

# Nucleophilic Substitution of Alkyl Halides by Electrogenerated Polysulfide Ions in *N,N*-dimethylacetamide

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The reactions between a series of alkyl halides RX: X=I, R=CH<sub>3</sub> (1), C<sub>3</sub>H<sub>7</sub> (2); X=Br, R=C<sub>4</sub>H<sub>9</sub> (3), 2-C<sub>4</sub>H<sub>9</sub> (4), 3-C<sub>5</sub>H<sub>11</sub> (5), PhCH<sub>2</sub> (6); X=Cl, R=PhCH<sub>2</sub> (7), C<sub>6</sub>H<sub>13</sub> (8), and electrogenerated S<sup>1/3-</sup> ions (S<sub>6</sub><sup>2-</sup> ⇌ S<sub>3</sub><sup>-</sup>) have been investigated by spectroelectrochemistry in *N,N*-dimethylacetamide at 20 °C. RX substrates react in two steps: (i) nucleophilic substitution of S<sup>1/3-</sup> ions (S<sub>x</sub><sup>2-</sup> process) yielding RS<sub>x</sub><sup>-</sup> ions ( $\bar{x}=5.2$ , R=alkyl;  $\bar{x}=4.8$ , R=PhCH<sub>2</sub>); (ii) subsequent substitutions of RS<sub>x</sub><sup>-</sup> ions lead to RS<sub>z</sub>R polysulfanes ( $\bar{z}\approx 3.5$ ), probably through partial disproportionation of the anionic species. On a preparative scale, mixtures of CH<sub>3</sub>S<sub>z</sub>CH<sub>3</sub> ( $z=2-6$ ,  $\bar{z}=3.9$ ) or PhCH<sub>2</sub>S<sub>z</sub>CH<sub>2</sub>Ph ( $z=2-5$ ,  $\bar{z}=3.7$ ) were obtained from chemical reactions between 1, 6 and S<sub>6</sub><sup>2-</sup> ions, or electrochemical syntheses. Kinetic studies at 20 °C of the reactions between S<sub>3</sub><sup>-</sup> ions and substrates 4, 5, 7 and 8 imply that the dianions S<sub>6</sub><sup>2-</sup> are the nucleophilic agents in the first step rather than S<sub>3</sub><sup>-</sup> radical anions.

Organic polysulfanes RS<sub>x</sub>R ( $x\geq 2$ ) have attracted considerable attention because of their practical applications which have been reviewed.<sup>1</sup> Among numerous methods,<sup>1</sup> RS<sub>x</sub>R compounds have been prepared in protic media from the nucleophilic substitution of alkyl halides, by direct addition to alkali-metal polysulfides M<sub>2</sub>S<sub>x</sub> (M=Na, K;  $x=2-5$ ),<sup>2-4</sup> or by reactions with sulfur in basic aqueous solutions.<sup>5,6</sup> The latter mode is applied to the industrial production of polysulfide polymers.<sup>7</sup> However, these means of access to RS<sub>x</sub>R species are not reliable in terms of selectivity and reproducibility, since S<sub>x</sub><sup>2-</sup> ions have an increasing tendency to decompose in protic solvents by chain scissions and disproportionations.<sup>7</sup>

In aprotic dipolar media (DMF, HMPA, DMSO, acetonitrile, etc.) the stabilisation of S<sub>x</sub><sup>2-</sup> ions ( $x=4, 6, 8$ )<sup>8</sup> seemed an attractive way to obtain organic polysulfanes with long sulfur chains. Reactions of electrogenerated polysulfide ions, from sulfur in *N,N*-dimethylacetamide (DMA),<sup>9</sup> or by the use of a carbon-sulfur sacrificial electrode (DMF),<sup>10</sup> with RX substrates (X=I, Br) led to RS<sub>z</sub>R mixtures containing predominantly tri- and tetra-sulfanes. However, the mechanistic pathway from S<sub>x</sub><sup>2-</sup> ions to RS<sub>z</sub>R compounds has not been yet clearly revealed in the absence of appropriate experimental data. As recently reported by our group,<sup>11</sup> the addition of

sulfur to thiolate ions entails the preponderant formation of RS<sub>x</sub><sup>-</sup> ions ( $x=2-5$ ) which could be implicated in the former processes.

The present paper reports an investigation on the complex mechanism that may be involved in the course of substitutions of polysulfide ions S<sup>1/3-</sup> (S<sub>3</sub><sup>-</sup> ⇌ S<sub>6</sub><sup>2-</sup>) which were electrochemically generated in DMA, on a series of alkyl halides RX: X=I, R=CH<sub>3</sub> (1), C<sub>3</sub>H<sub>7</sub> (2); X=Br, R=C<sub>4</sub>H<sub>9</sub> (3), 2-C<sub>4</sub>H<sub>9</sub> (4), 3-C<sub>5</sub>H<sub>11</sub> (5), PhCH<sub>2</sub> (6); X=Cl, R=PhCH<sub>2</sub> (7), C<sub>6</sub>H<sub>13</sub> (8). The known spectroelectrochemical characteristics of sulfur/polysulfide ions and of RS<sub>x</sub><sup>-</sup> species in DMA enabled the reactions to be followed by UV-VIS spectrophotometry coupled with voltammetry. The results were then confirmed on a preparative scale with methyl iodide (1) and benzyl bromide (6) as substrates.

## Results and discussion

There is now a general agreement concerning the nature of the colored polysulfide ions in dipolar aprotic media.<sup>8,12</sup> In DMA, the first step of the electrochemical reduction of sulfur is expressed by a bielectronic wave R<sub>1</sub> at a rotating gold-microelectrode<sup>12</sup> [ $E_{1/2}(R_1)=-0.40$  V, vs. ref.], eqn. (1). In our opinion, the overall bielectronic electroreduction (1) is likely to proceed through reactive S<sub>2</sub> molecules in equilibrium (2) with

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cyclooctasulfur.<sup>12</sup>



However the exhaustive electrolysis of sulfur at the first step  $R_1$  occurs via disproportionation (3)<sup>12</sup> of  $S_8^{2-}$  ions ( $\lambda_{\max 1} = 515$  nm,  $\epsilon_{515}^8 = 3800$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>;  $\lambda_{\max 2} = 360$  nm,  $\epsilon_{360}^8 = 9000$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), up to the stable  $S^{1/3-}$  species [eqn. (4)], i.e.  $S_6^{2-}$  ions ( $\lambda_{\max} = 465$  nm,  $\epsilon_{465}^6 = 3100$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) in equilibrium (5) with the blue radical-anion  $S_3^{.-}$  ( $\lambda_{\max} = 617$  nm,  $\epsilon_{617}^3 = 4400$  dm<sup>3</sup> mol<sup>-1</sup>).<sup>12</sup>



$$K_1(297 \text{ K}) = [S_3^{.-}]^2[S_6^{2-}]^{-1} = 0.043 \text{ mol dm}^{-3} \quad (6)$$

The total concentration of  $S^{1/3-}$  ions is expressed as  $[S_3^{.-}]_T$  with respect to  $S_3^{.-}$  ions, from eqns. (5) and (6):

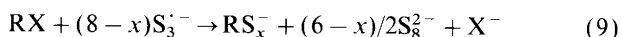
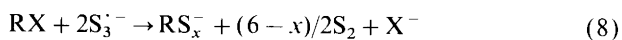
$$[S_3^{.-}]_T = [S_3^{.-}] + 2[S_6^{2-}] = [S_3^{.-}] + 2[S_3^{.-}]^2 K_1 \quad (7)$$

UV-VIS absorption spectra (250–750 nm) of  $S_8$ ,  $S_6^{2-}$ ,  $S_3^{.-}$ ,  $S_8^{2-}$  species, and constants of equilibria (2) and (3) to be used here for data treatment have previously been reported.<sup>11</sup>

$S_8^{2-}$  and  $S^{1/3-}$  ( $S_6^{2-} \rightleftharpoons S_3^{.-}$ ) ions oxidize ( $O_1$ ) and reduce ( $R_2$ ) at the same potentials<sup>8,12</sup> [ $E_{1/2}(O_1) = -0.20$  V;  $E_{1/2}(R_2) = -1.10$  V]. In dilute solutions  $[S_6^{2-}]$  remains low in comparison with  $[S_3^{.-}]$  (e.g.  $[S_6^{2-}] = 0.42 \times 10^{-3}$  mol dm<sup>-3</sup> at total concentration  $[S_3^{.-}]_T = 5.0 \times 10^{-3}$  mol dm<sup>-3</sup>).

The reactivity of electrogenerated  $S_3^{.-}$  ( $\rightleftharpoons S_6^{2-}$ ) ions towards alkyl halides was at first studied from  $A = f(\lambda)$  and  $i = f(E)$  recordings in the course of the progressive addition of RX (1–8) to diluted  $S^{1/3-}$  solutions (see Experimental). The reactions were initially fast under

our experimental conditions with  $CH_3I$  (1),  $C_3H_7I$  (2),  $C_4H_9Br$  (3) and  $PhCH_2Br$  (6) as substrates. The same changes in the spectra and the voltammograms are illustrated in Figs. 1, 2 and 3, relative to the addition of benzyl bromide 6 to a solution  $[S_3^{.-}]_T^0 = 6.15 \times 10^{-3}$  mol dm<sup>-3</sup>; as long as the ratio  $y = [RX]_{ad}/[S_3^{.-}]_T^0$  remains less than 0.31 (Fig. 1),  $A_{617}$  ( $S_3^{.-}$ ) decreases in favor of  $A_{485}$  and  $A_{360}$  (shoulder) with two isosbestic points at 525 nm and 294 nm, and with no appearance of sulfur on voltammograms. For  $0 < y < 0.25$ , the consumption of  $S^{1/3-}$  ions  $\Delta[S_3^{.-}]_T/[RX]_{ad}$  keeps the constant values 3.3 (RX =  $PhCH_2Br$ ) and 2.80 (RX =  $CH_3I$ ,  $C_3H_7I$ ,  $C_4H_9Br$ ) in agreement with the overall balance (9) = (8) + (6-x)/2 × (3b) giving average numbers  $\bar{x}$  of S-atoms in the chain,  $\bar{x} = 4.7$  (R =  $PhCH_2$ ) and 5.2 (R =  $CH_3, C_3H_7$ ) in  $RS_x^-$  species:



We showed earlier<sup>11</sup> that successive formation of  $RS_x^-$  ions (R = alkyl,  $x = 2-5$ ) result from the addition of sulfur to thiolate ions  $RS^-$  according to the shifts (f) of equilibria (10):



The formation of  $RS_x^-$  ions could not be clearly resolved, but is supposed to occur in low proportions: the last addition of sulfur to  $RS^-$  solutions led to the detection of  $S_8$  (appearance of its  $R_1$  wave).  $RS_4^-$  and  $RS_5^-$  ions, whose spectra were calculated to be in the range 260–600 nm,<sup>11</sup> gave a broad maximal absorption at 460–470 nm [ $\epsilon_{460}(RS_4^-) = 850$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>,  $\epsilon_{460}(RS_5^-) = 1500$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>].

In Fig. 1, the ‘mixed’ maximal absorbance  $A_{485}$  is that of  $RS_x^-$  ions [ $\bar{x} \approx 5$  ( $\lambda_{\max} = 460-470$  nm)], and of  $S_8^{2-}$  ions ( $\lambda_{\max} = 515$  nm), which also include the growth of the absorption between 300 and 400 nm. The experimental values of  $A_{485}$  as a function of  $y$ , are consistent with

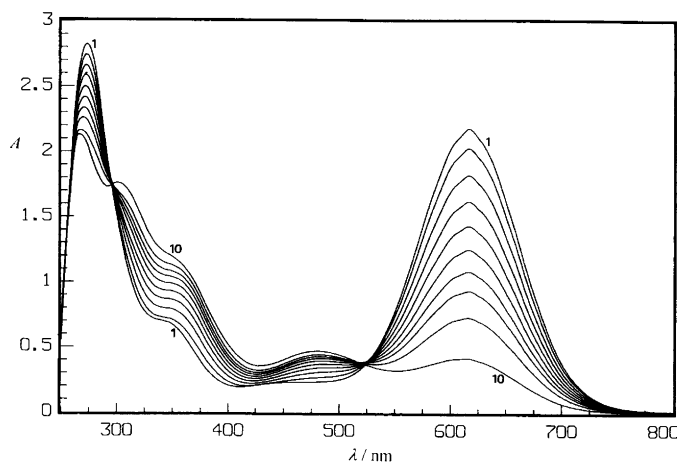


Fig. 1. Dependence of UV-VIS spectra on the addition of benzyl bromide to an  $S^{1/3-}$  solution  $[S_3^{.-}]_T^0 = 6.15 \times 10^{-3}$  mol dm<sup>-3</sup>.  $y = [RX]_{ad}/[S_3^{.-}]_T^0 = 0$  (1); 0.020 (2); 0.052 (3); 0.078 (4); 0.104 (5); 0.130 (6); 0.155 (7); 0.180 (8); 0.22 (9); 0.315 (10). Thickness of the cell = 0.1 cm; scan rate = 1000 nm min<sup>-1</sup>.

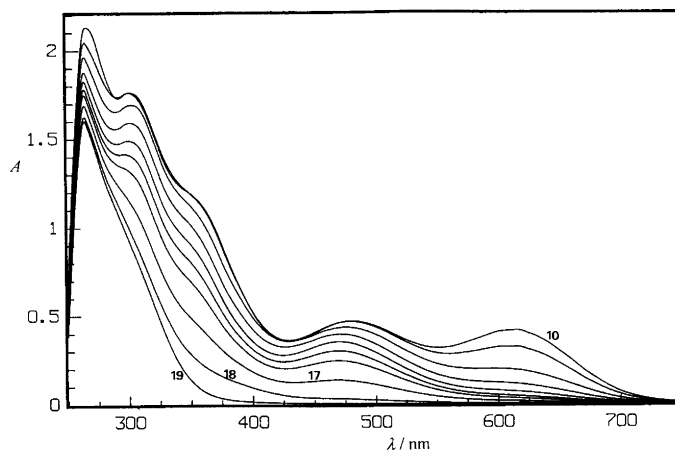


Fig. 2. UV-VIS spectra in the course of the reaction between benzyl bromide and  $S^{1/3-}$  ions. Same conditions as for Fig. 1.  $y=0.315$  (10); 0.35 (11); 0.415 (12); 0.495 (13); 0.565 (14); 0.63 (15); 0.70 (16); 0.83 (17); 0.96 (18); 1.02 (19). Recordings at equilibrium reached within 5–15 min.

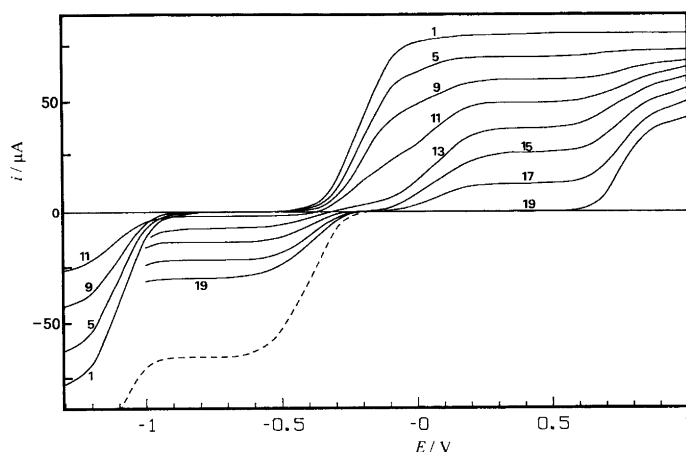
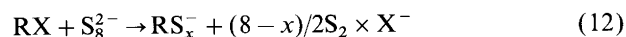


Fig. 3. Changes in voltammograms during the reaction of benzyl bromide with  $S^{1/3-}$  ions. Same conditions as for Fig. 1. Dotted curve of  $[S_8]_i=2.31 \times 10^{-3} \text{ mol dm}^{-3}$  leading to  $[S_3^{2-}]_T^0$ . Rotating gold-disc electrode,  $\Omega=1000 \text{ rev min}^{-1}$ , diameter = 2 mm. Scan rate =  $10 \text{ mV s}^{-1}$ .

values calculated by relationship (11) and the stoichiometry of eqn. (9) [ $\epsilon(\text{RS}_x^-) \approx 1200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,<sup>11</sup>  $\epsilon_1$  ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) of polysulfide ions:<sup>11</sup>  $\epsilon_8 \approx 3500$ ;  $\epsilon_6 \approx 2900$ ;  $\epsilon_3 \approx 100$ ].

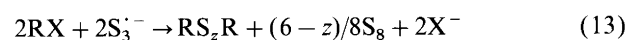
$$A_{485}/l = \epsilon(\text{RS}_x^-)[\text{RS}_x^-] + \epsilon_8[\text{S}_8^{2-}] + \epsilon_6[\text{S}_6^{2-}] + \epsilon_3[\text{S}_3^{2-}] \quad (11)$$

Beyond  $y \approx 0.31 \approx 1/3.3$  (Figs. 2 and 3)  $A_{485}$  and  $A_{360}$  begin to fall also because of the consumption of  $\text{S}_8^{2-}$  ions [eqn. (12)], perhaps through displacement (f) of equilibrium (3):



However, as soon as RX is added to the polysulfide ions,  $A_{617}$  immediately decreases, then slowly increases to a small extent (<5%), the absorbances being stabilized within 15 min (*vide infra*). Sulfur is now detected by its reduction wave  $R_1$  ( $E_{1/2} = -0.40 \text{ V}$ ), and the maximal absorbance  $A_{485}$ , of  $\text{S}_8^{2-}$  ( $\epsilon_8 = 3500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and  $\text{RS}_x^-$  ions, progressively shifts to  $A_{470}$  ( $\text{RS}_x^-$ ,

$\epsilon_{\text{max}} \approx 1500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) as shown by curves 10–13. For  $y=0.50$  ( $\text{RX} + 2\text{S}_3^{2-}$ ) the oxidation current of  $\text{RS}_x^-$  ions ( $E_{1/2} \approx +0.06 \text{ V}$ )<sup>11</sup> attains its maximal value; spectra and  $i=f(E)$  recordings (curve 13) are the same as those which we obtain by the addition of sulfur to  $\text{RS}_x^-$  ions ( $\text{R} = \text{C}_3\text{H}_7$ ,  $\text{PhCH}_2$ ) at a ratio  $8[\text{S}_8]_{\text{lad}}/[\text{RS}_x^-]_0 = 5$ , with  $[\text{RS}_x^-]_0 \equiv 0.5[\text{S}_3^{2-}]_T^0$ . For  $0.5 < y \leq 1.0$  (Figs. 2 and 3, curves 14–19),  $\text{RS}_x^-$  and residual  $\text{S}_8^{2-}/\text{S}_3^{2-}$  ions react in turn with RX substrates as shown by decreases in  $A_{470}$  and  $A_{617}$ , and sulfur continues to be released [increase of  $i(\text{R}_1)$ ] up to the decoloration of the solutions ( $[\text{RX}]_{\text{lad}}/[\text{S}_3^{2-}]_T^0 = 1$ ) according to the overall eqn. (13).



At that point ( $y=1$ ), the only oxidation wave of  $\text{X}^-$  ions ( $3\text{X}^- \rightarrow \text{X}_3^- + 2e^-$ ) is observed at anodic potentials [Fig. 3, curve 19,  $E_{1/2}(\text{Br}^-) \approx +0.75 \text{ V}$ ] with a limiting current in agreement with the value obtained after calibration with a solution of  $\text{NBU}_4\text{X}$  ( $\text{X} = \text{I}, \text{Br}$ ). The average length of the sulfur chains  $\bar{z}$  of dialkyl polysulfanes  $\text{RS}_z\text{R}$

(Table 1, RX = 1–3, 6, 7) was easily deduced from eqn. (13), by comparison between initial sulfur concentration  $[S]_i = 3[S_3^{2-}]_i^0$  with recovered sulfur,  $[S]_f = 8[S_8]_f$  which was obtained from  $i(R_1)$  measurements at  $y = 1$ .

The above results have been applied on a preparative scale with substrates  $CH_3I$  (1) and  $PhCH_2Br$  (6): (i) 1 and 6 were added to chemically generated  $S^{1/3-}$  ions from the quantitative oxidation (14) of anhydrous  $Li_2S$  by sulfur<sup>13,14</sup> in DMA:



(ii) sulfur was electrolyzed at controlled potential ( $E = -0.80$  V,  $R_1$ ) in the presence of  $PhCH_2Br$ , on the basis of eqn. (15) up to  $1$  F  $mol^{-1}$  RX:



The percentage molar distributions of polysulfanes  $RS_zR$ , listed in Table 2, were determined by  $^1H$  NMR spectroscopy. Chemical shifts due to the methyl groups in  $CH_3S_zCH_3$  ( $z = 2-6$ ), and methylene in  $PhCH_2S_zCH_2Ph$  ( $z = 2-5$ ) agree with those reported by Grant and Van Wazer;<sup>15</sup>  $\delta_H$  for  $RS_2R$  and  $RS_3R$  were the same as for authentic samples and mixtures thereof.  $CH_3S_zCH_3$  ( $z = 2-5$ ) and  $PhCH_2S_zCH_2Ph$  ( $z = 2, 3$ ) were, moreover, identified by GC-MS, this method being unsuccessful for higher polysulfanes because of their thermal decomposition.<sup>1</sup>

The sulfur rankings  $\bar{z} = 3.9$  ( $R = CH_3$ ) and  $3.7$  ( $R = PhCH_2$ ) are similar to those estimated by spectroelectrochemical studies (Table 1,  $R =$  alkyl,  $\bar{z} = 3.5$ ;  $R = PhCH_2$ ,  $\bar{z} = 3.3$ ). The electrochemical oxidation of an initial solution of benzylthiolate ions added with sulfur at  $y = 8[S_8]/[RS^-]_0 = 5$  gave a mixture of the same species  $RS_zR$  ( $z = 2-5$ ,  $\bar{z} = 3.6$ ) as those obtained by nucleophilic substitution of  $S^{1/3-}$  ions on  $PhCH_2Br$  (Table 2). So, in spite of different distributions of polysulfanes, the maximal average rankings  $\bar{z}$  were nearly the same whichever way the synthesis was carried out.

The predominant yield of tri- and tetra-sulfanes with respect to the formation of  $RS_5^-$  as the major anionic species from the first substitution step is worthy of further discussion. On the one hand, greatly enhanced nucleophilic character can be assumed for  $RS_x^-$  ions in equilibria (10) as  $x$  decreases ( $RS_3^- > RS_4^- > RS_5^- > RS_6^-$ ), the order being the same as for the nucleophilic abilities for  $S_x^{2-}$  ions<sup>16,17</sup> ( $S_4^{2-} > S_6^{2-} \gg S_8^{2-}$ ). On the other hand the disproportionations of  $RS_x^-$  ions ( $x = 4, 5, 6?$ ) must also be con-

Table 1. Average sulfur rankings of organic polysulfanes produced from reactions between polysulfide ions and alkyl halides in dilute solutions of DMA.

	RX				
	1	2	3	6	7
$[S]_f/[S]_i^a$	0.41	0.42	0.42	0.45	0.44
$\bar{z}^b$	3.55	3.5	3.5	3.3	3.35

<sup>a</sup> $[S]_f/[S]_i \pm 0.01$ . <sup>b</sup> $\bar{z}(\pm 0.1) = 6(1 - [S]_f/[S]_i)$ .

Table 2. Chemical shifts  $\delta_H$  (ppm vs. TMS) and molar composition (%) of  $CH_3S_zCH_3$  and  $PhCH_2S_zCH_2Ph$  synthesized mixtures.

R		z					$\bar{z}^d$
		2	3	4	5	6	
$CH_3$	$\delta_H$ (6 H)	2.38	2.53	2.62	2.64	2.67	3.9
	% <sup>a</sup>	11	33	25	18	13	
	% <sup>b</sup>	4	40	34	22	—	
$PhCH_2$	$\delta_H$ (4 H)	3.65	4.02	4.14	4.19	—	3.7
	% <sup>a</sup>	8	37	30	25	—	
	% <sup>b</sup>	26	24	12	38	—	

<sup>a</sup>Chemical synthesis. <sup>b</sup>Electrochemical reduction of sulfur in the presence of  $PhCH_2Br$ . <sup>c</sup>Electrochemical oxidation of  $PhCH_2S_x^-$  ions. <sup>d</sup> $\bar{z} \pm 0.2$  from % values.

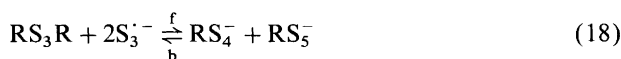
sidered: reactions (16), with related constants  $K_2$ , were studied by our group<sup>11</sup> from direct additions of a series of dialkyl disulfides to  $S^{1/3-}$  ions; absorbances of the solutions reached equilibria within 15 min for  $[S_3^{2-}]_T^0 = 2 \times 10^{-3}$  mol  $dm^{-3}$ .



$$K_2 = [RS_4^-]^2 [RS_2R]^{-1} [S_3^{2-}]^{-2} \quad (17)$$

For the example  $R = PhCH_2$ ,<sup>11</sup>  $K_2 = 1.2 \times 10^4$   $dm^3$   $mol^{-1}$ ; this value leads, for example, to the following solution composition:  $[RS_4^-]_0 = 6.0 \times 10^{-3}$  mol  $dm^{-3}$ ;  $[RS_2R] = 0.75 \times 10^{-3}$  mol  $dm^{-3}$ ,  $[S_3^{2-}] = 1.5 \times 10^{-3}$  mol  $dm^{-3}$ ,  $[RS_4^-] = 4.5 \times 10^{-3}$  mol  $dm^{-3}$ .

These results have been extended in the present work to the reactivity of  $S_3^{2-}$  ions towards trisulfides  $RS_3R$  ( $R = C_3H_7, PhCH_2$ ). In both cases  $RS_3R$  added to  $S^{1/3-}$  solutions (example of Fig. 4,  $R = C_3H_7$ ,  $[S_3^{2-}]_T^0 = 2.58 \times 10^{-3}$  mol  $dm^{-3}$ ) initially causes the fast consumption of  $S_3^{2-}$  ions leading to increased  $RS_x^-$  formation (decrease of  $A_{617}$  and increase of  $A_{465}$  through an isosbestic point at 524 nm). For  $[RS_3R]_{ad}/[S_3^{2-}]_T^0 < 0.30$  (curves 2–4) the calculated variations of  $A_{617}$  and  $A_{465}$  coincide with the experimental ones, with  $\Delta[S_3^{2-}]_T/[RS_3R]_{ad}$  close to  $-2$ , in accordance with eqn. (18) and constants  $K_3$  ( $\pm 20\%$ ).



$$K_3 = [RS_4^-][RS_5^-][RS_3R]^{-1}[S_3^{2-}]^{-2} \quad (19)$$

$K_3$  ( $Pr^n$ ) =  $1.0 \times 10^4$   $dm^3$   $mol^{-1}$ ; ( $Bz$ ) =  $2.5 \times 10^4$   $dm^3$   $mol^{-1}$ . At a ratio  $[RS_3R]_{ad}/[S_3^{2-}]_T^0$  greater than  $\approx 0.30$  (curves 5 and 6),  $RS_x^-$  ( $x = 4, 5$ ) solutions evolved after reaction (18f) within 10 min which led to a low regeneration of  $S_3^{2-}/S_8^{2-}$  ions, with the loss of the isosbestic point due to the dissociation (16b) of  $RS_4^-$  ions, and probably that of  $RS_5^-$  according to equilibrium (20).



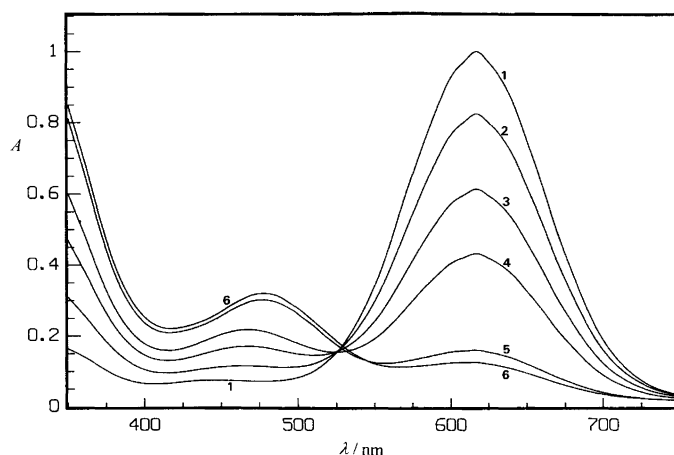


Fig. 4. Dependence of VIS spectra on the addition of dipropyl trisulfide to a solution  $[S_3^{2-}]_T^0 = 2.58 \times 10^{-3} \text{ mol dm}^{-3}$ .  $[RS_3R]_{ad.}/[S_3^{2-}]_T^0 = 0$  (1); 0.093 (2); 0.21 (3); 0.30 (4); 0.84 (5); 2.42 (6). Curves (5) and (6): recordings at equilibrium, 10 min after addition of  $RS_3R$ .

In processes (16b), (18b) and (20f), dissociations (21) of  $RS_x^-$  ions ( $x=4, 5$ ) could be the rate-determining steps, with subsequent fast dimerizations of  $RS_2^{\cdot-}$  and  $RS_2^-$  into  $RS_3R$  and  $RS_2R$ ,<sup>11</sup> in the latter case the release of sulfur from conversion of  $RS_2^-$  into  $RS_2R$ , as observed during the course of oxidations of  $RS_2^-$  ions,<sup>11</sup> results in the partial formation (3b) of  $S_8^{2-}$  ions ( $\lambda_{max} = 515 \text{ nm}$ ) and a related shift of the VIS absorption towards  $\approx 480 \text{ nm}$  (Fig. 4, curves 5, 6).



Isolated organic tetrasulfanes are not readily available because of their instability. Nevertheless, the additional equilibrium (22) may occur, in a similar way to eqns. (16) and (18) occurring through dissociation (21).



During the course of the reactions  $RX + S^{1/3-}$  the partial disproportionations of  $RS_x^-$  ions ( $x=4, 5$ ) into  $RS_zR$  ( $z=2, 3, 4$ ) and polysulfide ions also explain the slow regeneration of  $S_3^{2-}$  which was observed at a ratio  $y$  greater than 0.30. These disproportionations remain negligible when  $S_3^{2-}$  ions are the predominant species in the solutions ( $y < 0.25$ ), with only the formation of  $RS_x^-$  ions ( $\bar{x}=5.2$ ,  $R=\text{alkyl}$ ;  $\bar{x}=4.7$ ,  $R=\text{PhCH}_2$ ). This was applied to a kinetic study of the slower processes in order to determine the nature of the nucleophilic  $S^{1/3-}$  agent: the anion-radical  $S_3^{\cdot-}$ , or the dianion  $S_6^{2-}$ . The rates of reaction decreased from the first step (8) for 2- $C_4H_9Br$  (4), 3- $C_5H_{11}Br$  (5) and  $C_6H_{13}Cl$  (8) as substrates, whereas *tert*- $C_4H_9Br$  was unreactive. The processes bear the qualitative characteristics of an  $S_N2$  mechanism, with a reactivity order  $1^\circ > 2^\circ \gg 3^\circ$  for substrate while  $I > Br \gg Cl$  is the order for the leaving group. In a similar way, superoxide ions  $O_2^{\cdot-}$  were found to react with alkyl halides under aprotic conditions, accord-

ing to the following scheme.<sup>18-22</sup>



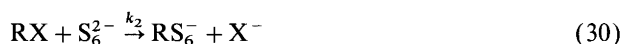
The primary step occurs via an  $S_N2$  displacement of halide. The resulting peroxy radical is reduced by a fast homogenous electron transfer to  $RO_2^-$ , which acts as a nucleophile towards  $RX$  species. With  $S^{1/3-}$  polysulfide ions one mechanistic possibility yielding  $RS_6^-$  ions before dissociation (10b) would also be the initial attack of  $S_3^{\cdot-}$  [eqn. (26)].



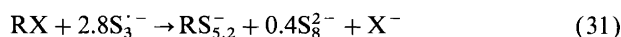
$RS_6^-$  ions could result either from coupling between radicals [eqn. (27)] or from electron transfer (28).



An alternative mechanism might involve the direct substitution (30) of  $S_6^{2-}$  on the functional carbon as rate-determining step.



In order to investigate these options, kinetic studies were carried out from  $A_{617}(S_3^{\cdot-})$  recordings as a function of time after the addition of  $RX$  substrates 4, 5 and 8 to  $[S_3^{\cdot-}]_T^0$  solutions at  $20^\circ\text{C}$ . As long as  $\Delta[RX]/[S_3^{\cdot-}]_T^0$  remains less than 0.25, the overall reaction (31) can be considered alone [eqn. (9),  $R=\text{alkyl}$ ,  $\bar{x}=5.2$ ].



In nucleophilic processes, the reactivity of the least reducing polysulfide ions  $S_8^{2-}$  was negligible in compar-

ison with that of  $S^{1/3-}$  species.<sup>16,17</sup> Here again the rates of reactions were greatly decreased when RX substrates were added to  $S^{1/3-}$  solutions saturated with sulfur; the rate equation can therefore be expressed by eqns. (32), and (33) from constant  $K_1$ .

$$v_t = -\frac{d[RX]_t}{dt} = -\frac{1}{2.8} \frac{d[S_3^{2-}]_t}{dt} = k_{\text{obs}}[RX]_t[S_3^{2-}]^n \quad (32)$$

$$v_t = -\frac{1}{2.8} (1 + 4[S_3^{2-}]_t/K_1) \frac{d[S_3^{2-}]_t}{dt} \quad (33)$$

$[RX]_t$  and  $[S_8^{2-}]_t$  are easily expressed as a function of  $[S_3^{2-}]_t$  by the use of initial concentrations  $[RX]_0 = a$  and  $[S_3^{2-}]_0^0 = b$ , and of stoichiometry (31).

$$2.8[RX]_t = (a - b) + [S_3^{2-}]_t + 2[S_3^{2-}]_t^2/K_1 \quad (34)$$

$$13[S_8^{2-}]_t = b - [S_3^{2-}]_t + 2[S_3^{2-}]_t^2/K_1 \quad (35)$$

$[S_3^{2-}]_t$  is attained from  $A_{617}$  measurements.

$$A_{617}^t/l = \varepsilon_3[S_3^{2-}]_t + \varepsilon_8[S_8^{2-}]_t \quad (36)$$

The kinetic equation (37) was then deduced from eqn. (32) and tested by assuming first or second order ( $n = 1, 2$ ) with respect to  $[S_3^{2-}]_t$  (denoted  $s$ ).

$$Y = -\int_{s_0}^s \frac{(K_1 + 4s \cdot l) ds}{[K_1(2.8a - b) + K_1s + 2s^2]s^n} = k_{\text{obs}}t \quad (37)$$

In all cases (RX = **4**, **5**, **8**) orders 2, relative to  $S_3^{2-}$  which were obtained from integrations  $Y = f(t)$  (Fig. 5), led us to propose  $S_6^{2-}$  as the effective nucleophilic agent in  $S_N2$  reactions (8). This fact was also noted during the course of the slow reactions between  $S^{1/3-}$  ions and nitroaromatic halides ( $S_NAr$ ),<sup>16</sup> *vic*-dibromides ( $E_2$ )<sup>17</sup> or *S*-phenyl thiol esters.<sup>23</sup> It could be explained by a more localized charge on the terminal sulfurs of  $S_6^{2-}$  ( $-0.50$ ) compared with those of  $S_3^{2-}$  ( $-0.38$ ) according to calculations made by Meyer *et al.*<sup>24</sup> The rate constants

Table 3. Rate constants  $k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$  of the reactions between  $S_6^{2-}$  ions and alkyl halides at  $20 \pm 0.5^\circ\text{C}$ . Ionic strength =  $0.1 \text{mol dm}^{-3}$ .

	RX			
	4	5	7	8
$k_2^a$	2.35	3.7	65	0.20

<sup>a</sup>Mean values  $\pm 5\%$  except for **7**,  $\pm 10\%$  from deviation of several kinetic runs.

$k_2 = k_{\text{obs}} \times K_1$  of the reactions between  $S_6^{2-}$  ions and alkyl halides **4**, **5**, **8**, and **7** ( $1RX + 3.3S_3^{2-} \rightarrow RS_{4,7}^-$ ) at  $20^\circ\text{C}$  are listed in Table 3. The nucleophilicity of  $S_6^{2-}$  ions towards *sec*-alkyl bromides in DMA can be placed between that of  $O_2^{2-}$  and  $\text{PhS}^-$  from kinetic data in DMF (298 K):  $k(O_2^{2-} + 2\text{-BuBr}) = 174 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ ,<sup>22</sup>  $k(\text{PhS}^- + 2\text{-PrBr}) = 0.20 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ .<sup>25</sup>

## Conclusions

In summary,  $S_6^{2-}$  ions in equilibrium with  $S_3^{2-}$  readily react with alkyl iodides and bromides in *N,N*-dimethylacetamide. The  $S_N2$  processes involve the initial formation of organic polysulfanide ions  $RS_x^-$  ions ( $\bar{x} \approx 5$ ) which were previously obtained by direct addition of sulfur to thiolate ions. Mixtures of dialkyl polysulfanes  $RS_2R$  ( $z = 2-6$ ,  $\bar{z} \approx 3.8$ ) result from subsequent reactions on RX substrates. This complex second step probably involves disproportionations of  $RS_x^-$  ions ( $x = 4, 5$ ), which have been proved by the study of the reactions between dialkyl di- or tri-sulfides and  $S^{1/3-}$  ions. Our results are currently applied to the synthesis of polysulfide polymers with high average sulfur rankings, by polycondensation of alkyl halides with electrogenerated polysulfide ions in dipolar aprotic media.

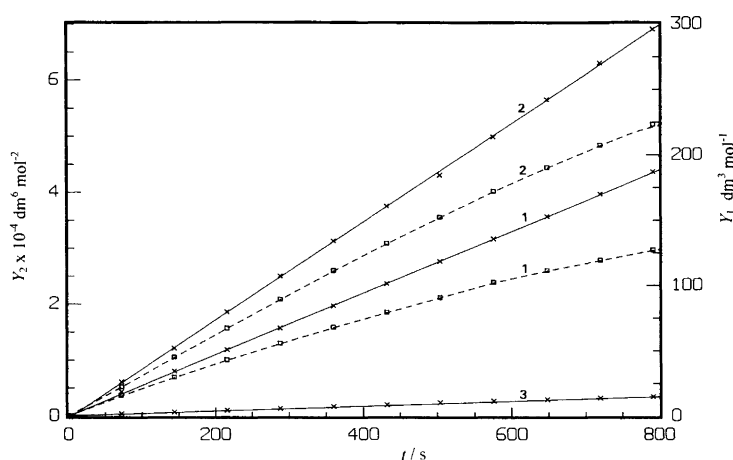


Fig. 5. Kinetic studies of the reactions between alkyl halides **4**, **5** and **8** and  $S^{1/3-}$  ions. Initial conditions:  $[2\text{-C}_4\text{H}_9\text{Br}]_0 = 2.63 \times 10^{-3} \text{mol dm}^{-3}$ ,  $[S_3^{2-}]_0^0 = 5.01 \times 10^{-3} \text{mol dm}^{-3}$  (1);  $[3\text{-C}_5\text{H}_{11}\text{Br}]_0 = 2.79 \times 10^{-3} \text{mol dm}^{-3}$ ,  $[S_3^{2-}]_0^0 = 5.78 \times 10^{-3} \text{mol dm}^{-3}$  (2);  $[C_6H_{13}Cl]_0 = 1.89 \times 10^{-2} \text{mol dm}^{-3}$ ,  $[S_3^{2-}]_0^0 = 4.98 \times 10^{-3} \text{mol dm}^{-3}$  (3). Calculations assuming first order ( $Y_1$ , dotted curves) and second order ( $Y_2$ ) with respect to  $S_3^{2-}$  ions.

## Experimental

**Materials and equipment.** *N,N*-Dimethylacetamide, alkyl halides, benzyl trisulfide, propanethiol and  $\alpha$ -toluenethiol were purchased from Aldrich. Lithium sulfide was obtained from Alfa. Propyl trisulfide was kindly supplied by ELF-Atochem. Distilled DMA was stored over molecular sieves (4 Å) after addition of the supporting electrolyte, tetrathylammonium perchlorate (Fluka, 0.1 mol dm<sup>-3</sup>). RX compounds 1–8 were distilled just before use. The thermostatted (20.0 ± 0.5 °C) flow-through cell and the two-compartment preparative cell were the same as previously described.<sup>17,26</sup> Current–potential curves at a rotating gold disc electrode (diameter 2 mm, 1000 rev min<sup>-1</sup>) were recorded with the use of an EGG-PAR 273 unit. The counter electrode was a platinum foil in a separated compartment. All the potentials referred to the Ag/AgCl(s), KCl saturated in DMA–N(Et)<sub>4</sub>ClO<sub>4</sub> 0.1 mol dm<sup>-3</sup> electrode. Absorption spectra were obtained with a Kontron Uvikon 930 spectrophotometer (thickness of the cell  $l=1$  mm). The mixtures of dialkylpolysulfanes were analysed by <sup>1</sup>H NMR spectroscopy (200.132 MHz, Bruker AC 200 spectrometer) with CDCl<sub>3</sub> as the solvent (Me<sub>4</sub>Si as standard) and GC–MS (Hewlett-Packard 5989 A, EI 70 eV).

**Generation of S<sup>1/3</sup> and S<sub>8</sub><sup>2-</sup> ions, and kinetic studies.** Solutions of alkyl halides 1–3, 6, 7 in DMA were added to S<sup>1/3-</sup> solutions ( $v_0=40$  cm<sup>3</sup>,  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup> < [S<sub>3</sub><sup>-</sup>]<sub>T</sub><sup>0</sup> <  $6.2 \times 10^{-3}$  mol dm<sup>-3</sup>) in two sets of experiments: (i)  $0 < [RX]_{ad}/[S_3^{-}]_T^0 \leq 1$ , from twenty successive additions of RX ( $v_{max}=4$  cm<sup>3</sup>) as illustrated in Figs. 1, 2; (ii)  $0 < [RX]_{ad}/[S_3^{-}]_T^0 \leq 0.35$ , with thirty additions of RX ( $v_{max}=5$  cm<sup>3</sup>) in order to obtain accurate variations of  $\Delta[S_3^{-}]_T/[RX]_{ad}$ . S<sup>1/3-</sup> ions were readily generated by electro-reduction of sulfur to S<sub>4</sub><sup>2-</sup> ions<sup>26</sup> at controlled potential ( $E=-1.3$  V) on the plateau of its second reduction wave R<sub>2</sub> at a large gold grid electrode. S<sub>4</sub><sup>2-</sup> ions, which reoxidize to S<sup>1/3-</sup>/S<sub>8</sub><sup>2-</sup> ions in the presence of sulfur, are in part protonated to H<sub>2</sub>S<sub>4</sub> by traces of non-electroactive acidic impurities in the solvent.<sup>27</sup> H<sub>2</sub>S<sub>4</sub> polysulfane, which disproportionates according to eqn. (38),<sup>28</sup> was eliminated by the nitrogen-bubbling:

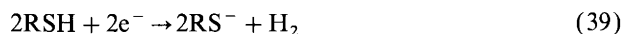


When the absorption reached a maximum at 617 nm, S<sup>1/3-</sup> ions were the only species in solution.

The kinetic studies were performed at 20 °C from  $A_{617}=f(t)$  recordings after addition of concentrated solutions of RX substrates ( $v_{max}=0.5$  cm<sup>3</sup>) to solutions ( $v=40$  cm<sup>3</sup>) of S<sup>1/3-</sup> ions (RX=4, 5, 7, 8). The dead time due to mixing and transfer of the reaction medium to the spectrophotometric cell took ca. 10 s. Under these conditions the rate constants of the reactions  $RX + S_8^{2-}$  can be evaluated for  $k_2 < 200$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

Thiolate ions ( $[RS^-]_0=2.07 \times 10^{-3}$  mol dm<sup>-3</sup>, R = C<sub>3</sub>H<sub>7</sub>;  $3.10 \times 10^{-3}$  mol dm<sup>-3</sup>, R = PhCH<sub>2</sub>) were obtained, before addition of sulfur (1RS<sup>-</sup> + 5S), by

electrolysis ( $E \approx -1.8$  V) of thiols RSH according to eqn. (39) as previously reported:<sup>11</sup>



**Syntheses of organic polysulfanes.** Mixtures of polysulfanes CH<sub>3</sub>S<sub>z</sub>CH<sub>3</sub> ( $z=2-6$ ) or PhCH<sub>2</sub>S<sub>z</sub>CH<sub>2</sub>Ph ( $z=2-5$ ) were yielded by reactions of S<sub>8</sub><sup>2-</sup> ions with methyl iodide and benzyl bromide. S<sub>8</sub><sup>2-</sup> were chemically generated in DMA by heating a solution (200 cm<sup>3</sup>) of Li<sub>2</sub>S with a stoichiometric quantity of sulfur [eqn. (14)] at 50 °C for 30 min under an N<sub>2</sub> atmosphere. RX substrates, which were dissolved in 25 cm<sup>3</sup> of DMA, were then added at room temperature, up to decoloration of the orange–blue polysulfide solutions. After extraction<sup>9,17</sup> of the oily products, sulfur was eliminated by column chromatography on silica gel (two successive times with hexane as the eluent for R = CH<sub>3</sub>, hexane then hexane–diethyl ether 80:20 for R = PhCH<sub>2</sub>).

CH<sub>3</sub>S<sub>z</sub>CH<sub>3</sub>. Li<sub>2</sub>S, 0.997 g (21.5 mmol); S<sub>8</sub>, 3.40 g (106 mmol S); CH<sub>3</sub>I, 6.2 g (43.6 mmol). Products: CH<sub>3</sub>S<sub>z</sub>CH<sub>3</sub>,  $z=2-6$  from  $\delta_H$  (6 H, s) (see Table 2), 2.13 g (64% with respect to  $\bar{z}=3.9$ );  $z=2$ ,  $m/z$  96 ( $M^+_{+2}$ , 11), 94 ( $M^+$ , 100%), 79 (55), 64 (12), 61 (24), 48 (25), 47 (40), 46 (55) and 45 (86);  $z=3$ ,  $m/z$  128 ( $M^+_{+2}$ , 13), 126 ( $M^+$ , 100%), 111 (17), 80 (22), 79 (59), 78 (12), 64 (22), 61 (15), 47 (48), 46 (26) and 45 (66);  $z=4$ ,  $m/z$  160 ( $M^+_{+2}$ , 15), 158 ( $M^+$ , 88), 111 (12), 94 (27), 79 (100), 64 (33), 61 (10), 47 (58), 46 (29) and 45 (78);  $z=5$ ,  $m/z$  190 ( $M^+$ , <2%), 158 (46), 126 (10), 94 (22), 79 (89), 64 (53), 61 (12), 47 (79), 46 (45) and 45 (100).

PhCH<sub>2</sub>S<sub>z</sub>CH<sub>2</sub>Ph. Li<sub>2</sub>S, 0.475 g (10.2 mmol); S<sub>8</sub>, 1.63 g (50.8 mmol S); PhCH<sub>2</sub>Br, 3.35 g (19.6 mmol). Products: PhCH<sub>2</sub>S<sub>z</sub>CH<sub>2</sub>Ph,  $z=2-5$  from  $\delta_H$  (4 H, s) (Table 2), 2.20 g (72% with respect to  $\bar{z}=3.7$ );  $z=2$ ,  $m/z$  246 ( $M^+$ , 6%), 91 (100), 65 (14) and 45 (12);  $z=3$ ,  $m/z$  278 ( $M^+$ , 2%), 91 (100), 65 (16) and 45 (18).

PhCH<sub>2</sub>S<sub>z</sub>CH<sub>2</sub>Ph mixtures (compositions in Table 2) were also electrochemically synthesized (i) from reduction of sulfur in the presence of PhCH<sub>2</sub>Br [eqn. (18)], and (ii) by oxidation of PhCH<sub>2</sub>S<sup>-</sup> ions added with sulfur at  $y=8[S_8]/[RS^-]_0=5$ . (i) PhCH<sub>2</sub>Br (1.44 g, 8.4 mmol) was dissolved in 120 cm<sup>3</sup> of the catholyte N(Et)<sub>4</sub>ClO<sub>4</sub> 0.5 mol dm<sup>-3</sup> and then added with solid sulfur beyond saturation (0.655 g, 20.4 mmol S). The potential of the large gold grid as cathode was kept at the R<sub>1</sub> step ( $-0.8$  V <  $E$  <  $-0.6$  V) in order to retain the Faradaic current near 250 mA. The reduction was extended as long as the solution became colored as a result of the formation of S<sub>8</sub><sup>2-</sup> after the full consumption of RX (electric yield 92%). The reaction products (0.87 g, 69%,  $\bar{z}=3.74$ ) were obtained in the same way as for chemical syntheses, after filtration of N(Et)<sub>4</sub>Br produced by the electrolysis. (ii) PhCH<sub>2</sub>S<sup>-</sup> ions were generated by electro-reduction ( $-1.7$  V <  $E$  <  $-1.4$  V) of  $\alpha$ -toluenethiol (1.06 g, 8.5 mmol in 120 cm<sup>3</sup> of the catholyte). After the addition of sulfur (1.35 g, 42 mmol S), exhaustive electro-oxidation of PhCH<sub>2</sub>S<sub>x</sub><sup>-</sup> ions was performed at controlled

potential ( $-0.3 \text{ V} < E < -0.1 \text{ V}$ ) up to decoloration of the solution. Products: 0.69 g (55%,  $\bar{z}=3.6$ ).

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