

Polymaleinimide Formation in the Electron Transfer Reaction Between *N*-Bromosuccinimide and Succinimide Anion

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The electron transfer reaction between *N*-bromosuccinimide (SBr) and succinimide anion (S^-) gives predominantly succinimide (SH, *ca.* 65 %) but also a small percentage (*ca.* 10 %) of a polymeric material, the nature of which has now been elucidated. By NMR spectral comparison with authentic specimens, the polymer was shown to be of the polymaleinimide type. The build-up and decay of maleinimide during the SBr/ S^- reaction could be followed (NMR). Also, the development of the characteristic, base-induced yellow-red colour of polymaleinimide could be followed kinetically and the effect of additives studied. Finally, the SBr/ S^- reaction exhibited weak chemiluminescence.

These findings further strengthen the hypothesis that the initial step of the reaction is ET between SBr and S^- , forming a cage radical ion/radical pair. Nitrogen–bromine bond cleavage within the cage produces a pair of S^\cdot , which react with disproportionation to give SH and maleinimide. The latter then undergoes predominant radical polymerization.

The reaction between *N*-chlorosuccinimide and S^- also gave polymaleinimide (40 %) in addition to SH (47 %).

In connection with a study¹ of the cathodic reduction of *N*-bromosuccinimide (SBr), aimed at probing new and simple ways to generate succinimidyl radical,² we found that SBr undergoes a relatively fast homogeneous reaction with succinimide anion (S^-) formed according to eqn. (1).



Preliminary studies¹ indicated that the homogeneous SBr/ S^- reaction is of the electron transfer (ET) type, ET taking place within an initially formed [SBr S^-] complex [eqns. (2)–(4)].

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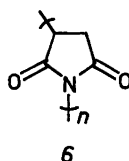
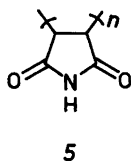
A number of such *N*-bromoimide/imide ion complexes, including $Bu_4N^+[SBrS^-]$ have been isolated and characterized.³ The products from reactions 2–4 were SH (65±3 %) and bromide ion (88±4 %).¹

The finding that SBr possibly can act as an ET oxidant toward an easily oxidizable species like S^{\cdot} is of considerable interest and turned out to be applicable to other compounds as well. Thus ferrocene ($E^0=0.60$ V vs. NHE)** is rapidly oxidized to ferricinium ion and *N,N,N',N'*-tetramethylphenylenediamine ($E^0=0.38$ V) to its radical cation (Wurster's Blue). Similar findings were recently reported by Koshechko *et al.*⁴ who obtained radical cations from several easily oxidizable compounds and SBr, *e.g.*, from tris(4-methoxyphenyl)amine ($E^0=0.72$ V) and 5,10-dihydro-5,10-dimethylphenazine ($E^0=0.35$ V).

In the following, we shall concentrate on two aspects of the SBr/ S^{\cdot} reaction, namely that a) a polymeric product is invariably formed in significant amounts and b) the reaction in most cases is accompanied by the development of an eventually deep red-yellow colour, very close to that of bromine. In fact our preliminary kinetic runs were partly made by monitoring the development of this colour¹ (shoulder at 360 nm) and it therefore was of some interest to elucidate its possible origin. As will be demonstrated, polymer and colour formation are intimately connected as part of a common reaction pathway: A cage reaction between two S^{\cdot} gives SH and maleimide which undergoes S^{\cdot} catalyzed polymerization to give polymaleinimide. It is a characteristic and well-known property of this polymer to produce deeply coloured species upon treatment with bases of different kinds.^{5–9}

RESULTS AND DISCUSSION

Polymer, formation and structure. All reactions between $S-X$ ($X=Cl,^{***} Br$) gave low to fair yields (3–40 %) of amorphous, coloured (light tan to red-brown) solids of polymeric nature (1–4, see Table 1) which had the characteristic features of polymaleinimide. Authentic samples of polymaleinimide can be prepared by either radical or base initiated polymerization of maleinimide,¹⁰ and consist of C–to–C and/or C–to–N bonded succinimide recurring units (5 and 6, respectively). The radical initiated process gives



* The E^0 value of the S^{\cdot}/S^- couple can be estimated¹ at <0.8 V vs. the normal hydrogen electrode in acetonitrile.

** Normal hydrogen electrode; all potentials are referred to this standard in the following.

*** SCl reacts with S^- in the same way as SBr, and we therefore include one SCl/ S^- derived polymer sample (3) in Table 1 for the sake of completeness. The reaction will be described in more detail elsewhere.¹¹

Table 1. Polymers from the reaction between succinimide anion and *N*-halosuccinimide (X-S) in acetonitrile.

| Origin | Yield/% ^a | Elemental analysis/% ^b | | | | | ¹ H NMR/ppm vs. TMS | | | ¹³ C NMR/ppm vs. TMS | | | IR, cm ⁻¹ (KBr) |
|--|----------------------|-----------------------------------|------|------|------|----------------|--------------------------------|--------------------------------|-------------------------|---------------------------------|----------------|-------------------------------|-------------------------------|
| | | C | H | N | O | X ^c | Residual | Bu ₄ N ⁺ | S _n | Bu ₄ N ⁺ | S _n | IR, cm ⁻¹ (KBr) | |
| SBr+Bu ₄ N ⁺ S ⁻ (1) | 9 | 45.1 | 5.98 | 8.30 | 25.4 | 14.4 | 0.8 | 0.95 (t,6) | 2.72 (bm) | 13.8 | 29.2 | 3410 (broad) | |
| | | | | | | | | 1.45 (m) | 3.6 (bm) | 20.3 | 52.1 | 1720 | |
| | | | | | | | | 3.12 (t) | (in CD ₃ CN) | 24.3 | 177.2 | 1640 | |
| | | | | | | | | 59.3 | (in CD ₃ CN) | | | | |
| SBr+Na ⁺ S ^{-d} (2) | 11 | 43.3 | 2.74 | 12.2 | 34.2 | 6.8 | 0.8 | 2.7 (b) | | | 28.6 | | |
| | | | | | | | | 2.87 (s) | | | 127.2 | | |
| | | | | | | | | 3.75 (b) | | | 257.5 | | |
| | | | | | | | | 4.23 (b) | | | 163.5 | | |
| | | | | | | | | 11.8 (bs) | | | 173.2 | | |
| | | | | | | | | (in DMSO-d ₆) | | (in DMSO-d ₆) | 173.6 | | |
| SCl+Bu ₄ N ⁺ S ⁻ (3) | 40 | 49.9 | 4.75 | 11.2 | 34.0 | - | 0.2 | 0.96 (t,6) | 2.6 (b) | 14.0 | 29.2 | | |
| | | | | | | | | 1.45 (m) | 2.72 (s) | 20.5 | 51.5 (b) | | |
| | | | | | | | | 3.04 (m) | 3.7 (bm) | 24.4 | 170-180 (m) | | |
| | | | | | | | | | 5.4 (bm) | 59.3 | | | |
| | | | | | | | | (in CD ₃ CN) | | (in CD ₃ CN) | | | |

^a Calculated for polymaleinimide (C₄H₃NO₂)_n. ^b For polymaleinimide (C₄H₃NO₂)_n, one calculates C 49.4, H 3.1, N 14.3, O 33.0. ^c X=Br for 1 and 2. ^d A similar polymeric material (4) was obtained from the reaction between SBr and Li⁺S⁻ in ca. 3% yield. Its ¹H NMR spectrum in DMSO-d₆ had a broad singlet at 3.52 ppm and a very broad one at 11.0 ppm.

Table 2. Spectral data of low molecular weight reference compounds.

| Compound | ¹ H NMR/ppm vs. TMS | | Solvent | ¹³ C NMR/ppm vs. TMS | | Ref. | |
|---|--------------------------------|----------|---|---------------------------------|-------------------------------------|------|------------------|
| | Bu ₄ N ⁺ | S | | Bu ₄ N ⁺ | S | | |
| Bu ₄ NBF ₄ | 0.98 (t,6) | | CDCl ₃ | 13.5 | | 15 | |
| | 1.49 (m) | | | 19.5 | | | |
| | 3.19 (t) | | | 23.7 | | | |
| Succinimide (SH) | | 2.58 | CD ₃ CN/D ₂ O CD ₃ CN | 30.5 | CD ₃ CN/D ₂ O | 15 | |
| | | 2.64 | | 181.6 | | | D ₂ O |
| Bu ₄ N ⁺ 5 | 0.96 (t,6) | 2.35 | CD ₃ CN | 13.8 | CD ₃ CN | 16 | |
| | 1.49 (m) | | | 20.4 | | | |
| | 3.14 (t) | | | 24.4 | | | |
| | | | | 59.5 | | | |
| Et ₄ N ⁺ S ⁻ | | 2.42 | CD ₃ CN/D ₂ O | 32.9 | CD ₃ CN/D ₂ O | 15 | |
| Maleinimide | | 6.71 | CD ₃ CN | 198.3 | Dioxane | 16 | |
| N-Chlorosuccinimide | | 2.80 | CD ₃ CN | 135.7 | CD ₃ CN | 16 | |
| N-Bromosuccinimide | | 2.82 | CD ₃ CN | 172.6 | | | |
| 2,2'-Bisuccinimide | | 2.91 (m) | D ₂ O | 28.8 | CD ₃ CN | 16 | |
| | | 3.60 (m) | | 172.9 | | | |
| 2-(Phthalimido)glutarimide | | 5.2 (q) | DMSO-d ₆ | 29.5 | DMSO-d ₆ | 16 | |
| | | | | 175.6 | | | |
| | | | | 35.5 | | | |
| | | | | 43.6 | | | |
| | | | | 183.3 | | | |
| | | 184.6 | | | | | |
| | | 22 | | | | | |
| | | 30.9 | | | | | |
| | | 48.9 | | | | | |

Table 3. NMR parameters and 5/6 ratios in polymaleinimide samples of different origin. Solvent, DMSO-*d*₆ unless otherwise stated.

| Polymaleinimide sample | Initiation by | ¹ H NMR shift/ppm vs. TMS | 5/6 ratio |
|------------------------|--|--|-----------|
| 1 | See Table 1 | | >95:5 |
| 2 | See Table 1 | | >95:5 |
| 3 | See Table 1 | | 50:50 |
| 4 | See Table 1 | | >95:5 |
| 7 ^a | Benzoyl peroxide | 3.38 (s) 2.3-4.4 (vb) | >98:2 |
| 8 | Azobisisobutyronitrile | 3.43 (s) 2.3-4.4 (vb) | >98:2 |
| 9 ^b | NaOEt in DMF/EtOH | 2.78 (d,16) ^c 3.58 (s) ^c 4.0 (bm) ^c | 33:67 |
| 10 | NaOEt in CH ₃ CN | 5.13 (bs) 2.78 (bs) 3.56 (bs) | 58:42 |
| 11 | Pyridine in water | 5.28 (bs) 2.7 (m) 3.48 (bs) | 87:13 |
| 12 | Bu ₄ NS (0.1 M) in CH ₃ CN | 5.10 (b) 2.73 (bs) 3.3 (bm) | 52:48 |
| 13 | Bu ₄ NS (0.015 M) in CH ₃ CN | 5.28 (bs) 2.70 (bm) 3.39 (bs) | 42:58 |
| 14 | Bu ₄ NS (0.002 M) in CH ₃ CN | 5.28 (bs) 2.76 (bm) 3.37 (bs) | 47:53 |
| 15 | Bu ₄ NS (0.015 M) in DMF | 5.29 (bs) 2.80 (d,16) ^c 3.34 (s) ^c | 39:61 |
| 16 | Bu ₄ NS (0.067 M)+SBr (0.067 M) in CH ₃ CN | 5.28 (bs) 2.7 (sh) 3.6 (bm) 5.19 (bs) | 63:37 |

^a ¹³C shifts/ppm vs. TMS: 42 (b, partly obscured by the DMSO signal), 178.6 (b). ^b ¹³C shifts/ppm vs. TMS: 30-50 (several signals, partly obscured by the DMSO signal), 160-180 (several signals). ^c Superimposed upon a very broad absorption between 2.3 and 4.5 ppm.

predominantly the C-to-C bonded variety, whereas the base-catalyzed (alkoxide in *N,N*-dimethylacetamide) polymerization gives polymers with a ratio of 5/6 of *ca.* 25/75.^{12,13} It has however been shown that pyridine catalysis in water can give almost exclusively 5.⁵

Characteristic spectral features of the C-to-C bonded polymer are clearly seen in the model compound, 2,2'-bisuccinimide,¹⁴ (see Table 2, which gives spectral data for a number of low molecular weight reference compounds), especially the ¹H signal at *ca.* 3.6 ppm due to the CH-CH protons; the corresponding ¹³C signal appears at 43.6 ppm. Similar ¹H NMR signals appear in the radical derived polymaleinimide (see Table 3; 7 and 8), superimposed upon a very broad structureless absorption in the region of 2.3-4.4 ppm. The CH-CH signal at 3.4 ppm appears as a broad singlet. Similar characteristics are displayed in published^{5,12} ¹H NMR spectra of polymaleinimide. A broad signal in the ¹³C NMR spectrum at *ca.* 42 ppm is indicative of the CH-CH bonding arrangement (see Table 3).

Unfortunately, it proved impossible to reproduce a published recipe¹⁷ for the synthesis of 2-succinimido(succinimide), a model compound for the C-to-N bonded polymer 5. Instead the NMR spectrum of 2-phthalimido(glutarimide) (thalidomide)* gave the desired NMR parameters for the N-CH intermonomer bonding arrangement, the ¹H and ¹³C signals appearing at 5.2 and 48.9 ppm, respectively. An authentic specimen¹⁰ of the base derived polymer very clearly showed these signals (5.2 and 30-50 ppm, respectively) in addition to a weaker signal at 3.58 ppm due to CH-CH bonding (see 9, Table 3). In addition, the CH₂ signal of 5 appears as a sharp doublet (*J*=16 Hz) at 2.78 ppm, as shown previously.¹²

Both polymer types are known⁵⁻⁹ to undergo spectacular colour changes upon treatment with base, in keeping with the findings to be discussed below. A dark-red specimen (*11*, Table 3) of low molecular weight polymaleinimide (*MW ca.* 1000), prepared by pyridine catalyzed polymerization⁵ in aqueous solution (procedure 2d of Table 1, Ref. 5) had features analogous to those of radical polymerized polymaleinimide, with a weak component of C-to-N bonding (<15 %) visible at 5.1 ppm in the ¹H NMR spectrum.

In addition to known initiation modes for maleinimide polymerization, the different components of the SBr/S⁻ system were tried as initiators by themselves or in combination. SBr alone did not cause any polymerization, whereas S⁻ at the 0.1 M concentration level (Table 3, *12*) in acetonitrile rapidly gave a precipitate of the polymer and a deep-red solution. Even at [S⁻]=0.002 M (Table 3, *14*), polymer formation is noticeable after a few h at room temperature and almost complete after *ca.* 40 h. Also the SBr/S⁻ reaction (Table 3, *16*) rapidly polymerized maleinimide, with the same colour development as in the more dilute solutions used in the kinetic experiments; the colour of the solution immediately turned yellow-red and became very deeply red during 2 h (510 nm [sh], 410 nm [sh]). The UV/VIS spectrum was similar to that of the solutions of the kinetic runs. Upon work-up a polymeric material (Table 3, *16*, 52 % yield, based on the combined amount of S⁻ and S-Br used) with all the characteristics of polymaleinimide (1 Bu₄N⁺ per *ca.* 30 monomer units; C-to-C to C-to-N bonding ratio 63:47). The significantly higher yield of polymer indicates that polymerization of the added maleinimide has been initiated by intermediates formed in the reaction between S⁻ and S-Br.

We can now discuss the polymers *1-4* (Table 1; see also Table 3) in the light of the spectral data given in Tables 2 and 3 and referred to above. In general, the elemental analyses of *1-3* do not agree very well with the ones calculated for polymaleinimide. For *1* and *2* we ascribe this to a) bromination of the polymer by S-Br and b) for *1* the presence of

* Obtained by courtesy of Dr. K. Wetterlin, AB Draco, Lund, Sweden.

tetrabutylammonium ion, probably connected both to an ionized S^- of *4* and to bromide ion (the purification of *1* was exceedingly laborious and complicated*). Polymer *3* is most well-behaved from this point of view; it should be noticed that a low nitrogen analysis for some reason is often found for samples of the authentic polymer.^{5,10}

Neither *1* nor *2* showed any evidence for the presence of C-to-N bonded units (lack of the 5.2 ppm signal in the 1H NMR spectrum) but had the requisite absorption for CH-CH at *ca.* 3.6 ppm. Polymer *3* showed evidence of both polymerization modes, with the approximate proportion of 1:2 between *5* and *6*. Polymer *1* contained 1 Bu_4N^+ unit per 55 carbon bonded hydrogens, corresponding to *ca.* 20 monomer units per Bu_4N^+ . Polymer *4* was almost identical to *1* and *2* with respect to its NMR spectrum.

Mass spectral examination of *1-4* (direct inlet) did not give any particularly useful additional information. The highest *m/e* generally were <500, and below that peaks around the dimer (196) and monomer (99) unit were prominent. In mass spectra of *1* and *3*, characteristic peaks originating from Bu_4N^+ (*m/e* 185 and 142) were also detectable.

The reaction could also be monitored by NMR analysis (0.60 M Bu_4NS and 0.41 M SBr in CD_3CN at 35 °C) which showed several interesting features. Immediately upon mixing of the S^- and SBr solutions, the original S^- and SBr peaks at 2.38 and 2.82 ppm, respectively, merged to a single peak at 2.54 ppm due to the very rapidly equilibrating complexation process of eqn. (2) (shown already¹ by IR to be displaced to the right). With time, the chemical shift of this signal moved toward lower field, eventually ending up at the shift of the SH α -hydrogens, 2.63 ppm. No separate signal from SH appeared since it in its turn exists in rapid equilibrium with $S-H\cdots S^-$ [eqn. (5)].



Thus the α hydrogen of all three "S" species are NMR equivalent on the timescale involved.

More importantly, [MH] could be monitored at (initially) 6.54 ppm, a signal that was also displaced slightly toward lower field (ending at 6.68 ppm) due to the changing acid/base relationship during the run. The variation of [MH] with time is seen in Fig. 1, showing that

* A simpler work-up procedure for the SBr/ S^- reaction (essentially the same as that described for the isolation of *3* from SCI/S^-) gave apart from SH (*ca.* 60 %) and bromide ion (100 %) a dark, very viscous oil, containing one tetrabutylammonium ion per *ca.* three succinimide units of the C-to-C bonded polymer (yield *ca.* 40 %, calculated for polymaleinimide). By trituration with diethyl ether a small proportion of solid was obtained from the oil; its composition corresponded to one tetrabutylammonium ion per four succinimide units of the C-to-C bonded polymer.

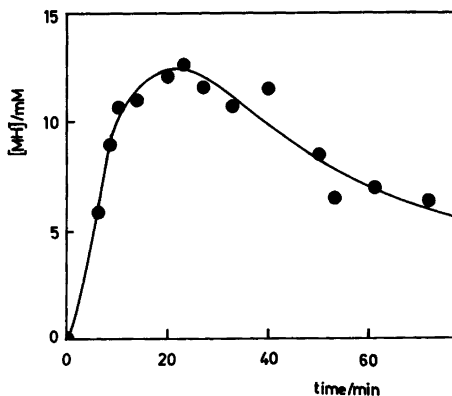
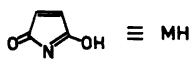
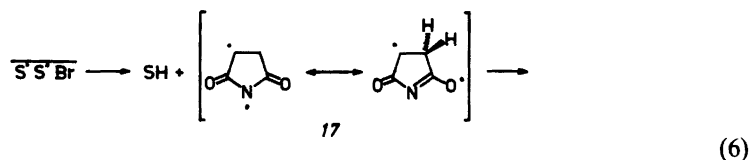


Fig. 1. Plot of [MH] vs. time during the reaction between 0.6 M Bu_4NS and 0.41 M SBr in acetonitrile at 35 °C.

$[\text{MH}]_{\text{max}}$ under these conditions is reached after *ca.* 25 min at *ca.* 0.013 M. It was also possible to detect signals from the polymer at the end of the run (only around 2.8 ppm; the signals from 5 are completely obscured by the $\text{N}-\overset{+}{\text{C}}\text{H}_2$ signal, and nothing was detectable around 5.4 ppm).

We conclude this section by emphasizing that the mechanism of eqns. (2)–(3) nicely accommodates the formation of maleinimide (MH) and hence the polymer; in fact it is almost imperative that ET and N–Br bond breaking are spaced in time so as to allow for the formation of the cage radical pair of eqn. (3). From this, MH can be formed by disproportionation or, rather, intracage H atom abstraction by one S^{\cdot} from an α C–H bond of the other one to give SH and diradical 17 which is assumed to undergo a 1,3 hydrogen shift to give ultimately MH [eqn. (6)]. It is difficult to assume that the same process might occur *via* second-order recombination of escaped S^{\cdot} . Thus, polymaleinimide formation is in itself strongly indicative of the ET mechanism. That the cage recombination reaction does not produce *N,N'*-bisuccinimide by N–to–N coupling is entirely in agreement with earlier experience of this reaction; no N–to–N coupling of S^{\cdot} has so far been proven successful.¹⁸



The polymerization mode in the $\text{S}^{\cdot}/\text{SBr}$ reaction (Table 3, 1, 2, and 4) is C–to–C within the limits of experimental error, whereas the S^{\cdot} initiated samples (12–15) show 40–50 % C–to–C coupling only. A significant increase (to 63 %) is found in 16, prepared by adding excess maleinimide to an $\text{S}^{\cdot}/\text{SBr}$ solution. It therefore seems safe to conclude that radical initiation (by S^{\cdot} or radicals along its decay pathway) is the predominant polymerization mode in the $\text{SBr}/\text{S}^{\cdot}$ reaction.

Chemiluminescence of the $\text{SBr}/\text{S}^{\cdot}$ reaction. As seen from Table 1, only *ca.* 10 % yield of polymer is obtained, whereas complete adherence to eqn. 5 would require a 50 % yield. Obviously, S^{\cdot} can escape from the cage species of eqn. 3 and form SH by hydrogen abstraction from other species. In addition, one might anticipate diffusion of S^{\cdot} away from the first-formed cage species, the radical-radical anion pair [eqn. (7)].



Since $\text{SBr}^{\cdot-}$ has a finite life-time,¹⁹ we now have the possibility to consider that it will donate back its electron to another odd-electron species (S^{\cdot} or another electron-deficient radical along its decay pathway). If the transferred electron is placed in the LUMO of the radical, we obtain an excited state that might emit a photon in order to reach the ground state. This would then constitute a case of the so-called CIEEL pathway (Chemically Initiated Electron Exchange Luminescence) of chemiluminescence, well-known in, *e.g.*, peroxide/ArH reactions.²⁰

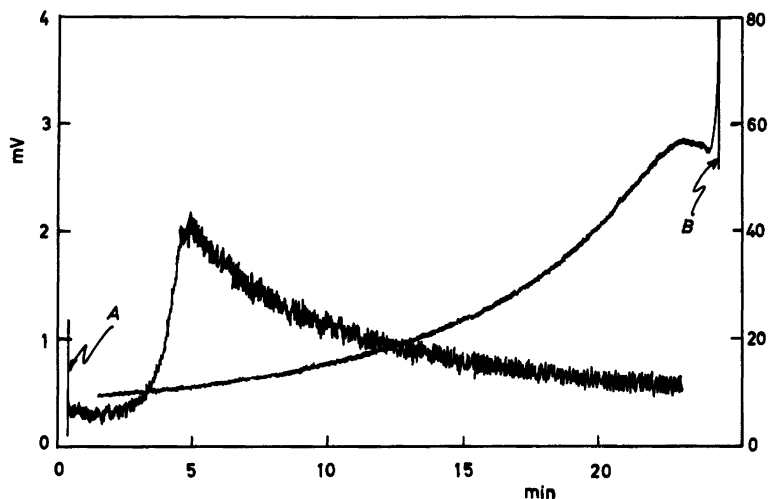


Fig. 2. Light intensity (mV) vs. time (min) for A: 0.1 M Bu₄NS, 0.01 M SH and 0.0032 M SBr (left ordinate axis) and B: 0.5 M Bu₄NS and 0.016 M SBr (right ordinate axis) in acetonitrile at 25.0 °C.

Indeed, very weak light emission was detectable (Fig. 2) from an acetonitrile solution of 0.1 M Bu₄Ns, 0.01 M SH (to “stabilize” the solution for monitoring the rate of colour development; see below) and 0.0032 M SBr. The light emission starts after *ca.* 2.5 min and reaches a maximum after *ca.* 4.5 min. The decay curve is exponential with a rate constant of 0.28(1) min⁻¹ at 25 °C (2 runs).

To increase the yield of light the concentrations of [S⁻] and [SBr] were increased five-fold and the SH left out. If the light emission is dependent upon second-order reactions between transient intermediates, its maximum intensity would be expected to increase by a factor of 5²=25; the observed ratio is 28 which is very satisfactory in view of all possible sources of error. Again, the decay of the light signal was exponential, with a rate constant of 0.17(1) min⁻¹. At this concentration level, there is an initial stronger burst of light, followed by attainment of the local maximum after *ca.* 60 s.

Blind experiments with SBr/MH and S⁻/MH established that no light was emitted from these solutions on a timescale ≥4 h. In connection with studies of the effect of added MH upon the rate of colour development from the SBr/S⁻ reaction (see below), the same stock solutions (0.1 M S⁻, 0.01–0.06 M MH in acetonitrile) were tested for light emission. The results are shown in Table 4.

We note that the light decay process is slower (by a factor of *ca.* 0.07) than in the experiments described above, and the lag period longer. With increasing [MH] *k*₁ increases [according to eqn. (8)] whereas the lag period decreases.

$$k_1 = 0.014 + 0.31[\text{MH}] \quad (r = 0.96) \quad (8)$$

Presently, we have few clues as to which effect added reagents should have on the light emitting reaction(s). Therefore, we are content to conclude that one of the best characteristics of an ET mechanism, chemiluminescence, is exhibited by the SBr/S⁻ reaction, and we leave this phenomenon aside for future exploration in a wider context.

Table 4. Light emission characteristics of the reaction between Bu₄NS (0.1 M) and SBr (0.0032 M) in acetonitrile at 25.0 °C in the presence of maleinimide.

| [MH]/M | k_1^a/min^{-1} | Lag period ^b /min |
|--------|-------------------------|------------------------------|
| 0 | 0.0124 | 24 |
| 0.010 | 0.020 | 21.1 |
| 0.020 | 0.019 | 14.8 |
| 0.030 | 0.021 | 10 |
| 0.040 | 0.029 | 5.0 |
| 0.050 | 0.029 | 2.5 |
| 0.060 | 0.032 | 0.5 |

^a k_1 =rate constant for the exponential decay of light.

^b From start of reaction to maximum of light emission.

Factors in colour development. Our preliminary study¹ of the kinetics of the SBr/S⁻ reaction was partly based on the idea that the colour development (an initial, fast process with $k_1 \sim 2 \text{ min}^{-1}$ followed by a much slower one with $k_1 \sim 0.035 \text{ min}^{-1}$ at 23 °C) was due to formation of the complex of eqn. 2 (k_1), followed by its decomposition (k_2). At that time this assumption seemed perfectly reasonable since neither had the polymer been detected, nor did we suspect that the brilliant yellow-red colour of the SBr/S⁻ solutions could originate from anything else than a complex of the charge-transfer type!

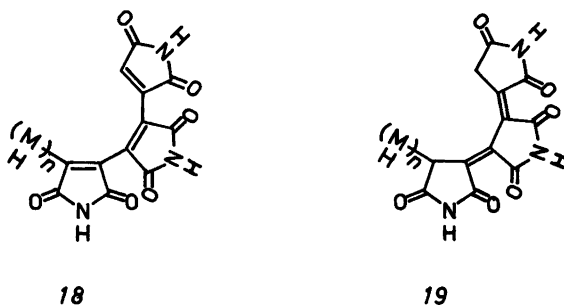
During attempts to perform a more detailed kinetic study along the lines just mentioned, it became obvious that the colour appearance could not be connected with the formation of a CT complex. After almost two years of intensely frustrating experimentation, it had been established that both the intensity and quality of the colour were strongly dependent on the purity of the acetonitrile and the history of a given stock solution of Bu₄NS. Thus the following causal relationships were found eventually between colour development of SBr/S⁻ and the quality of the acetonitrile.

| | |
|--|---------------------------|
| Ultra-pure (analytical grade, twice-distilled over KMnO ₄) | No colour |
| HPLC or UV quality, directly used | No colour or lemon yellow |
| Ordinary analytical grade | Yellow-red |
| HPLC quality, aged with 0.1 M S ⁻ ≥ 40 –50 h at 20 °C | Yellow-red |

To add complexity, the colour development was dependent upon the initial [SBr]; if this is too high, the colour simply seemed to be bleached by SBr in the first half of the reaction, resulting in a rather bizarre absorbance/time curve.

Once the problem of the formation and structure of the polymer had been elucidated the behaviour described above immediately became intelligible. Polymaleinimide or copolymers of maleinimide give brilliant colours upon treatment with bases,^{5–9} such as hydroxide, alkoxide, unpurified DMF, pure DMF+pyridine, and aliphatic amines. It has been suggested^{6*} that the colour formation is dependent upon base-catalyzed oxidation (air) of structure 5 at the terminal S units, resulting in a conjugated system along the backbone of

* See, however, also Ref. 9.



the polymer, formulated as *18*. Even more congenial with the strong colourforming tendency would be a fulgide-like arrangement of double bonds (*19*), known as a very strong chromophore.²¹

We thus will assume that the following picture of the colourforming process is valid: As MH starts to form *via* the reaction between two S^- [eqn. (6)], it begins to polymerize to give oligomers of different sizes. By attack of so far unknown – but oxidatively removable – basic impurities in the solvent and an oxidant (most likely, SBr) coloured oligomers start to build up as the reaction proceeds.

Kinetics of colour development. Given that the solvent has the appropriate level of basic components for the brilliant yellow-red colour to develop normally, can we assume that the colour is an accurate marker for determining the extent of reaction 6 and thus can be used for conveniently monitoring the kinetics of the SBr/ S^- reaction? Let us examine the available facts before we attempt to answer this question,.

As before, the reaction was followed at 20.0 ± 0.1 °C by monitoring the absorbance at 360 nm *vs.* time, with $[S^-] = 0.10$ M and $[SBr]_0$ generally at 0.0032 M. Fig. 3 shows the appearance of a reconstituted run over a complete reaction period of *ca.* 1 h. This “trace” was best analyzed as two consecutive 1:st order reactions, one very fast (k_1 , half-life ~ 1 min) and one relatively slow (k_2 , half-life ~ 30 min). The dissection of the trace of Fig. 3 into these two processes is shown in Fig. 4, and for the latter two traces, the best exponential curve was

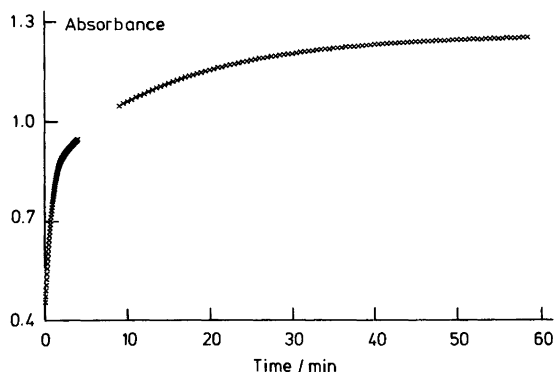


Fig. 3. Absorbance (360 nm) *vs.* time behaviour for a solution of Bu_4NS (0.1 M), SH (0.01 M), Bu_4NBF_4 (0.25 M) and SBr (0.0032 M) in acetonitrile at 20.0 °C. The two periods of data collection (100 data pairs/run) are separated by 5 min $\equiv 7$ half-lives of the first process (k_1).

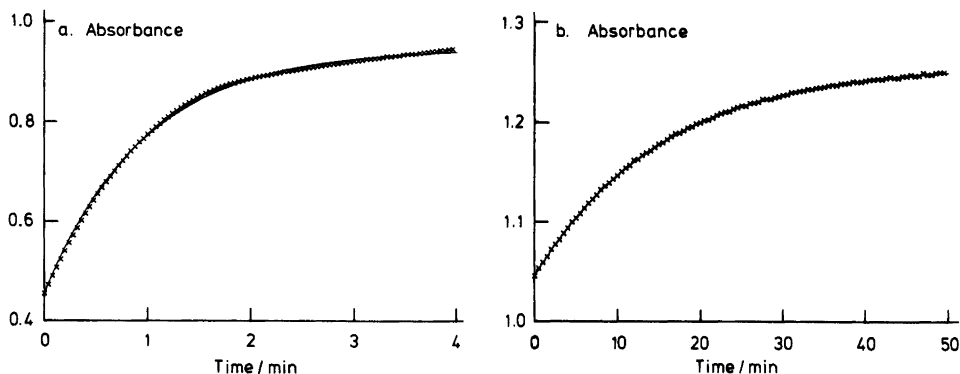


Fig. 4. Absorbance vs. time behaviour for the two reaction periods of Fig. 3. The curves correspond to the best exponential functions fitting to the data points; (a) $k_1=1.03(1) \text{ min}^{-1}$; (b) $k_2=0.0643(3) \text{ min}^{-1}$. Stock solution IV.

evaluated by a non-linear regression method (solid lines in Figs. 4a and 4b). Under these conditions the fit to a first-order increase in absorbance generally was good to excellent. Most of the measurements have been designed to determine k_1 , since k_2 turned out to be much less sensitive to additives.

Fig. 5 shows how k_1 obtained from different stock solutions or after different ageing periods but with otherwise identical conditions varies for two typical situations. For case A, the average k_1 is $1.4(3) \text{ min}^{-1}$ and for B $1.1(3) \text{ min}^{-1}$. It should be noticed that the filled triangle of Fig. 5 is not included in case A; it represents a run with stock solution XIII (a less pure acetonitrile) and has a considerably lower rate constant (*ca.* 0.3 min^{-1}).

The addition of SH decreased the rate constant, Fig. 6 showing the $\log(k_1)/\log[\text{SH}]$ behaviour obtained from rate determinations on three stock solutions. The slope of the regression line is $-0.4(2)$.

As expected, added maleinimide had a strong accelerating effect upon k_1 (Fig. 7; *cf.* also the chemiluminescence results above). The $\log k_1/\log[\text{MH}]_0$ plot had a slope of $2.1(0.6)$, a result that was well reproducible in a second set of runs.

The initial concentration of SBr, $[\text{SBr}]_0$, had a certain effect on k_1 (reaction order $-0.6(5)$) and k_2 (reaction order $0.4(2)$), although this effect was difficult to study over an extended range of $[\text{SBr}]_0$. At $[\text{SBr}]_0 > \text{ca. } 7 \text{ mM}$ in 0.1 M S^- , the colour development is impeded, presumably *via* the same mechanism as suggested for the inhibition of colour

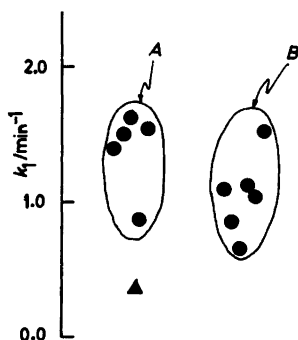


Fig. 5. Showing the spread of k_1 for repeated observations in A: $0.1 \text{ M Bu}_4\text{NS}$ and 0.0032 M SBr , and B: $0.1 \text{ M Bu}_4\text{NS}$, 0.01 M SH , and 0.0032 M SBr in Baker analytical grade acetonitrile at 20.0°C . ●, from stock solution I-IX; ▲, from XIII.

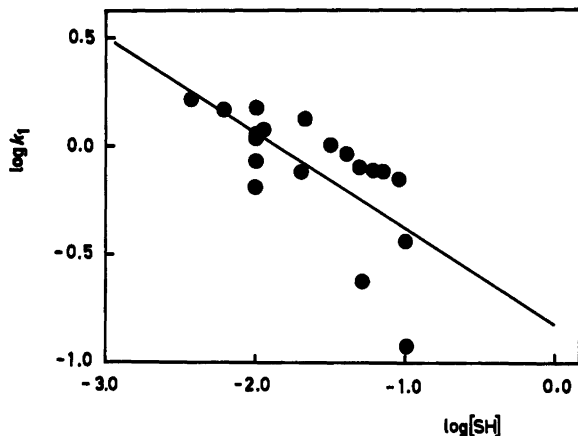


Fig. 6. Log/log plot of k_1/min^{-1} vs. $[\text{SH}]/\text{M}$. The slope of the regression line is $-0.4(2)$ at the 95 % confidence level. Stock solutions VI–VIII.

development from polymaleinimide pretreated by *t*-butyl hypochlorite.⁶

A few kinetic runs were also performed with presynthesized $\text{Bu}_4\text{NS}-\text{SBr}$ complex.³ Rate determinations at three concentrations of the complex gave $k_1=0.18(1)$, $0.35(2)$ and $0.41(2)$ min^{-1} at $[\text{complex}]=2.6$, 3.9 , and 5.2 mM, respectively, corresponding to a reaction order of $1.2(2)$.

Other variations were to check for the effect of added Bu_4NBF_4 (0.25 M, no effect), Bu_3N (up to 0.6 M, no effect), and Bu_4NBr (up to 0.2 M, slight decrease).

According to a kinetic scheme involving fast, reversible and complete formation of a complex (C), followed by its rate-determining conversion to product(s) [eqns. (8) and (9)], a simple first-order equation for formation of P should be obeyed when one of the reactants is present in large excess.

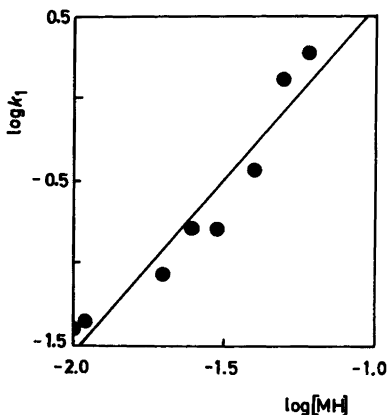


Fig. 7. Log/log plot of k_1/min^{-1} vs. externally added $[\text{MH}]/\text{M}$. The slope of the regression line is $2.1(6)$ at the 95 % confidence level. Stock solution IX.

The colour-producing process (k_1) deviates from this behaviour ($[SBr]_0$ affects k_1) and thus cannot truly be invoked as a marker for the disappearance of SBr. On the other hand, the retardation by SH observed would be expected for the above mechanism, if $SH \cdots S^-$ [eqn. (5)] is kinetically inactive, and the second-order dependence upon $[MH]$ would also be a consequence of it. MH enters both as a kinetically active initiator (by forming M') and after the k_2 step (in the polymerization process). Thus we conclude that although the colour development reaction does not truly map the disappearance of SBr, its kinetics nevertheless give some useful information, not the least in the form of the slightly erratic behaviour to be expected from a rather complex free-radical polymerization mechanism.

Summary. The deceptively simple reaction between SBr and S^- has turned out to be rather complex. We now have good experimental evidence for a mechanism in which the $SBrS^-$ complex is formed first in a fast, reversible step with a high equilibrium constant (IR, NMR, complex isolated), followed by ET within the complex (calculated ET rate constant agrees fairly well with the experimental one). The first formed cage radical/radical ion pair can dissociate (SH isolated, chemiluminescence detected) or undergo N-Br bond cleavage to give a cage radical pair of two S' . From this maleinimide is formed (NMR) by eqn. (6), and it then undergoes polymerization to give polymaleinimide, a powerful colour inducer under the conditions employed (kinetics).

It now remains to connect the above findings to the kinetics of the actual process, as followed by monitoring $[SH]$ or $[SBr]$, and to quantitatively determine the source of hydrogen atoms in the formation of SH. Moreover, a comparison with the very similar behaviour of SCl is of interest.¹¹ Such studies are under way and will be reported shortly.

A final comment with respect to the nature of S' , as generated by the reaction between $S-X$ and S^- , is pertinent in view of the discussion around this subject². As far as we can see now, S' from SX/S^- has the character of S'_π ; its reaction modes are limited to hydrogen atom abstraction to give SH and initiation of maleinimide polymerization. There is no sign of formation of ring-opened products, a characteristic property of S'_σ . Of some interest in this connection is the novel pathway to the maleinimide system *via* the bimolecular reaction between two S'_π .

EXPERIMENTAL

General Methods. NMR spectra were recorded on a JEOL MH-100 instrument for 1H and a JEOL-JNM FX-60 instrument for ^{13}C . Chemical shifts are given downfield from internal TMS.

Kinetic experiments were performed in the thermostatted cuvette holder (20.0 or 25.0 °C, ± 0.1 °C, as checked by a digital thermometer) of a Cary 219 UV/VIS spectrophotometer, connected to an HP-85 microcomputer, or an Ultrospec (LKB Instruments, Sweden) equipped in the same way. Generally 200 absorbance/time readings were collected at regular intervals over the main reaction period (3-4 half-lives). After this, absorbance readings were made with 10 times larger intervals for a further period of *ca.* 10 half-lives. In most cases the reaction was followed at 360 nm, but in more optically dense solutions (the MH runs, Fig. 7) it was necessary to go up to 420-460 nm. The automatically stored data (tape) were then transferred to an HP-9835 desk-top computer and first-order rate constants evaluated by a non-linear regression method, developed by Marquardt.

For reactions of more normal reproducibility, *e.g.* tungstocobalt(III)ate oxidation of 4-methoxytoluene,²² the two set-ups gave very satisfactory interexperimental agreement, *i.e.*, within ± 2 %. For the reaction at hand, the reproducibility is limited by its chemical peculiarities and thus no comparison was attempted.

The chemiluminescence measurements were made using the Luminometer 1250 from LKB-Wallac, Sweden. The cell holder was thermostatted and kept at 25.0 ± 0.2 °C.

Mass spectra were recorded on a Finnigan 4021 instrument at 70 eV using a heated (up to ~350 °C) inlet.

Elemental analyses were performed at the Microanalytical Laboratory of the Chemical Center.

Chemicals. All chemicals, except for $\text{Bu}_4\text{N}^+\text{S}^-$ (see below), were of highest commercial quality available. *N*-Bromosuccinimide gave similar results before and after recrystallization (water) and therefore was used directly. The following acetonitrile qualities were used to make up stock solutions, always 0.100 M in Bu_4NS and 0.010 M in SH whenever appropriate. Stock solutions are numbered by Roman numerals, and the number within parentheses is the number of h of ageing that at least is required to give good first-order appearance of the yellow-red colour.

- I–III. Baker analytical grade (0)
- IV. Baker analytical grade (150)
- V. Baker analytical grade, twice distilled over KMnO_4 (300)
- VI. Baker analytical grade (48)
- VII–IX. Baker analytical grade (24)
- X. Merck UVASOL (no colour)
- XI. Baker HPLC (no colour)
- XII. Eastman 488 (no colour)
- XIII. Eastman 488 (24, but slower reactions)

Tetrabutylammonium succinimide. Succinimide (0.50 mol) and tetrabutylammonium hydrogen sulfate (0.50 mol) were dissolved in dichloromethane (600 ml). Then sodium hydroxide (1.00 mol) in the form of a 50 % aqueous solution was added dropwise with efficient stirring during 20 min, dried sodium sulfate (30–40 g) was added, and the resulting mixture stirred for additional 40 min. After filtration, the dichloromethane was evaporated from the filtrate in a rotating evaporator. The residual oil was kept at oil pump pressure (room temperature) for ca. 24 h during which period it slowly crystallized to a semi-solid mass. Recrystallization (twice) from analytical grade ethyl acetate (ca. 400 and 250 ml, respectively) gave after filtration in a dry atmosphere a slightly yellow solid (NMR spectrum, see Table 2). The salt is extremely hygroscopic and must be kept in a desiccator over Siccapent or concentrated sulfuric acid.

Polymer samples from the reaction between S-X and S^- . (a) Sample 1 was obtained in the following way: Tetrabutylammonium succinimide²³ (0.0954 mol) in 195 ml of Eastman 488 grade acetonitrile was added to SBr (0.0954 mol) in 250 ml of the same solvent. After standing 1 week at room temperature the solvent was evaporated at the water pump (100 mm). The dark residue was dissolved in 360 ml of dichloromethane and extracted with five 100 ml portions of water. The solid isolated from the aqueous extract was recrystallized from acetone–ether–hexane to give 15.4 g of tetrabutylammonium bromide (50 %).

After drying over magnesium sulfate the dichloromethane solution was chromatographed on a column of silica gel. The chromatogram was developed and eluted by changing solvents successively in the following order: dichloromethane; 1:1 dichloromethane–acetonitrile; acetonitrile; 1:1 methanol–acetonitrile; methanol. The progress was monitored by IR analysis of the residue on evaporation of the eluates. Those fractions which contained the desired product were combined and rechromatographed on silica gel from 1:1 dichloromethane–acetonitrile. The solvent was changed successively in the following order: CH_3CN ; $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$; CH_3OH . The fractions were monitored as above. The largest amount of product was eluted by $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$. The residue on evaporation was dissolved in a small amount of CH_3CN and treated cautiously with ether. The precipitate was filtered with suction, triturated with ether with a mortar and pestle to give a more powdery consistency and refiltered (1). The sample (1.81 g, 9 % yield as polymaleinimide) began to darken and decompose at 95 °C but had no definitive melting point below 300 °C.

Sample 2: A solution prepared from 2.35 g (0.102 mol) of sodium and 250 ml anhydrous methanol, shown by analysis to contain 0.0993 mol of sodium methoxide, was treated with 9.84 g (0.0993 mol) of succinimide followed by 100 ml of benzene. Distillation at the water pump gave a white residue of sodium succinimide. A vigorously stirred suspension of this substance in 200 ml of acetonitrile was heated to 70 °C and treated over a 5 min period with a

solution of 17.6 g, (0.0993 mol) of SBr in 150 ml of acetonitrile. A condenser and drying tube replaced the addition funnel and the mixture was stirred at 70 °C for 24 h. At this time a negative test for SBr was obtained.

After standing for 48 h at 20 °C, the mixture was filtered and the solid washed with a small amount of acetonitrile. A total of 13.3 g of tan solid was obtained. A total of 92 % of the theoretical Br⁻ was found by analysis (the solid had 0.0826 mol Br⁻ and the filtrate had 0.0087 mol Br⁻). Analysis of the filtrate by IR spectroscopy indicated 12.9 g (65.5 %) succinimide.

The tan solid was stirred repeatedly with acetone and the decanted acetone was filtered and evaporated to give 0.56 g of solid, which mostly consisted of succinimide and a small proportion of polymeric material.

To remove sodium bromide, the solid remaining after the acetone extraction was stirred with 100 ml of water for 1 h and filtered to give a dark solid. Airdrying and grinding gave 1.42 g (2) of a tan powder. The material was not soluble in acetonitrile and a solution of it in hot DMF-acetonitrile gave, on precipitation with ether, a solid whose IR spectrum was identical to that before solution.

The original acetonitrile filtrate was distilled at the water pump and the solid residue was distributed between dichloromethane and water. The extract was washed with water, dried over magnesium sulfate and distilled to give 0.67 g off-white solid. Reprecipitation from acetonitrile-ether did not appreciably alter the spectrum. This solid was very similar to 2 in its IR and NMR spectral behaviour. The combined yield of polymeric material was 11 % (calculated as polymaleinimide).

Sample 3: To a solution of 12.8 g (0.096 mol) of SCl in 100 ml of acetonitrile was added 200 ml of 0.480 M tetrabutylammonium succinimide²³ in acetonitrile. After three days at room temperature, the resultant dark solution (negative starch/iodide test) was analyzed for chloride ion (96 % by Volhard titration, 101 % by GLC²⁴) and succinimide (47 % by IR). The acetonitrile was distilled off at 100 mmHg and the residue dissolved in 360 ml of dichloromethane. After washing with 5×100 ml of water, the solution was dried over magnesium sulfate and the solvent distilled off from a water-bath. The last traces of solvent were removed at the water pump, 7.43 g of a dark, semi-crystalline solid being obtained (3, 40 % yield as polymaleinimide).

Sample 4: Lithium succinimide (0.100 mol) was prepared as described above for the sodium compound. It was stirred at 70 °C with a solution of 0.100 mol of SBr in 350 ml of acetonitrile (Baker, analytical grade) for 30 h and then kept at 20 °C for 48 h. Similar work-up as for sample 2 gave 0.62 g (3.1 % yield, calculated as polymaleinimide) of polymeric material (4).

Samples 7 and 9: These were prepared according to literature procedures.¹⁰

Sample 8: Maleinimide (2.0 g) and azobisisobutyronitrile (0.03 g) in 25 ml of acetonitrile were refluxed for 8 h and then left for 12 h at 20 °C. The precipitate (1.8 g, 90 %) was collected (8).

Sample 11: This was prepared according to procedure 2d of Table 4 in Ref. 5

Sample 12: Maleinimide (0.50 g) was dissolved in 10 ml of 0.1 M Bu₄NS solution at 20 °C. After 2–3 min the solution was yellow-red and after 20 min a precipitate started to form from a dark-red solution. After standing overnight, water (20 ml) was added and the solid collected (12, 0.37 g after drying, 74 %).

Sample 13: To maleinimide (1.0 g) in 5 ml of acetonitrile was added 0.15 ml of 0.475 M Bu₄NS in acetonitrile. After standing over night at 20 °C a precipitate (13, 1.0 g, 100 %) had formed.

Sample 14: Maleinimide (2.0 g) was dissolved in 50 ml of acetonitrile and 1 ml of 0.1 M Bu₄NS in acetonitrile was added. After 1 h the pink solution turned turbid and a precipitate started to form. It was collected (14, 1.5 g, 75 %) after standing for ca. 150 h.

Sample 15: Maleinimide (2.0 g) was dissolved in 5 ml of analytical grade DMF and 0.15 ml of 0.475 M Bu₄NS in acetonitrile added. After standing over night at 20 °C the solution had become dark-red and the polymer (15, 1.3 g, 65 %) was obtained by pouring it into 100 ml of methanol.

Sample 16: Bu₄NS (1.7 g, 5.0 mmol) and SBr (0.90 g, 5.0 mmol) in 25 ml of acetonitrile were immediately mixed with maleinimide (4.9 g, 50 mmol) in 50 ml of acetonitrile. A strong yellow-red colour instantaneously developed, slowly deepening to dark-red. After 2 h at

20 °C the solvent was evaporated, and the remaining solid triturated with methanol. The solid (16, 0.51 g, 52 % yield, based upon total S in the initiator system) was collected by filtration.

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