Polymer modification and synthesis using sulphenyl derivatives: 9. Addition of alkylsulphenyl chlorides to *cis*-1, 4-polybutadiene

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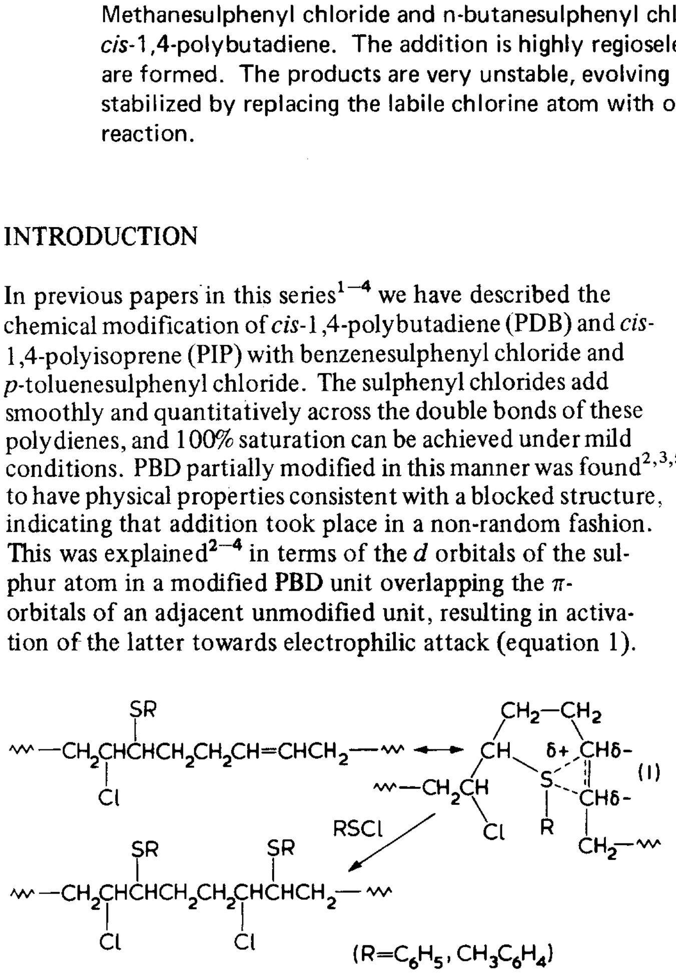
Methanesulphenyl chloride and n-butanesulphenyl chloride add readily across the double bonds in *cis*-1,4-polybutadiene. The addition is highly regioselective so that long sequences of saturated units are formed. The products are very unstable, evolving hydrogen chloride on standing, but can be stabilized by replacing the labile chlorine atom with other nucleophiles in a phase transfer catalysed reaction.

INTRODUCTION

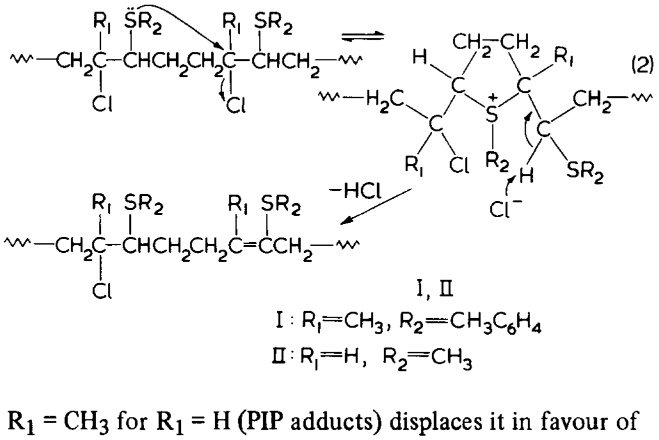
In previous papers in this series[1–4] we have described the chemical modification of *cis*-1,4-polybutadiene (PDB) and *cis*-1,4-polyisoprene (PIP) with benzenesulphenyl chloride and *p*-toluenesulphenyl chloride. The sulphenyl chlorides add smoothly and quantitatively across the double bonds of these polydienes, and 100% saturation can be achieved under mild conditions. PBD partially modified in this manner was found[2,3,5] to have physical properties consistent with a blocked structure, indicating that addition took place in a non-random fashion. This was explained[2–4] in terms of the *d* orbitals of the sulphur atom in a modified PBD unit overlapping the π-orbitals of an adjacent unmodified unit, resulting in activation of the latter towards electrophilic attack (equation 1).


(1)

($R=C_6H_5, CH_3C_6H_4$)

Firm chemical evidence for a regioselective addition came from the reaction of PIP with toluenesulphenyl chloride[4]. In this case it was impossible to measure the physical properties of the adducts, as they decomposed at room temperature with loss of hydrogen chloride. However, it was established[4], by reference to model compounds, that this decomposition took place *via* equation (2) ($R_1 = CH_3$, $R_2 = CH_3C_6H_4$). In other words, it stemmed directly from the saturation of successive double bonds along the polymer chain, and the extent of decomposition was too great to be compatible with a random addition.

Substituents on the polydiene backbone evidently exert a profound effect on the equilibrium in equation (2). The PBD adducts ($R_1 = H$, $R_2 = CH_3C_6H_4$) show good thermal stability, and the equilibrium lies to the left, but substituting $R_1 = CH_3$ for $R_1 = H$ (PIP adducts) displaces it in favour of the cyclic sulphonium ion I, from which irreversible loss of hydrogen chloride readily takes place.


(2)

I, II

I : $R_1=CH_3$, $R_2=CH_3C_6H_4$

II : $R_1=H$, $R_2=CH_3$

There remained to be studied the influence of the sulphenyl substituent, R_2, on the equilibrium, and in particular the behaviour of alkylsulphenyl chlorides towards polydienes. Theory predicts that substitution of a strongly bridging alkylthio group for an arylthio group should enhance both the neighbouring group activation in equation (1) and the cyclic sulphonium ion formation in equation (2); we now present evidence that methanesulphenyl chloride (MSC) and butanesulphenyl chloride (BSC) indeed react with polydienes in a highly regioselective fashion, and that the resulting adducts decompose very rapidly *via* equation (2), even when $R_1 = H$, so much so that the labile chlorine atom can be replaced almost quantitatively by a variety of nucleophiles, forming a wide range of novel polymers and copolymers.

EXPERIMENTAL

Product numbers refer to *Tables 1* and *2*.

N.m.r. spectra were recorded on a Varian HA-100 instrument from $CDCl_3$ solutions, using tetramethylsilane as internal standard; i.r. spectra were obtained on a Perkin–Elmer Model 177 grating spectrometer for films cast from chloroform solution, unless otherwise indicated.

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Table 1 Composition of product polymers from the reaction $\left(-CH_2CH{=}CHCH_2\right)_n \xrightarrow[(2)\ X^{-b}]{(1)\ RSCl^a}$

Product number	X^-	Mol % RSCl used	Elemental analysis (%) C	H	Cl	N	S	Composition (%)[f] $-CH_2CH{=}CHCH_2-$	$-CH_2\overset{Cl}{CH}\underset{SR}{CH}CH_2-$	$-CH_2\overset{X}{CH}\underset{SR}{CH}CH_2-$	$-CH_2CH{=}\underset{SR}{C}CH_2-$	Calculated[g] C and H (%) C	H
1a[c]	–	50	73.0	9.4	7.5	–	9.9	78.6	14.6	–	6.8	73.1	9.5
1b	$2-NO_2C_6H_4CO_2^-$	50	55.5	5.4	–	4.7	13.7	5.0	–	75.0	20.0	55.4	5.2
2	$C_6H_5CO_2^-$	66	69.7	8.4	2.2	–	11.1	46.5	9.4	39.5	4.6	69.9	–
3	$4-NO_2C_6H_4CO_2^-$	50	64.4	7.5	1.2	3.2	9.1	56.9	5.1	34.7	3.3	64.5	7.4
4	CN^-	66	69.7	9.3	–	5.3	15.1	47.2	–	42.4	10.4	70.1	8.9
5	$C_6H_5O^-$	66	71.7	9.0	1.3	–	12.3	42.7	5.5	46.6	5.2	72.6	–
6	$Cl_3CO_2^-$	20	68.5	8.5	14.8	–	5.3	85.9	3.3	10.8	–	67.3	8.6
7	$Cl_3CO_2^-$	66	47.5	6.3	28.4	–	10.0	43.9	12.1	44.0	–	47.6	6.2
8[d]	$Cl_3CO_2^-$	66	45.9	6.1	29.0	–	9.8	43.8	9.1	47.1	–	47.0	6.1
9	$C_6H_5CH_2O^-$	66	72.4	9.5	2.0	–	11.3	36.7	7.8	23.5	32.0	71.5	–
10a[e]	$Cl_3CO_2^-$	20	77.3	9.3	6.9	–	2.7	94.5	1.9	3.6	–	78.7	10.0
10b[e]	$Cl_3CO_2^-$	20	55.3	6.7	22.4	–	8.4	67.7	9.5	22.8	–	56.0	7.3

[a] R = n-C_4H_9 except for 1a and 1b where R = CH_3; [b] except for products 1a and 1b, step (2) involved phase transfer catalysis; [c] product from supernatant liquid (see Experimental); [d] after 2 days reaction; [e] from fractionation of product 6; [f] calculated from Cl, S, N or Cl, S, H as appropriate; [g] calculated from % composition

Materials

PBD was a sample of Cariflex BR 1220 supplied by the Dunlop Rubber Co. It consisted of 96–97% *cis*-1,4-linkages, and was purified by precipitation from toluene into methanol.

Analar grade toluene and chloroform were dried over sodium and calcium chloride respectively, then distilled. Dichloromethane was dried over molecular sieves, and sulphuryl chloride was distilled immediately before use.

MSC was prepared by the method of Britzinger and coworkers[6] and BSC by the dropwise addition at –15°C of one equivalent of sulphuryl chloride to the calculated amount of n-butyl disulphide, both in dichloromethane solution. After warming to room temperature, the solvent and dissolved gases were removed under reduced pressure, and the residue dissolved in chloroform for immediate use.

All other chemicals were used as supplied by the manufacturers.

Addition of MSC to PBD

PBD (2% solution in toluene) was treated dropwise, with stirring at –15°C with the desired amount of MSC in toluene solution. A grey, gelatinous precipitate formed immediately, and turned brown with evolution of hydrogen chloride when allowed to warm up to room temperature. The supernatant liquid was decanted into methanol, yielding a white, sticky precipitate which also developed an odour of hydrogen chloride on storage.

Treatment of PBD/MSC adduct with ClO_4^-

A sample of PBD was treated with one equivalent of MSC as described above. The supernatant liquid was discarded and the precipitate stirred at room temperature with a solution of excess lithium perchlorate in THF until no more material dissolved. After filtering off the small amount of residual gel on glass wool, the clear solution was left for 3 days at room temperature, by which time a white precipitate had formed. The latter was collected, reprecipitated from acetonitrile into water, and dried at 50°C *in vacuo* to constant weight.

Treatment of PBD/MSC adduct with sodium 2-nitrobenzoate

A sample of PBD was treated with one half-equivalent of MSC as described above. The supernatant liquid was decanted into methanol and the resulting spongy precipitate collected and dried at 50°C *in vacuo* for 24 h (product 1a).

The original precipitate was stirred at room temperature for 2 days with a solution of excess sodium 2-nitrobenzoate in DMF. After standing for a further 2–3 weeks at room temperature, the insoluble material was removed and the filtrate added to methanol. The product was collected, reprecipitated from chloroform into light petroleum, and dried at 50°C *in vacuo* to constant weight (product 1b). The compositions of both products were calculated from their elemental analyses.

Addition of BSC to PBD with nucleophilic displacement of Cl^-

PBD (2% solution in chloroform) was treated dropwise with stirring at –15°C with the desired amount of BSC in chloroform. The phase transfer catalyst Aliquat 336 (approximately 5 mol% of the amount of BSC used) was then added to the solution of the adduct, followed by a

Table 2 Spectral data of product polymers

	I.r.		N.m.r.	
Product no	$\nu_{C=O}$ (cm^{-1})	Other (cm^{-1})	δ $-\overset{\vert}{C}H-X$ (ppm)	Other (ppm)
1b	1730	1540 ($-NO_2$) 1590 (aromatic)	5.30*	2.15 ($-SCH_3$) 2.84 ($-CHSR$) 7.40–8.00 (aromatic)
2	1710	1600 (aromatic) 1580	5.20	7.90 (*o*-aromatic) 7.35 (remaining aromatics)
3	1715	1600 (aromatic) 1525 ($-NO_2$)	5.30*	8.15 (aromatics)
4	–	2230 ($-C{\equiv}N$)	2.30 (?)†	–
5	–	1590 (aromatic)	4.35	8.15 (*o*-aromatic) 7.85 (remaining aromatics)
6, 7, 8	1755	–	5.05	–
9	–	1060 (ether)	3.48	4.50 ($Ph-CH_2-O-$) 7.28 (aromatics)

*Overlapping olefinic signal; †obscured by methylene/$-CH-SR$ envelope

five to ten-fold excess of the appropriate nucleophile (as its sodium salt) in concentrated aqueous solution. The mixture was stirred vigorously at room temperature overnight, diluted with water, stirred for a further 5–10 min, the layers separated, and the organic layer added to methanol. The precipitated product was dissolved in toluene, centrifuged to remove adhering salts, reprecipitated from methanol and freeze-dried from benzene. In this way, products 2–8 were prepared, the compositions being calculated from the elemental analyses.

When trichloroacetate was used as the nucleophile, a reaction time of 2 days was found to be preferable (products 7 and 8). With the benzyloxyanion as nucleophile (product 9) the following procedure was adopted. After treatment of the PBD with BSC, the Aliquat 336 was added, together with a ten-fold excess of benzyl alcohol and a concentrated aqueous solution of 7.5 equivalents of sodium hydroxide. Thereafter the normal procedure was followed.

Fractionation of product 6

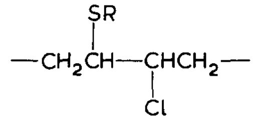
A sample of product 6 was weighed into a soxhlet thimble, then immersed in light petroleum (b.p. 60–80°) (100 ml) with the top of the thimble extending above the surface of the liquid. After extraction for 3 days at room temperature, the solvent was decanted into methanol (850 ml) cooled to −15°C. The resulting precipitate was collected on a weighed sintered glass crucible (porosity 3), and the procedure repeated until no more precipitate was obtained (7 times). The extract and residue (products 10a and 10b respectively) were dried to constant weight at room temperature, and their compositions calculated from their elemental analyses.

RESULTS AND DISCUSSION

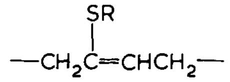
In contrast to the arylsulphenyl chlorides, MSC produced a precipitate immediately on contact with a toluene solution of PBD. When less than one equivalent of MSC was used, a second product could be isolated from the supernatant liquid, resembling unreacted PBD in appearance and texture. This suggested that a highly regioselective addition might be taking place to give a precipitate of highly modified polymer, leaving slightly modified and unreacted PBD in solution.

This precipitate was insoluble in toluene, benzene and chloroform, but was soluble in THF, dioxane, pyridine, DMF and methanol, suggesting a highly polar structure for the adduct, and this in turn suggested a high concentration of cyclic sulphonium ions II in the sequences of modified units. The extreme instability of the product was also consistent with cyclic sulphonium ion formation. The precipitate rapidly discoloured at room temperature with evolution of hydrogen chloride–behaviour reminiscent of the adducts of PIP with toluenesulphenyl chloride, which had been shown[4] to decompose *via* sulphonium ion I. When the precipitate was treated with excess lithium perchlorate in THF, a product was obtained that showed no tendency to decompose at room temperature, and which was soluble in acetonitrile but insoluble in THF, the reverse of the behaviour of the original product. The i.r. spectrum of this product (CH_3CN solution) showed a very strong, broad absorption at 1100 cm^{-1}. All these observations point to incorporation of perchlorate ion in the polymer and provide strong evidence for sulphonium ion formation. The extent of perchlorate ion incorporation was difficult to determine accurately, but on the basis of the n.m.r. spectrum, it must have been of the order of a few per cent. Apart from resonances at δ 2.15 ($-SCH_3$), 2.95 ($>CHSR$), and 4.30 ppm ($>CHCl$), a small peak at 3.15 ppm was attributable to $>\overset{+}{S}-CH_3$ (CD_3CN solution).

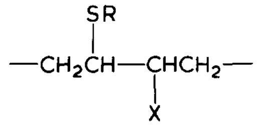
It was clearly desirable to perform elemental analyses on the two fractions obtained from the addition of MSC to PBD in order to compare their respective compositions. This was not feasible, however, in the case of the precipitate owing to its rapid decomposition. A possible solution to the problem lay in substituting the labile chlorine atoms with some other nucleophile, such as a carboxylate, in the hope of obtaining a stable polymer with a well-defined structure. Sodium 2-nitrobenzoate was available in the laboratory, and combined the advantage of solubility in DMF (a good solvent for the substrate polymer) with the presence of groups easily detected by i.r. and n.m.r. PBD was therefore treated with one half-equivalent of MSC and the supernatant liquid separated from the precipitate. Work-up of the former gave a soft, rubbery product (1a in *Table 1*). From the Cl and S content, the average composition of 1a as shown in *Table 1* was calculated, in terms of modified units III and IV, the latter arising through loss of HCl from the former[4]. The C and H contents (last column in *Table 1*) calculated for such a composition agree well with the experimental values.


$\text{—CH}_2\overset{\text{SR}}{\text{CH}}\text{—}\underset{\text{Cl}}{\text{CH}}\text{CH}_2\text{—}$

(III)


$\text{—CH}_2\overset{\text{SR}}{\text{C}}\text{=CHCH}_2\text{—}$

(IV)


$\text{—CH}_2\overset{\text{SR}}{\text{CH}}\text{—}\underset{\text{X}}{\text{CH}}\text{CH}_2\text{—}$

(V)

Meanwhile, the precipitate was treated with excess sodium 2-nitrobenzoate in DMF to yield a stable, white polymer (1b) soluble in chloroform and other non-polar solvents. No signal for >CHCl could be detected by n.m.r. in 1b but a strong signal for aromatic protons appeared at δ 7.4–8.0, and the i.r. spectrum showed strong peaks at 1730 and 1540 cm^{-1} for the ester carbonyl and nitro groups respectively. Elemental analysis confirmed the absence of chlorine in the product, and from the figures for N and S, the average composition was calculated in terms of IV and V as the modified units (X = 2-nitrobenzoyloxy). The results are shown in *Table 1* (entry 1b).

There is clearly a large difference in composition between the two products obtained from the reaction designed to give a polymer of 50% overall modification. Starting with 2.16 g (0.04 monomer mol) PBD, the yield of 1a was 1.79 g, corresponding to 0.026 monomer moles of polymer with the average composition given in *Table 1*. It follows from this that 64 mol % of the butadiene units had reacted with 31.5 mol % of the available MSC to give 1a and that 36 mol % had reacted with 68.5 mol % of the MSC to give 1b. The addition of MSC to PBD was thus shown to be highly susceptible to neighbouring group activation as depicted in equation (1) ($R = CH_3$).

The fact that a comparatively weak nucleophile such as 2-nitrobenzoate could substitute cleanly and efficiently for the labile chlorine in the MSC–PBD adduct suggested that a wide range of novel polymers and copolymers should be accessible by similar nucleophilic substitutions. However, before a general synthetic method could be developed on this basis, there remained to be solved the problem of bringing together the polymer substrate and ionic reagent in the same solvent. The method used in the preparation of 1b was inefficient and inconvenient; the precipitate obtained from MSC and PBD in toluene was invariably in the process of decomposition, and this apparently led to crosslinking, since the material was seldom fully soluble in any solvent, and residual gel generally had to be removed. Furthermore, such a method restricted the choice of nucleophiles to those soluble in THF or DMF, the best solvents for the unstable adduct.

A more promising approach was that of phase transfer catalysis using a quaternary ammonium salt, a technique which recently has found widespread use in organic chemistry[7–10]. The method is based on the ability of quaternary ammonium salts containing long alkyl chains to migrate between aqueous and organic phases, so that anionic reagents can be extracted into organic solvents. Equations (3)–(5) show the course of a typical phase transfer catalysed nucleophilic substitution, where QY is the catalyst, X^- the reagent, and RY the substrate, although it should be emphasized that the technique is by no means restricted to this type of reaction[7–10].

$$QY_{(aq)} + X^-_{(aq)} \rightleftharpoons QX_{(aq)} + Y^-_{(aq)} \qquad (3)$$

$$QX_{(aq)} \rightleftharpoons QX_{(org)} \qquad (4)$$

$$QX_{(org)} + RY \longrightarrow RX + QY_{(org)} \qquad (5)$$

In equation (3), the equilibrium is driven to the right when X^- is present in a large excess, while the equilibrium in equation (4) is driven to the right by a suitable choice of organic solvent. The reactivity of X^- in the organic phase is usually greatly enhanced by the lack of solvating water molecules and so the method often gives high yields under mild conditions[7–10].

Before applying the method to the present system, two changes in procedure were introduced. Firstly, chloroform was substituted for toluene as the solvent for the polydiene–sulphenyl chloride reaction as it is more suitable for the phase transfer catalysed reaction[8,10], and secondly, n-butanesulphenyl chloride (BSC) was substituted for the noxious, volatile and highly unstable MSC. BSC was prepared immediately prior to use by treatment of the theoretical quantity of n-butyl disulphide with an equimolar amount of sulphuryl chloride. Addition of BSC to PBD took place almost instantaneously at −15°C without production of a precipitate, although the solution tended to gel at high degrees of modification unless vigorous mechanical stirring was employed.

The resulting solutions of BSC–PBD adduct were treated immediately with aqueous solutions of a variety of nucleophiles under conditions of phase transfer catalysis (experimental section). The catalyst used was Aliquat 336, which is nominally 'tricaprylylmethylammonium chloride', but actually contains a mixture of C_8–C_{10} alkyl chains[7]. In this way, products 2–9 were prepared, and their compositions calculated from their elemental analyses in terms of III, IV and V as the modified units (*Table 1*).

The i.r. and n.m.r. spectra of the products (*Table 2*) support these structures, strong carbonyl absorptions appearing in the i.r. spectra where appropriate, and >CH–Cl signals being absent or barely detectable in the n.m.r. spectra. New signals for >CH–X appeared where predicted, and in addition to the peaks listed in *Table 2*, the following signals were recorded for each product: δ 0.85 ppm (methyl protons of butylthio groups), 1.1–2.8 ppm (envelope comprising remaining butylthio protons, backbone methylenes and >CH–SR protons) and 5.40 ppm (olefinic protons). The relative intensities of the methyl and olefinic signals were consistent with the proposed structures.

The data in *Table 1* reveal that the content of unreacted butadiene units ($-CH_2CH{=}CHCH_2-$) was generally greater than predicted from the amount of BSC used. This could be explained by incomplete conversion of n-butyl disulphide to BSC, or partial decomposition of the latter through contact with atmospheric moisture and residual solvent moisture. The figures in *Table 1* indicate that nucleophilic substitution of chlorine took place efficiently, although rather less so when trichloroacetate was the nucleophile (product 7). In this case, a combination of low nucleophilicity and steric hindrance produced a slower reaction, but an extended reaction time (product 8) gave better results. Apart from this example, no effort was made to optimize yields, and presumably the proportion of III ($-CH_2CHClCHSRCH_2-$) in the polymer could be reduced by employing more vigorous reaction conditions.

Varying amounts of structure IV ($-CH_2CH{=}CSRCH_2-$) were detected in the products (*Table 1*). In principle, these could arise both by spontaneous decomposition of the initial PBD–BSC adduct and by elimination of hydrogen chloride as a side reaction to nucleophilic substitution. However, for products 6–8 the best fit to the analytical data was obtained assuming no contribution from IV, which suggests that spontaneous decomposition was insignificant. Certainly the proportions of IV shown in *Table 1* follow the trend predicted by the 'Principle of Hard and Soft Acids and Bases'[11] for an elimination taking place in competition with a substitution[12], with the 'softest' bases, trichloroacetate and 4-nitrobenzoate giving least elimination, and the 'hardest' base, benzyloxide, giving the most.

In the reaction of PBD with MSC, a crude fractionation of the polymer mixture took place spontaneously as a result of the insolubility of one of the fractions in toluene. No such process occurred in the corresponding reaction with BSC in chloroform, and so it was of interest to carry out a fractionation of one of the substituted products to determine whether BSC was as selective as MSC in its addition to PBD. Accordingly, a 20% adduct of BSC with PBD was prepared, and treated with trichloroacetate ion in the usual way (product 6). A sample of the product was extracted exhaustively with light petroleum (experimental section) to yield an extract (product 10a) and a residue (10b) whose analytical data and calculated compositions are shown in *Table 1*. From 2.48 g product 6 (0.029 monomer mol) there was obtained 1.00 g product 10a (0.015 monomer mol), from which it was calculated that 52.8 mol% of the PBD had reacted with 20.6 mol% of the available BSC to give 10a and 47.2 mol% of the PBD with 79.4 mol% of the BSC to give 10b.

CONCLUSIONS

The alkylsulphenyl chlorides MSC and BSC were shown to react with PBD in a highly regioselective fashion, there being a strong tendency for saturation of successive double bonds along the polymer chain in accordance with equation (1) ($R = CH_3$, $n-C_4H_9$). The resulting adducts were extremely unstable towards decomposition *via* equation (2), so much so that the labile chlorine could be replaced smoothly under mild conditions by a variety of nucleophiles. The nucleophiles listed in *Table 1* were chosen merely to demonstrate the scope and limitations of the method, but in principle a large number of reagents could be employed, allowing a wide range of functional groups to be attached to the polymer backbone.

The technique used to carry out the nucleophilic substitutions appears to be novel in polymer chemistry. Roovers[13] used a crown ether to catalyse the acetolysis of chloromethylated polystyrene, but to the best of our knowledge, no example exists in the literature of such transformations being effected by the cheaper, more convenient quaternary ammonium salts.

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