dots$)

growth characteristic of step polymerization as monomer is depleted by reaction. In the latter stage, radical transfer is again necessary for continued chain extension (Scheme 8), the reasons for this, and the predicted trends in variation of molar mass with time, being essentially the same as described for the $S_{RN}1$ -type mechanism.

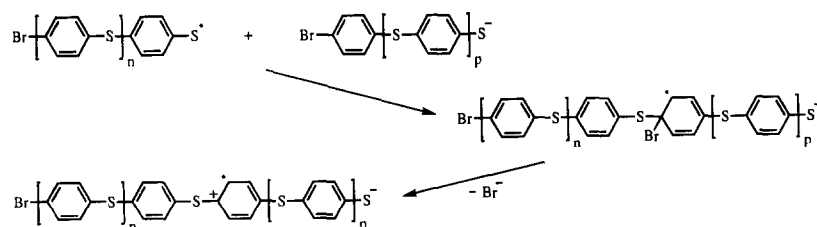
Processes involving SET from thiolate sulfur to the aromatic ring of a bromoaryl group, as shown in Scheme 9, are in accord with the reaction often invoked as the initiation step in $S_{RN}1$ mechanisms^{4,5} and are likely to contribute in CBT polymerization. Such reactions would lead not only to simultaneous initiation of the two propagation mechanisms, but also to an increase in the concentration of organic free radicals. The two mechanisms of polymerization may have other interactions, such as the reaction given in Scheme 10. This involves coupling of a bromoaryl radical-anion with a sulphenyl radical followed by loss of a bromide ion to yield a molecule of PPS, which subsequently could grow further via either of the proposed SET mechanisms.

As discussed so far, both of the proposed mechanisms of polymerization are consistent with observations (i)–

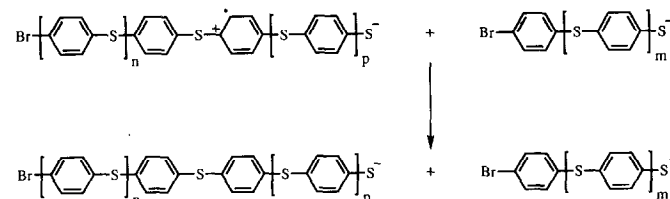


Scheme 9 A reaction leading to simultaneous initiation of the $S_{RN}1$ -type and free-radical mechanisms proposed in Schemes 3–8 ($n, p = 0, 1, 2, 3, \dots$)

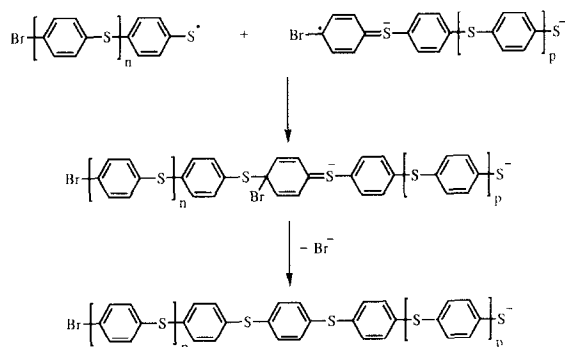
Coupling:



Transfer:



Scheme 8 Coupling and chain transfer reactions of chain species involved in the free-radical mechanism for polymerization of CBT ($n = 0, 1, 2, 3, \dots$ and $p, m = 1, 2, 3, \dots$)



Scheme 10 Chain growth by coupling of reactive species from the $S_{RN}1$ -type and free-radical mechanisms for polymerization of CBT ($n, p = 0, 1, 2, 3, \dots$)

(iv), (vii) and (viii). However, although simultaneous operation of the two mechanisms is possible, it is reasonable to assume that one will be favoured. The inference to be drawn from observations (v) and (vi) is that the $S_{RN}1$ -type mechanism dominates the early stages of the polymerization, with the free-radical mechanism contributing as the reaction progresses. On this basis, the principal contribution from the free-radical mechanism is to the step-wise chain extension of the oligomers formed during the first phase of the polymerization.

ACCOUNTING FOR OBSERVED EFFECTS

Effect of 1,3-dinitrobenzene on the polymerization of CBT

Since 1,3-dinitrobenzene is a free-radical scavenger¹⁵, the effects described as observation (ix) are consistent with an SET mechanism for polymerization of CBT and provide further evidence against the operation of an $S_{N}2Ar$ mechanism. An obvious interpretation of the effects is that 1,3-dinitrobenzene and CBT react in approximately 1:1 stoichiometry early in the polymerization to give non-polymeric products that are capable of subsequent growth into PPS chains. One possible reaction is addition to 1,3-dinitrobenzene of the aryl radical intermediate of the $S_{RN}1$ -type mechanism, as shown in *Scheme 11(i)*. If this reaction is efficient, monomeric aryl radical intermediates would be trapped

as they were generated and formation of PPS chains would be delayed. However, following complete reaction of the 1,3-dinitrobenzene the polymerization could proceed in the manner described in *Schemes 3–10* with the adducts participating in the polymerization because they possess a thiolate group. In this way, the reduction in PPS yield at short reaction times and the subsequent recovery of PPS yield to normal levels can be explained. Furthermore, growth of the adducts will give rise to PPS chains with a 1,3-dinitrobenzene residue at one chain end and a thiolate ion at the other, thereby explaining the low bromine contents and the presence of nitrogen in the PPS obtained.

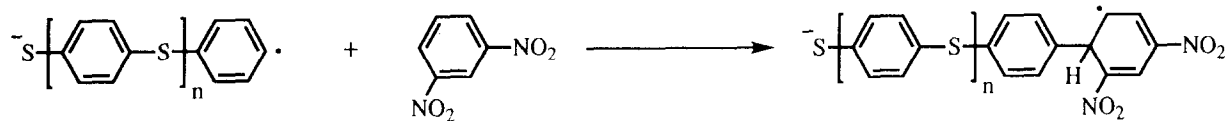
Scavenging of sulfenyl radical chain carriers (from the free-radical mechanism) by 1,3-dinitrobenzene is a further possibility and would also give adducts that could subsequently grow into PPS chains via the aryl bromide group in the adducts (*Scheme 11(ii)*). However, such a reaction is not consistent with the experimentally observed loss of bromine end-groups. Additionally, the free-radical mechanism is thought not to contribute significantly in the early stages of polymerization. Thus the effect of 1,3-dinitrobenzene on the polymerization of CBT can be assigned to the reaction shown in *Scheme 11(i)*.

Effect of u.v. radiation on the polymerization of CBT

U.v. radiation is known to promote reactions that proceed via an $S_{RN}1$ mechanism, whereas it has no significant effect on the $S_{N}1Ar$ and $S_{N}2Ar$ mechanisms^{4,5}. Thus observation (x) gives further support to the arguments for operation of an SET mechanism.

The evidence that the PPS formed in the presence of u.v. radiation has a low level of branching and that the branches have bromine end-groups is instructive. Clearly, this reveals the operation of additional reactions and, on the basis of the mechanisms proposed for CBT polymerization, indicates that the branches become attached to PPS chains via either a thiolate ion or a sulfenyl radical. *Scheme 12* shows reactions that are consistent with the observations, but require the formation of aryl radicals by loss of H^{\bullet} from a phenylene group of a PPS repeat unit. Under u.v. irradiation quinoline (the polymerization solvent) undergoes $\pi \rightarrow \pi^*$ excitation, leading to formation of quinolyl

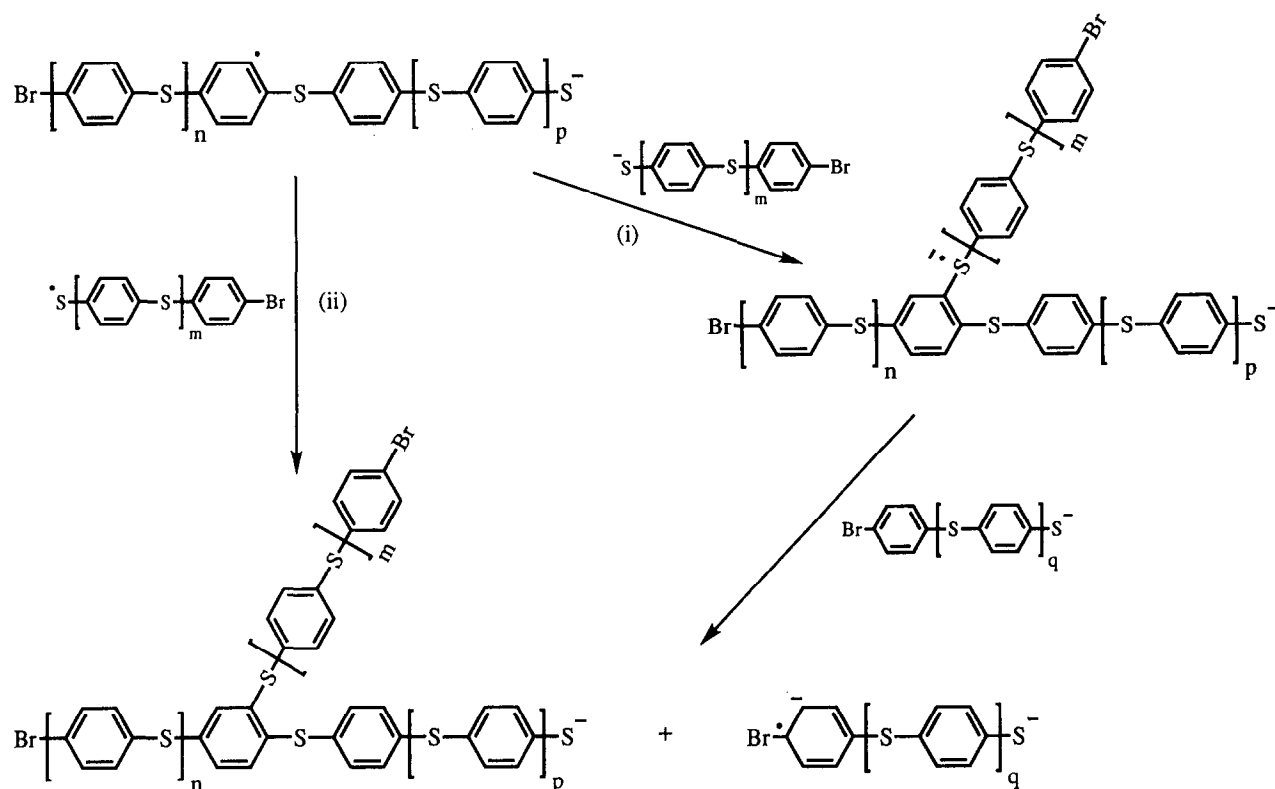
(i)



(ii)



Scheme 11 Reaction of 1,3-dinitrobenzene with reactive species from (i) the $S_{RN}1$ -type mechanism and (ii) the free-radical mechanism for polymerization of CBT ($n, p = 0, 1, 2, 3, \dots$)



Scheme 12 Reaction schemes for the formation of branched PPS molecules via (i) the $S_{RN}1$ -type mechanism and (ii) the free-radical mechanism for polymerization of CBT ($n, p, m, q = 0, 1, 2, 3, \dots$)

radicals that are known to abstract H^\bullet from cyclohexane¹⁶. On the basis of transfer constants for free radical polymerization of olefinic monomers¹⁷, H^\bullet abstraction from cyclohexane proceeds with approximately the same facility as H^\bullet abstraction from benzene. Thus it is not unreasonable to suggest that H^\bullet abstractions from phenylene groups in PPS repeat units could also occur as a consequence of u.v. excitation of quinoline.

Operation of the reactions shown in *Scheme 12* also explains the higher molar mass of the PPS formed in the presence of u.v. radiation, because the branching results in fewer PPS chains.

Debromination during polymerization of CBT

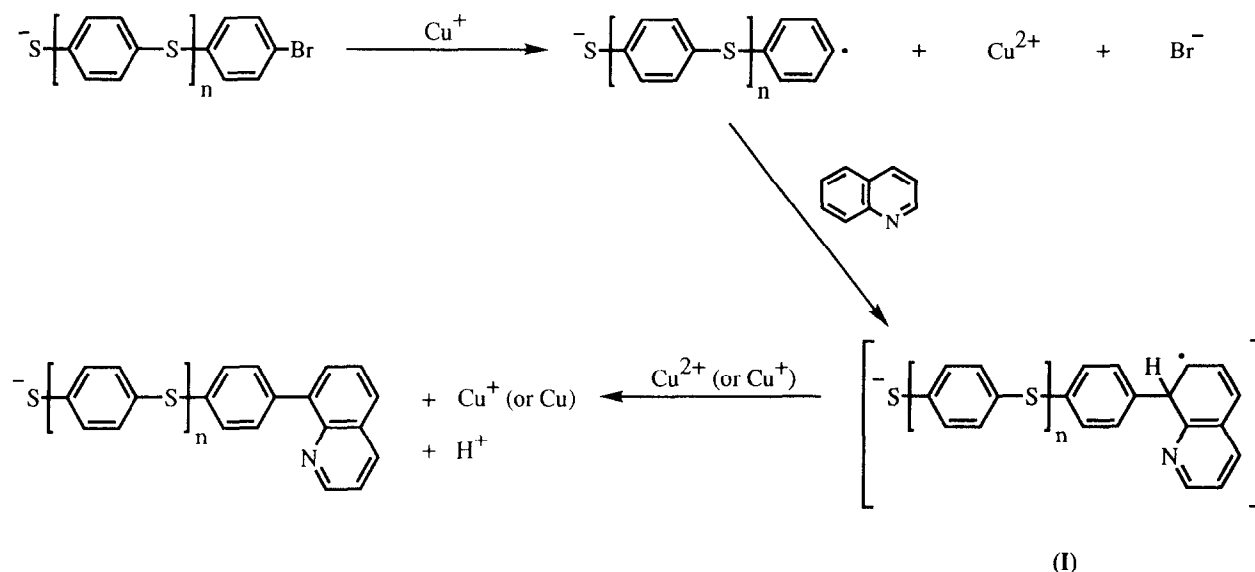
Loss of bromine end-groups (debromination) is a feature of CBT polymerization that has long been recognised^{2,3,7,8} but only recently investigated (observation (xi)). Model compound studies¹⁰ indicate that debromination proceeds at significant rates only in the presence of Cu^+ ions and when the reaction temperature is above $\sim 220^\circ C$. Consistent with these studies, recent work^{1,11} has shown that debromination during CBT polymerization is negligible when the temperature is controlled at $\leq 200^\circ C$.

On the basis of the experimental evidence from the model compound studies, the mechanism postulated¹⁰ for debromination involved formation of an aryl radical by SET from a Cu^+ ion to an aryl bromide chain end with subsequent loss of bromide ion (i.e. a reaction akin to initiation in the $S_{RN}1$ -type mechanism), this being followed by addition of the aryl radical to quinoline and loss of H^\bullet from the adduct to give a quinolyl end-group (*Scheme 13*). The mechanism is, therefore, in accord with

the $S_{RN}1$ -type polymerization mechanism proposed herein and provides a process that is competitive to propagation and chain extension.

Since quinoline, as solvent, is present at high concentration throughout the reaction, the absence of significant debromination at temperatures $\leq 200^\circ C$ indicates that the rate at which H^\bullet is lost from the adduct (I) is much lower than the rates of the rate-determining steps in the $S_{RN}1$ -type propagation and chain extension reactions. In view of the absence of H^\bullet acceptors in the reaction mixture, the reaction proposed¹⁰ for loss of H^\bullet was oxidation of the adduct by a Cu^{2+} ion (or a Cu^+ ion) to give a Cu^+ ion (or Cu metal) and H^+ as shown in *Scheme 13*. The low concentration of Cu^{2+} ions and the less favourable nature of oxidation by a Cu^+ ion suggest that such bimolecular reactions will be far less probable than the unimolecular loss of a bromide ion required in the $S_{RN}1$ -type propagation step (*Scheme 3*) and the bimolecular chain transfer process involved in continuation of chain extension (*Scheme 5*). The increase in debromination brought about by increasing the polymerization temperature above $220^\circ C$ presumably results from enhancement of the relative rate at which H^\bullet is lost from the adduct (I) and, on the basis of the mechanisms proposed, must be related to the activation energies for the competing processes. However, in order to be more definitive about the effect of temperature on debromination, more experimental data on model reactions are required than presently are available.

An important conclusion from consideration of debromination is that it is consistent with the $S_{RN}1$ -type mechanism, but cannot be interpreted in terms of the free-radical mechanism for PPS formation. The



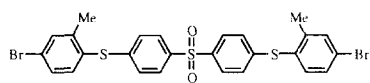
Scheme 13 Reaction scheme for the loss of bromine end-groups from PPS molecules during polymerization of CBT in quinoline ($n = 0, 1, 2, 3, \dots$) (from ref. 10)

observations, therefore, provide additional support in favour of the $S_{RN}1$ -type mechanism being the dominant SET mechanism.

Formation of poly(arylene sulfide) block copolymers

The formation of PPS(A)/PMPS(B) ABA triblock copolymers by the sequence of reactions shown in Scheme 2 occurs without formation of significant quantities of the homopolymers^{12,13}. Although these observations can be accounted for in terms of an S_N2Ar mechanism, as described in the original work¹² it also is possible to explain them on the basis of the SET mechanisms proposed here.

The first step in the formation of the block copolymers is the reaction of bis(4-bromophenyl) sulfone (BBS) with copper(I) 4-bromo-2-methylbenzenethiolate (CBMT) in the molar ratio 1:2. Since the sulfone group in BBS strongly activates the bromine atoms towards nucleophilic substitution, this first step in block copolymer formation undoubtedly proceeds via an S_N2Ar mechanism to give:

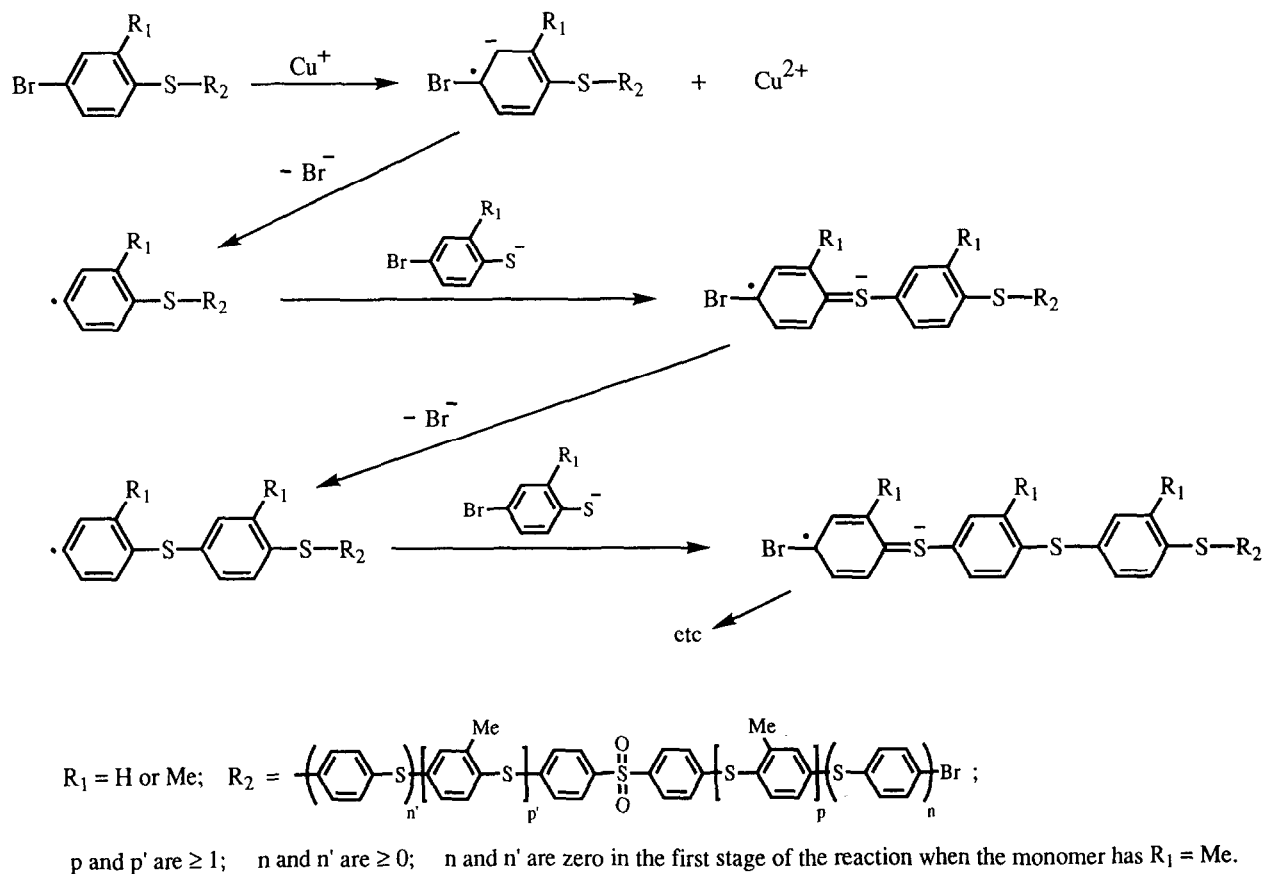


In the subsequent stages, monomer is added stepwise (at 30 min intervals) in amounts equimolar to the original amount of BBS bromine groups. In the first series of additions, aliquots of CBMT are added, and in the second series, aliquots of CBT. The influence of the sulfone group on the mechanism of reaction for these stages will be minor and the reactions can be expected to proceed via either or both of the SET mechanisms described in this paper. Although both mechanisms are consistent with the formation of block copolymer, the $S_{RN}1$ -type mechanism would yield block copolymer via

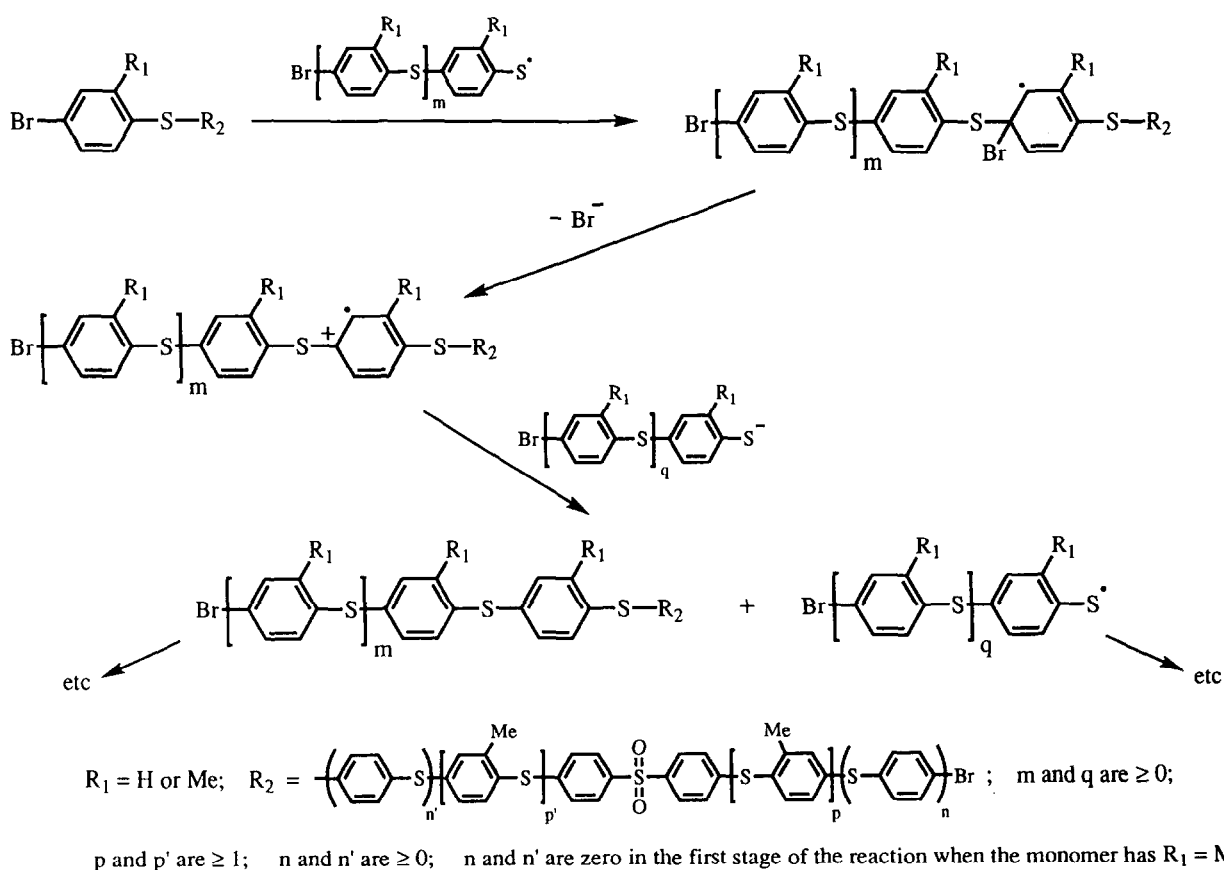
chain polymerization, whereas the free-radical mechanism can only proceed via step-wise processes. This is shown in Schemes 14 and 15.

The procedure and conditions used must be considered in order to explain the formation of block copolymer without significant amounts of homopolymer. On addition of an aliquot of monomer to the growing block copolymer, the monomer concentration equals the concentration of aryl bromide block copolymer chain ends. Hence, on a number basis, at the beginning of the reaction of a given aliquot of monomer, there is equal probability for reaction of monomer with monomer as for reaction of monomer with block copolymer. The important feature, however, is that throughout the reaction the concentration of aryl bromide block copolymer chain ends remains constant and relatively high, whereas during reaction of each aliquot of monomer added the monomer concentration reduces rapidly due to polymerization. Thus even though homopolymer chains can form, there is a very high probability that they will react with the block copolymer chain ends (hence becoming part of a block copolymer molecule) rather than with other homopolymer chain ends. For this reason, the procedure and conditions employed ensure that formation of block copolymers is relatively clean. A consequence of the mechanism of block copolymer formation is that there will be a distribution of block lengths and, therefore, of overall block copolymer composition, as observed experimentally^{12,13}.

The 30 min period allowed for reaction of an aliquot of monomer is sufficient for high conversion^{1,7,9} but, for the reasons described earlier in this paper, is too short to expect a significant contribution from the free-radical mechanism for polymerization. Even if the free-radical mechanism were to contribute, the growth of block copolymer via the $S_{RN}1$ -type mechanism would proceed at a much greater rate (chain *versus* step-wise growth, see Schemes 14 and 15 respectively). Thus it is reasonable to assume that block copolymer formation via the $S_{RN}1$ -type mechanism would be dominant.



Scheme 14 Growth of block copolymer molecules via the $\text{S}_{\text{RN}}1$ -type mechanism for polymerization of copper(I) 4-bromobenzenethiolates



Scheme 15 Growth of block copolymer molecules via the free-radical mechanism for polymerization of copper(I) 4-bromobenzenethiolates

MECHANISMS FOR POLYMERIZATION OF METAL(I) 4-HALOBENZENETHIOLATES

In the preceding sections a consistent explanation of the observations on solution polymerization of copper(I) 4-bromobenzenethiolate monomers has been presented based upon SET processes. In this section, the more general case of polymerization of metal(I) 4-halobenzenethiolates (MHTs) will be considered briefly in terms of the possible effects that changing the halogen and metal will have upon the mechanism(s) of polymerization operating.

The effects of halogen and metal upon the polymerization are summarized in observation (iii) with the reactivity order for the halogen ($I > Br > Cl, F$) arguing against the operation of an S_N2Ar mechanism. Provided that initiation is possible, the proposed $S_{RN}1$ -type and free-radical mechanisms provide a satisfactory explanation of all observations made on polymerizations of MHTs. As stated earlier in this paper, an $S_{RN}1$ mechanism has been proposed¹⁴ to explain the effect of diazonium salts in facilitating solution polymerization of sodium 4-bromobenzenethiolate at room temperature. However, in the absence of such free-radical sources, the principal initiation reaction proposed in *Scheme 3* for the $S_{RN}1$ -type mechanism involves an increase in the oxidation state of the metal ion, which, whilst being facile for Cu^+ , clearly is not realistic for Li^+ , Na^+ and K^+ . For MHTs of the latter metal ions the only feasible initiation process would be the reaction shown in *Scheme 9*, which would simultaneously initiate the $S_{RN}1$ -type and free-radical mechanisms. Thus the observation that the reaction is more facile with Cu^+ as the metal ion lends additional support to the arguments in favour of SET mechanisms, especially as the metal ion would not be expected to influence reactions proceeding via an S_N2Ar mechanism in this way. In view of the reactivities with respect to halogen and metal ions, therefore, the SET mechanisms proposed in this paper also are more consistent with the general observations on polymerizations of MHTs than is an S_N2Ar mechanism. The experimental data, however, are insufficient to be absolutely definitive about the mechanism(s) operating in MHT polymerizations across the complete range of halogens and metal ions. There is a possibility that both an SET mechanism and an S_N2Ar mechanism operate simultaneously in all MHT polymerizations, with one mechanism predominating dependent upon the particular halogen and metal ion, and also upon the reaction conditions. For example, recent work¹⁸ on the related solution polymerization of 1,4-dichlorobenzene with sodium sulfide in *N*-methyl-2-pyrrolidone at 200°C has provided strong evidence for domination by an S_N2Ar mechanism, with only a minor contribution from an $S_{RN}1$ -type mechanism. The operation of an S_N2Ar mechanism can be expected to become more probable (i.e. contribute to a greater extent) for MHT polymerizations in the order: (i) for the halogen substituent, $F > Cl > Br > I$; and (ii) for the metal ion, alkali-metal ions $> Cu^+$. In these terms, the changes in reactivity within the series of MHTs may simply reflect differences in the rate at which the SET mechanisms proceed as compared to an S_N2Ar mechanism.

CONCLUSIONS

The substantial body of experimental data on polymer-

izations of copper(I) 4-bromobenzenethiolates (CBTs) has been considered and shown to be consistent only with single-electron transfer (SET) mechanisms of polymerization. Two SET mechanisms have been proposed that are capable of explaining all the experimental observations in a self-consistent manner. An $S_{RN}1$ -type mechanism is thought to be dominant, with a possible contribution from a free-radical mechanism as the polymerization progresses. Both mechanisms have the characteristics of chain polymerization in the initial stages, but as the monomer concentration reduces due to polymerization the same chemistry leads to a change in the nature of the polymerization to step-wise growth. This is consistent with the observed two-stage variation of molar mass with reaction time and results from the fact that all species present (i.e. molecules of monomer, oligomer and polymer) are capable of growth by reaction at both chain ends. Reaction of monomer with monomer, oligomer or polymer proceeds via chain reaction mechanisms in which the newly added monomer end units automatically become active propagation sites, thus giving rise to the characteristics of chain polymerization. In comparison, the reactions between molecules of oligomer/polymer (which proceed by identical coupling processes to those for reaction of monomer with monomer) leave the active site at the point of coupling, i.e. remote from the chain end, thereby preventing immediate continuation of growth of the chain. These coupled oligomer/polymer molecules can transfer their activity to the end unit of another oligomer/polymer molecule, activating it towards further growth, hence continuing the kinetic chain of events and resulting in growth of the chains in a step-wise manner.

The experimental data in the more general area of polymerization of metal(I) 4-halobenzenethiolates (MHTs) also are most satisfactorily explained in terms of the SET mechanisms proposed in this paper. However, possible contributions from an S_N2Ar mechanism cannot be eliminated, especially for polymerizations of MHTs of alkali-metal ions with Cl or F as the halogen. A systematic, thorough experimental study of the polymerization of MHTs is necessary in order to elucidate the effects of halogen and metal ion upon the reaction mechanism and to establish whether or not an S_N2Ar mechanism operates in competition with the SET mechanisms described herein. It is clear, however, that SET mechanisms are dominant in polymerizations of CBTs.

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