Electron spin resonance studies of spin-labelled synthetic polymers: 13. Lithiation of copolymers of chloro- and bromostyrenes

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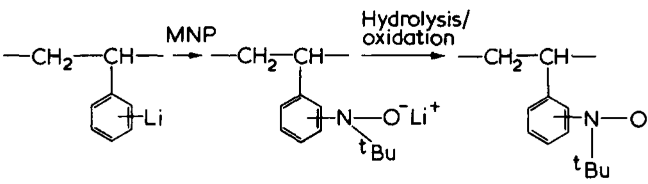
The products of the reaction between n-butyllithium, complexed with tetramethylethylenediamine or THF, and chloro- and bromostyrene copolymers were identified by trapping the lithiated sites with 2-methyl-2-nitrosopropane. From the e.s.r. spectra of the resulting nitroxide-labelled polymers it was concluded that bromostyrene units undergo direct lithium–bromine exchange. Styrene–bromostyrene copolymers are therefore useful precursors to labelled polystyrene. Chlorostyrene units, by contrast, react with butyllithium to yield intermediate benzynes to which another molecule of butyllithium adds. The product contains a mixture of lithiated sites, each carrying a n-butyl group *ortho* to the lithium atom; the resulting nitroxide-labelled polymers are unsuitable for dynamic studies. The observations on halogenated styrene copolymers were complemented by experiments on small model molecules.

INTRODUCTION

A convenient method of spin-labelling polystyrene in the aromatic ring with a nitroxide radical is to react the lithiated polymer with 2-methyl-2-nitrosopropane (MNP[1]). The resulting lithium salt of the hydroxylamine is readily hydrolysed and oxidized to the t-butyl nitroxide:



If the lithiation step can be controlled the point of attachment of the nitroxide group is unambiguously defined. This synthesis has been utilized to prepare polystyrene labelled in the *para*- and *meta*-positions[1,2]. For the former, the polymer was first iodinated in the *para*-position and the iodine was then exchanged for lithium by reaction with n-butyllithium (BuLi) under fairly mild conditions. For the latter, direct lithiation of the polymer with BuLi complexed with tetramethylethylenediamine (TMEDA) was employed. The iodine–lithium exchange was uncomplicated by scission or cross-linking reactions and the products were very suitable for subsequent dynamic studies. Direct lithiation, on the other hand, always gave a small proportion of gel, indicating a crosslinking side reaction which makes this route to the *meta*-labelled polymer decidedly unattractive[2]. Furthermore, there is always a risk that if the direct reaction is carried out under prolonged or forcing conditions some lithiation may occur at other points on the aromatic ring, thus leading to impure products unsuitable for dynamic studies. These difficulties led us to investigate whether the lithium–halogen exchange reaction, which was successful with *para*-iodinated polystyrene, could be extended to polystyrenes containing comonomer units with chlorine or bromine atoms in the aromatic ring, particularly in the *meta*-positions. An attractive feature of this approach was that halogenated styrenes are readily available and can be incorporated in small, controlled amounts into polystyrene by radical copolymerization. Some optimism was engendered by a report that a butadiene–*ortho*-chlorostyrene copolymer was lithiated cleanly in a lithium–halogen exchange with BuLi/TMEDA[3].

EXPERIMENTAL

Materials

The monomers styrene, *meta*- and *para*-chlorostyrene, *meta*- and *para*-bromostyrene were purified by fractional distillation under reduced pressure of nitrogen.

The solvents benzene, toluene and cyclohexane were sodium dried and distilled. THF was purified as described previously[1].

TMEDA was purified by fractional distillation.

Butyllithium was prepared as before[1]. Benzyllithium solution, prepared by reaction of lithium metal on benzyl ethyl ether in a THF/ether solution[4], was used immediately.

Copolymers

Copolymers of styrene containing ~2% halogenated styrene were prepared as follows. Dry, degassed styrene (40g) and halo-styrene (0.7g) were distilled into a dilatometer containing benzoyl peroxide (1.9g). Polymerization was allow-

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ed to proceed to ~10% conversion at 60°C. The copolymers were purified by repeated precipitation from chloroform solution in methanol and were dried at room temperature under vacuum.

Lithiation and labelling reactions

The procedures for lithiating and labelling the copolymers with BuLi, BuLi/TMEDA and benzyllithium were essentially as described for the direct lithiation reaction[2]. Similar reactions were also conducted on the model compounds *para*-t-butylchlorobenzene and *para*-t-butylbromobenzene. The procedure was as follows. To a 250 ml, 3-necked flask fitted with a sealed stirrer, nitrogen inlet and septum cap, were added benzene (100 ml), n-BuLi (80 ml of 1 M solution in n-hexane) and TMEDA (12 ml). To this stirred mixture was then added slowly *para*-t-butylchlorobenzene (6.7g) or *para*-t-butyl bromobenzene (8.5 g). The reaction mixture warmed spontaneously and stirring was continued for 1 h when MNP (5 g) in benzene (200 ml) was added by syringe. The resulting solution was stirred for 10 min then the solvent was evaporated leaving a red oil which was dissolved in benzene (10 ml) and shaken for 10 min with silver oxide. After removal of the benzene by evaporation, the residue was chromatographed on a silica gel column. With benzene as eluant, a red oil (5.2 g from *para*-t-butylchlorobenzene, 6.2 g from *para*-t-butylbromobenzene) containing an aryl nitroxide and some starting material, was obtained. On changing the eluant to chloroform another red-oil fraction containing a dialkyl nitroxide was obtained.

Model nitroxides

The two model nitroxides: 2,5-t-butylphenyl t-butyl nitroxide and 2,5-di-n-butylphenyl t-butyl nitroxide, were prepared via a Grignard reaction from the corresponding 2,5-dibutylbromobenzene. Magnesium turnings (0.18 g), dry THF (30 ml) and the 2,5-dibutylbromobenzene (2 g) were heated under reflux in a nitrogen atmosphere for 1 h by which time all the magnesium had reacted. MNP (1 g) in THF (10 ml) was added and the mixture stirred for 10 min when 20 ml of water was added. The resulting suspension was extracted with dichloromethane (4 x 50 ml). The extracts were combined, dried and the solvent evaporated, leaving a red oil which was dissolved in a few millilitres of benzene and shaken with silver oxide for 10 min. The oxidized product was purified by chromatography on silica gel with benzene as eluant from which the product, 2,5-dibutylphenyl t-butyl nitroxide was obtained as red crystals (yield ~73%).

Analysis. $C_{18}H_{30}NO$ requires C 78.2, H 10.9, N 5.0; found: 2,5-di-t-butylphenyl t-butyl nitroxide (m.p. 76°C): C 78.2, H 11.1, N 4.8; 2,5-di-n-butylphenyl t-butyl nitroxide (m.p. 63°C): C 78.5, H 11.2, N 4.8.

E.s.r. spectral data. 2,5-Di-t-butylphenyl t-butyl nitroxide: a_N, 40.47 ± 0.20 MHz; g_{iso}, 2.00586 ± 0.00004 (*Figure 7*). 2,5-Di-n-butylphenyl t-butyl nitroxide: a_N, 39.42 ± 0.19 MHz; g_{iso}, 2.00584 ± 0.00004 (*Figure 6*).

E.s.r. measurements

Spectra were recorded at room temperature or 60°C as described previously[1]. Toluene was used as solvent and e.s.r. tubes were 3 mm i.d. pyrex. For polymers the concentration was 5% w/v and for small molecule nitroxides $\sim 10^{-3}$M.

RESULTS AND DISCUSSION

If straightforward lithium–halogen exchange occurs when the *para*- or *meta*-halostyrene copolymers are treated with BuLi, then subsequent reaction with MNP, followed by hydrolysis and oxidation should yield a polymer labelled with a t-butyl nitroxide group in the *para*- or *meta*- position respectively. The e.s.r. spectra of polymers labelled in these positions are shown in Figures 1 of refs 1 and 2, respectively. These may be regarded as reference spectra in the discussion that follows.

Table 1 summarizes the essential details of the reactions investigated together with a description of the e.s.r. spectra and the spectral parameters of the products.

Table 1 Characteristics of e.s.r. spectra of products trapped with MNP after reaction of organolithium compounds with styrene–bromostyrene, styrene–chlorostyrene copolymers and small model compounds

Reaction conditions			E.s.r. spectral characteristics				
Organolithium compound	Polymer or model reactant	Solvent	No. of lines in e.s.r. spectrum	Figure	a_N (MHz)	a_H[*] (MHz)	g (±0.00004)
n-BuLi/TMEDA	*m*-Bromostyrene copolymer	Benzene	3 X 8	1	35.6 ± 0.3	$a_o = a_p = 5.0$ $a_m = 2.5$	2.00589
n-BuLi/TMEDA	*p*-Bromostyrene copolymer	Benzene	3 X 7	2	35.4 ± 0.25	$a_o = 5.56$ $a_m = 2.48$	2.00577
n-BuLi	*m*-Bromostyrene copolymer	Benzene	Complex spectrum	3	–	–	–
n-BuLi/TMEDA	*p*-Chlorostyrene copolymer	Benzene	3	4	39.69 ± 0.25	–	2.00586
n-BuLi/TMEDA	*m*-Chlorostyrene copolymer	Benzene	3 (small split in centre line)	5	39.70 ± 0.20	–	2.00585
n-BuLi/TMEDA	*m*-Chlorostyrene copolymer	Cyclohexane	3 (small split in centre line)	–	39.62 ± 0.22	–	2.00582
n-BuLi	*m*-Chlorostyrene copolymer	THF	3 (small split centre line)	–	39.66 ± 0.22	–	2.00586
n-BuLi/TMEDA	*Para*-t-butylbromobenzene	Benzene	3 X 7	8	34.98 ± 0.27	$a_o = 6.02 \pm 0.18$ $a_m = 2.66 \pm 0.16$	–
n-BuLi/TMEDA	*Para*-t-butylchlorobenzene	Benzene	6	9	39.48 ± 0.22[‡]	–	–
n-BuLi/TMEDA	*m*-Chlorostyrene copolymer	Toluene	6	10	41.56 ± 0.22	9.25 ± 0.16	2.00581
Deutero-BuLi/TMEDA[†]	*m*-Chlorostyrene copolymer	Toluene	6	–	41.54 ± 0.21	9.23 ± 0.18	2.00582
Benzyl Li/TMEDA	*m*-Chlorostyrene copolymer	Benzene	6	–	41.52 ± 0.21	9.21 ± 0.21	2.00584

[*] a_o, a_m and a_p refer to protons in positions *ortho, meta* and *para* respectively to the nitroxide group. [†] $CH_3(CH_2)_2CD_2Li$. [‡] For the more abundant nitroxide.

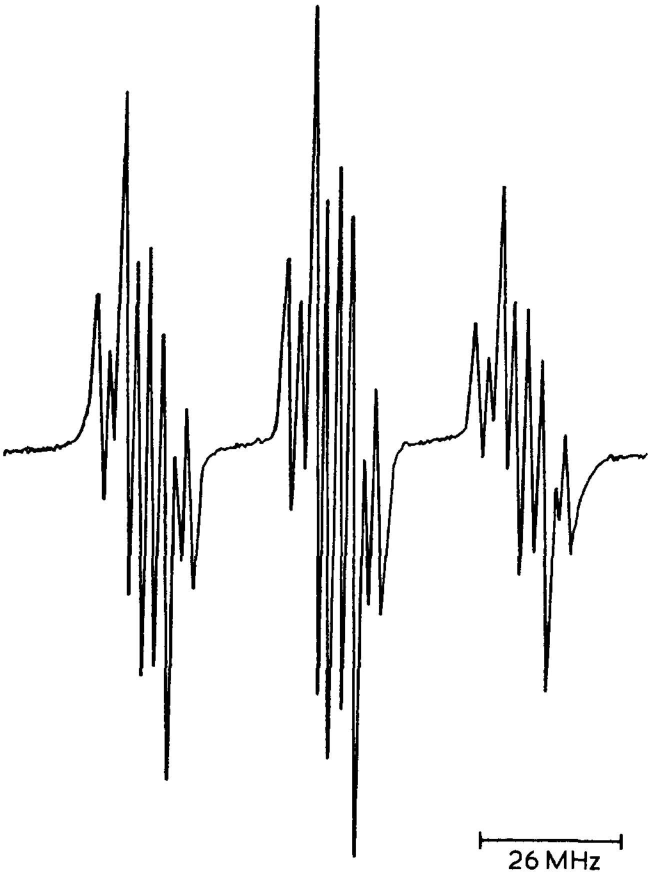


Figure 1 E.s.r. spectrum (at 60°C) of labelled polymer from *m*-bromostyrene copolymer after reaction with BuLi/TMEDA and MNP in benzene solution

Labelling of styrene–bromostyrene copolymers

The e.s.r. spectrum of the product when the *meta*-bromostyrene copolymer is subjected to the labelling routine (BuLi/TMEDA in benzene, addition of MNP, hydrolysis and oxidation) is shown in *Figure 1* which is identical with Figure 1 of ref 2, i.e. each nitrogen line is split into eight hyperfine lines in the intensity ratio 1:1:3:3:3:3:1:1 because of interaction of the unpaired electron with aromatic protons. Similarly the spectrum of the product from the *para*-bromo precursor, *Figure 2,* is identical with that of the *para*-labelled polymer in Figure 1 of ref 1. It is clear that with both isomers, bromine–lithium exchange occurs readily under the reaction conditions and there is no evidence from the e.s.r. spectra of the presence of contaminating nitroxides from side reactions at other points in the polymer molecule. Polymers containing aromatic bromine atoms can therefore be used as satisfactorily as their iodinated counterparts for preparing nitroxide-labelled derivatives. No crosslinking appears to occur during this procedure which is therefore a more satisfactory route to *meta*-labelled polystyrene than direct metallation described previously[2]. We note, however, that the BuLi must be complexed with TMEDA in order to effect a clean lithium–halogen exchange. If the TMEDA is omitted from the reaction routine the spectrum of the labelled polymer, as typified by *Figure 3,* is complicated and appears to arise from a mixture of products. This behaviour contrasts with that of *para*-iodostyrene units which are sufficiently reactive to exchange with BuLi in its uncomplexed, less basic form[1].

Labelling of styrene–chlorostyrene copolymers

The application of the labelling routine to the chlorostyrene copolymers did not yield the *meta*- or *para*-labelled products under any of the conditions tried here. With BuLi/TMEDA in benzene the spectra of the products from the *para*-chlorostyrene and *meta*-chlorostyrene copolymers are shown in *Figures 4* and *5* respectively. Both spectra consist essentially of three lines with no hint of proton hyperfine structure, although the spectrum of the polymer from the *meta*-chloro isomer shows some splitting of the centre line. BuLi/TMEDA in cyclohexane or BuLi in THF (in which the solvent also functions as a complexing agent) yielded products with the same type of spectra (see *Table 1*). When the spectrum of the labelled polymer from the *meta*-chlorostyrene copolymer was recorded at 60°C the small asymmetric splitting of the centre line disappeared, but reappeared on cooling to ambient temperature. This behaviour is inconsistent with proton hyperfine interaction which normally shows improved resolution, because of line-width narrowing, as the temperature is raised. The asymmetric centre-line splitting is there-

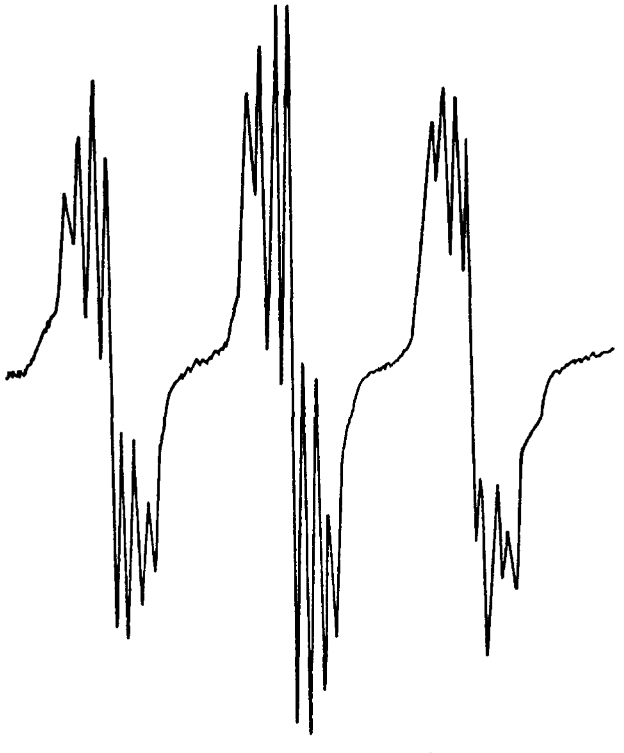


Figure 2 As for *Figure 1* but with *p*-bromostyrene copolymer

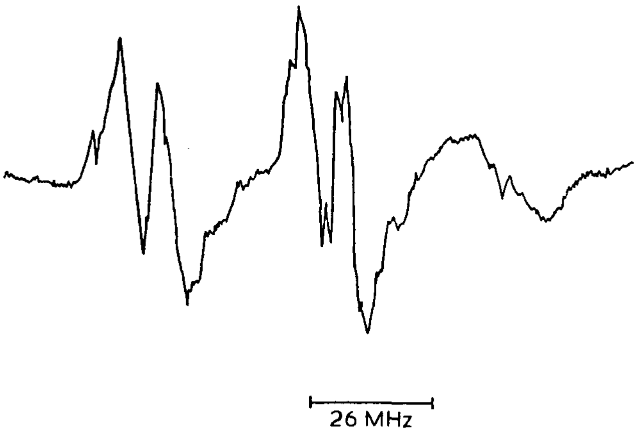


Figure 3 E.s.r. spectrum of labelled polymer from *m*-bromostyrene copolymer after reaction with BuLi and MNP in benzene solution

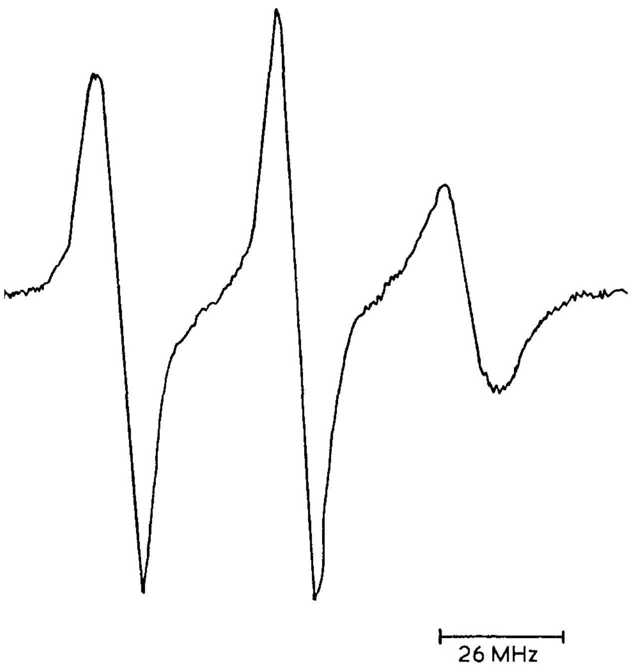
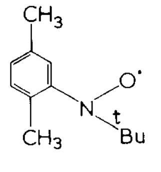


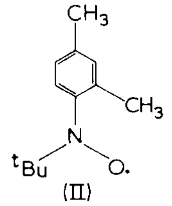
Figure 4 E.s.r. spectrum of labelled polymer from *p*-chlorostyrene copolymer after reaction with BuLi/TMEDA and MNP in benzene solution

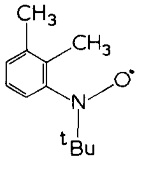
fore more likely to be due to the presence of two or more nitroxides, with slightly different *g*-values, in the reaction products. This splitting is not observed in the outer lines of the spectrum because of the greater line-width associated with $m_N = \pm 1$.

The a_N- and *g*- values of the spectra in *Figures 4* and *5* are identical indicating that the nitroxides are structurally similar. Significantly, this a_N value (~39.7 MHz) is rather high for an alkylaryl nitroxide in which the nitroxide group is in conjugation with the aromatic ring but is very close to the value for alkylaryl nitroxides in which rotation of the nitroxide group is hindered by an adjacent substituent on the aromatic ring (see later). It is rather low, however, to be a_N of a of a dialkyl nitroxide (usually ~42 MHz). The chlorine content of these copolymers is reduced by about 20% on reaction with BuLi and clearly these sites are involved in the lithiation reaction but this cannot occur by direct lithium–chlorine exchange, otherwise the spectra of the labelled polymers would show aromatic proton hyperfine structure as in *Figures 1* and *2*.

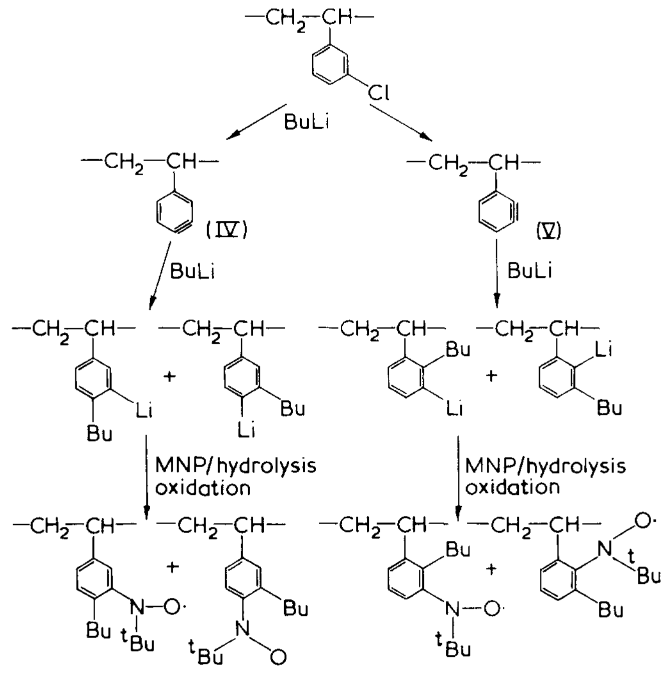
The above observations lead us to the conclusion that the labelled polymers derived from the chlorostyrene copolymers have the nitroxide groups on the styryl rings but that the unpaired electron is unable to couple significantly with the aromatic protons. This situation will arise if the nitroxide group on the aromatic ring is adjacent to another substituent which forces the nitrogen $2p\pi$ orbital out of conjugation with the ring. Thus, the dimethylphenyl t-butyl nitroxides below show very small aromatic proton hyperfine splittings in their e.s.r. spectra[5].


(I)


(II)


(III)

Structures similar to those above could be formed on the chlorostyrene units by the reaction sequence (1):



(1)

The important intermediates in this reaction scheme are the benzynes IV and V of which IV is likely to be produced in greater abundance because the proton in the *para*-position of the styryl ring is more acidic than the *ortho*-proton; furthermore the *ortho*-proton is in a sterically protected position. We would therefore expect nitroxides VII and VIII to be more abundant than IX and X. In VII, VIII and IX the t-butyl nitroxide group is adjacent to a n-butyl group on the aromatic ring. The steric effects on the nitroxide group are therefore likely to be very similar and the a_N- and *g*-values for these three isomers should also be similar. An analogous situation prevails with the

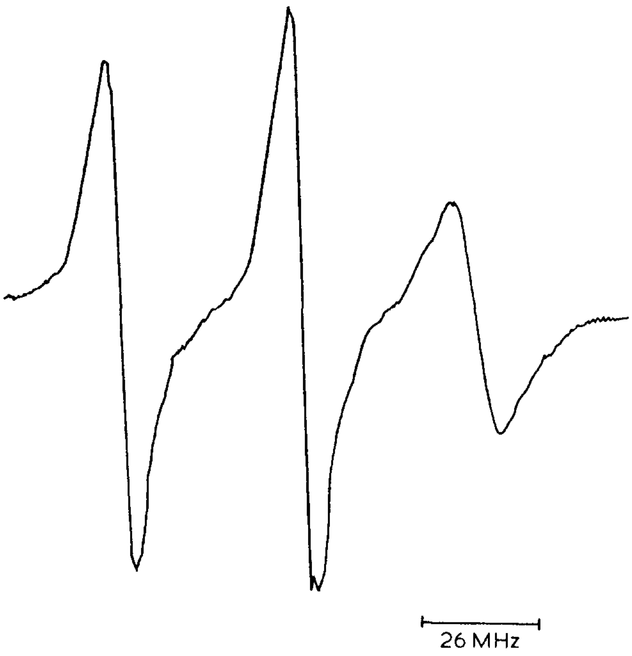


Figure 5 As for *Figure 4*, but with *m*-chlorostyrene copolymer

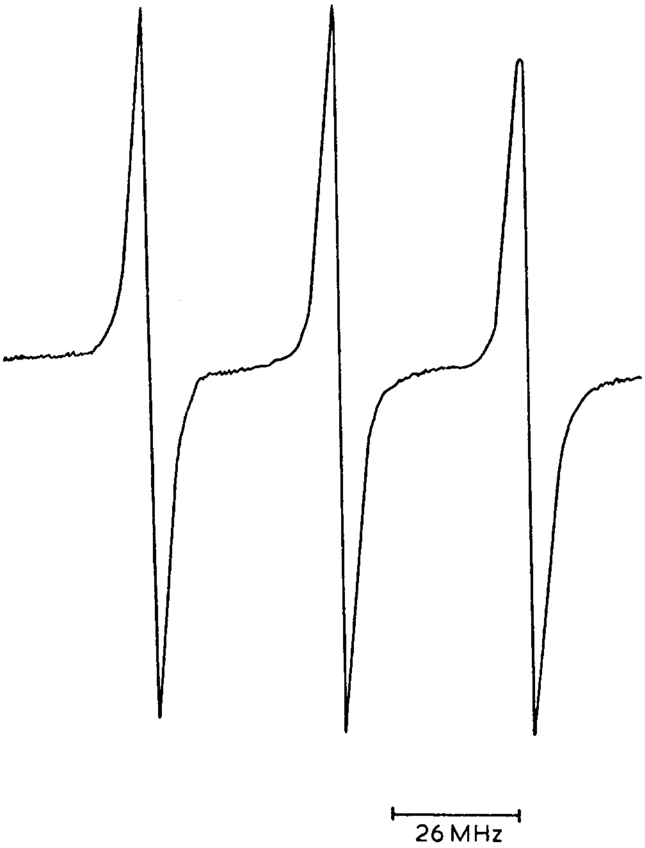


Figure 6 E.s.r. spectrum of 2,5-di-n-butylphenyl t-butyl nitroxide

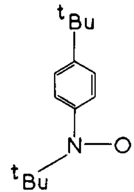
three dimethylphenyl nitroxides I, II, and III, the a_N values of which are almost identical[5]. In structure X by contrast, the nitroxide group is flanked on one side by a n-butyl group and on the other by the bulky polymer chain. The steric influences in this case are therefore much stronger than in VII, VIII and IX and it is reasonable to expect rather different g- and a_N- values for X. These differences could account for the small asymmetric centre-line splitting in the spectrum of the product from the *meta*-chlorostyrene copolymer (*Figure 5*) and for the simpler three-line spectrum of the product from the *para*-chlorostyrene copolymer (*Figure 4*) which, on the basis of the above scheme, can yield only VII and VIII.

The intermediate formation of benzynes in reactions between halobenzenes and strong bases is well documented[6]. For example, reaction of phenyllithium/TMEDA with chlorobenzene appears to go exclusively via a benzyne which reacts with another molecule of phenyllithium to form the biphenyl[7]. It has also been shown that BuLi reacts with benzyne to form *ortho*-lithiumbutylbenzene[8]. There is, therefore, ample evidence from the established chemistry of small molecule species to validate the above reaction sequence.

The hypothesis, that the products from chlorostyrene copolymers are labelled as in VII, VIII, IX or X, is supported by the spectral characteristics of the model 2,5-dibutylphenyl t-butyl nitroxides. The 2,5-di-n-butyl isomer may be regarded as a model for VII. Its e.s.r. spectrum (*Figure 6*) consists of three lines with no hyperfine structure and the a_N value, 39.42 MHz, is equal within the combined experimental errors to that of the labelled polymer. For 2,5-di-t-butylphenyl t-butyl nitroxide (spectrum in *Figure 7*) a_N is 40.74 MHz; again proton hyperfine structure is absent. These two a_N values, together with that of the dimethylphenyl nitroxide II (37.9 MHz), illustrate the effects of steric bulk of substituents *ortho* to the nitroxide group on an aromatic ring. An increase in a_N reflects a decrease in delocalization of the unpaired electron in the aromatic ring. Thus, the tendency to force the nitrogen $2p\pi$ orbital out of conjugation with the aromatic ring increases in the order methyl < n-butyl < t-butyl.

Labelling reactions on model compounds

Para-t-butylbromobenzene is a small molecule model for the *para*-bromostyrene copolymer. The e.s.r. spectrum of the aromatic nitroxide isolated after subjecting this model to the usual labelling routine is shown in *Figure 8*. The spectrum consists of three lines typical of a nitroxide; each line has a well resolved proton hyperfine structure of seven lines in the intensity ratio 1:2:3:4:3:2:1 which is consistent with the structure XI:



(XI)

The values of the coupling constants from *Figure 8* (see *Table 1*) correspond closely with published data for XI[9] which are a_N = 34.7 MHz, a_{ortho} = 6.18 MHz, a_{meta} = 2.8 MHz. There can be little doubt that XI is the product when *para*-t-butylbromobenzene is subjected to the labelling routine. This substantiates the observations on the same reaction as carried out on bromostyrene copolymers and confirms that straightforward bromine–lithium exchange occurs under the reaction conditions.

With *para*-t-butylchlorobenzene as starting material, the e.s.r. spectrum of the aromatic nitroxide product is shown

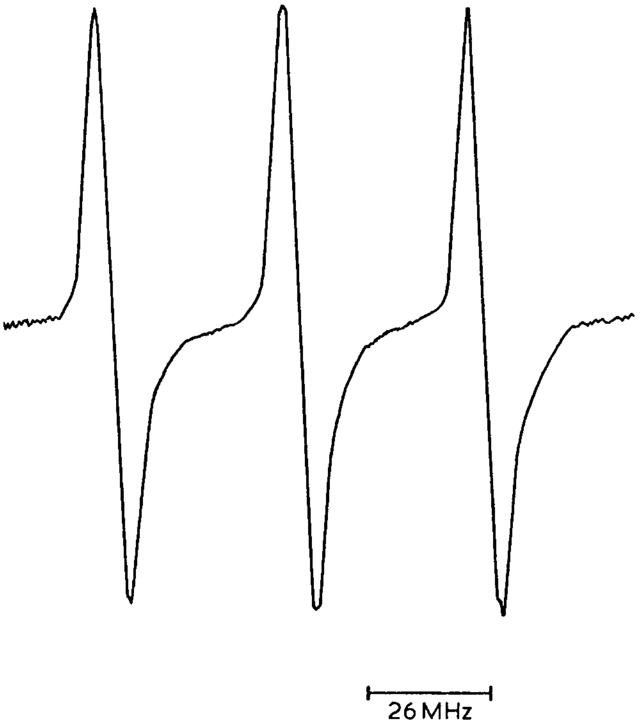


Figure 7 E.s.r. spectrum of 2,5-di-t-butylphenyl t-butyl nitroxide

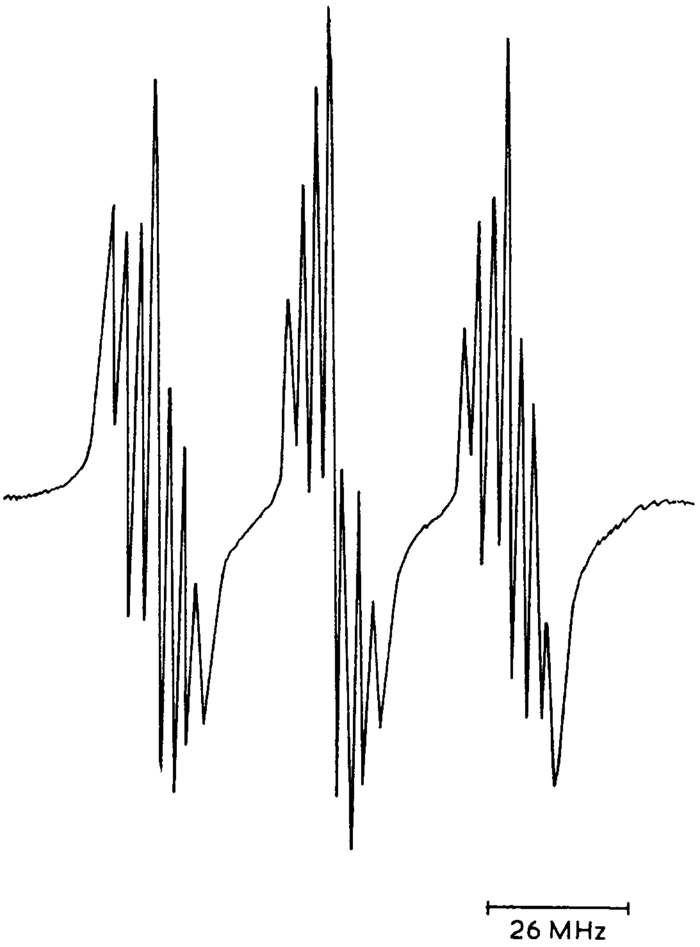
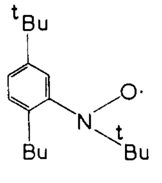
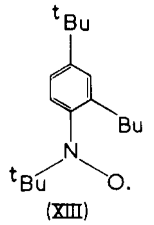


Figure 8 E.s.r. spectrum of nitroxide formed on reaction of *para*-t-butylbromobenzene with BuLi/TMEDA and MNP in benzene solution

in *Figure 9*. This product is definitely not XI. In fact it appears to consist of a mixture of two products each with a three-line e.s.r. spectrum and showing no proton hyperfine structure. The more abundant nitroxide has a_N = 39.48 ± 0.22 MHz which equals, within experimental error, the a_N value of the labelled products from the chlorostyrene copolymers. If this nitroxide is formed via a benzyne intermediate as postulated for the polymer, then it should be a mixture of XII and XIII:


(XII)


(XIII)

These two nitroxides should have virtually identical a_N values (as do the dimethylphenyl nitroxides I, II and III) and, since the original t-butyl group on the benzene ring is too far removed to influence the nitroxide, this a_N value should be very close to that of 2,5-di-n-butylphenyl t-butyl nitroxide. This is in fact the case, and it is safe to conclude that XII and/or XIII are major products of the reaction sequence. The other nitroxide spectrum in *Figure 9* has a_N = 41.13 MHz, which is rather high for an alkylaryl nitroxide. It is probably due to contamination by a dialkyl nitroxide formed when MNP reacts with the excess BuLi.

These results from model compounds accord well with those from the copolymers. They underline the contrasting behaviour of aromatic chlorine and bromine in reactions with complexed BuLi, and provide additional strong evidence that one or more benzyne intermediates are formed when chlorostyrene units are reacted with BuLi/TMEDA.

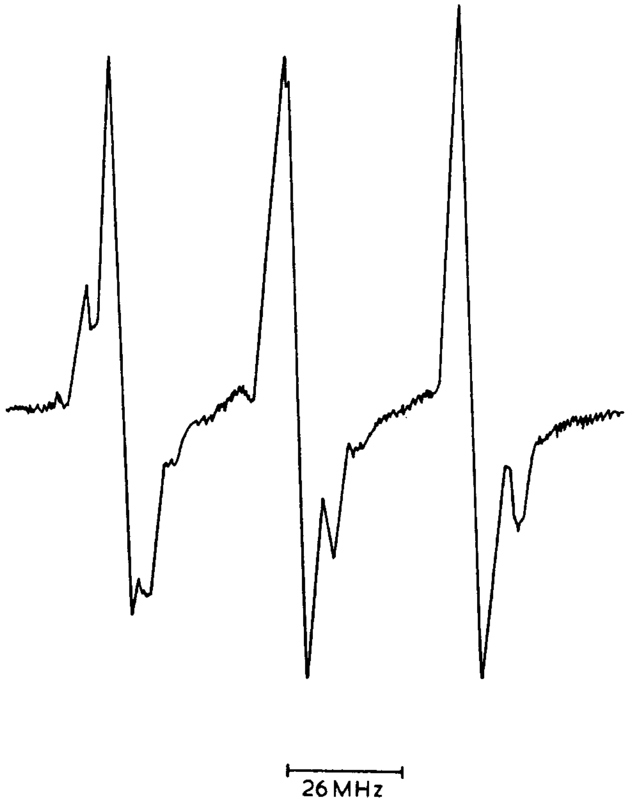


Figure 9 As for *Figure 8*, but with *para*-t-butylchlorobenzene

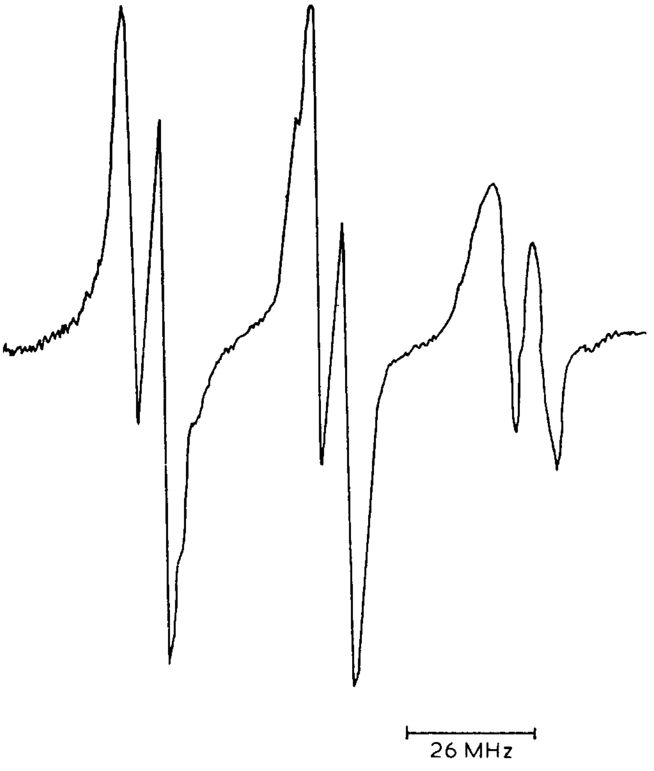
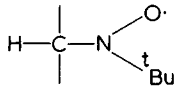


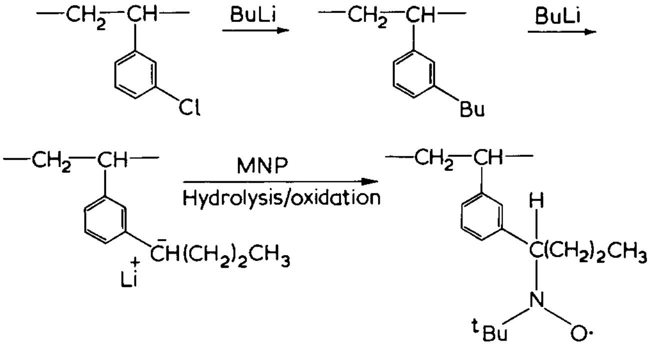
Figure 10 E.s.r. spectrum of labelled polymer from *m*-chlorostyrene copolymer after reaction with BuLi/TMEDA and MNP in toluene solution

Labelling of m-*chlorostyrene copolymers in toluene solution*

Toluene was also tried as a solvent in the metallation reaction of *meta*-chlorostyrene copolymers with BuLi/TMEDA. The e.s.r. spectrum of the resulting spin-labelled polymer is shown in *Figure 10*. The a_N-value from this spectrum, 41.56 MHz, together with the doublet splitting of the three nitroxide lines indicates that the product is aliphatic with the structure:



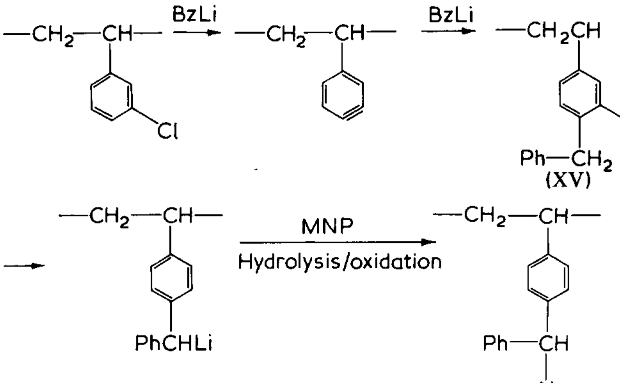
Initially it was thought that this structure could arise via replacement of the Cl atom by a n-butyl group and subsequent attack on this group by BuLi in a similar manner to the side reaction that occurs during end-labelling of poly(methyl methacrylate)[10]:



(XIV)

As has been discussed previously[10], substitution of the proton β to the nitroxide with a deuteron should convert the six-line to a three-line spectrum. However, replacement of BuLi by deuterated BuLi $[CH_3(CH_2)_2CD_2Li]$ yielded a product with a six-line spectrum identical to that in *Figure 10* (see *Table 1*). Evidently structure XIV cannot account for this spectrum.

It is known that toluene reacts rapidly with BuLi to yield benzyllithium[11]. If we assume that benzyllithium is the reactive agent in these experiments then the appearance of the six-line spectrum can be accounted for on the basis of benzylation via intermediate benzyne formation as before:



(XV) (2) (XVI) (XVII)

Scheme (2) differs from (1) in that the aromatic lithium derivative XV rearranges rapidly to the benzylic lithium substituent XVI before reaction with MNP. This is quite reasonable on energetic grounds and leads to the nitroxide XVII which has the required structure to give a six-line e.s.r. spectrum. In scheme (2) only benzylation in the *para*-position has been shown; *meta*- and *ortho*- substitutions are also possible although the latter is unlikely for steric reasons. The e.s.r. spectra of the *meta*- and *para*-isomers should be very similar. To check the feasibility of this reaction benzyllithium/TMEDA in benzene solution was employed as lithiating agent in the labelling procedure. The product had as e.s.r. spectrum identical to *Figure 10* (see *Table 1*). This result virtually proves that benzylation occurs with BuLi/TMEDA in toluene solution, although there is insufficient evidence available at present to define the position of substitution.

CONCLUSIONS

Lithium–halogen exchange between BuLi/TMEDA and the bromine atoms on *para*- and *meta*-bromostyrene units proceeds without detectable interference from side reactions, and provides a convenient route for preparing polystyrene labelled with t-butyl nitroxide groups. This is a particularly useful method for preparing *meta*-labelled polystyrene as it is uncomplicated by crosslinking.

Copolymers of *para*- and *meta*-chlorostyrene are unsuitable starting materials for preparing labelled polystyrene. Lithiation does occur but the final product almost certainly contains more than one type of labelled styrene unit in which the nitroxide group lies *ortho* to a n-butyl group.

The ease with which lithium–halogen exchange takes place on the aromatic styryl ring increases in the order Cl < Br < I. This is the order of decreasing electronegativity of the halogens.

In the preparation of lithiated polystyrene as a reactive precursor for grafting or similar preparations, *para*-bromostyrene copolymers are probably the most convenient starting materials, first because they can be lithiated cleanly and second because the *para*-position on the styryl ring is the most accessible point for the second stage of the preparation. Lithiated polymers can be prepared from chlorostyrene precursors but, as stated above, a mixture of lithiated products, each carrying a n-butyl group *ortho* to the lithium atom, is formed.

The experiments described in this paper illustrate again the potential value of MNP as a trap for identifying metallated sites or carbanions on organic molecules.

The comparison between reactions on the small-molecule models and on the polymers indicates that polymeric substrates may have advantages in testing certain organic reactions. Repeated dissolution/precipitation readily separates the reacted polymer from low molecular weight impurities formed in side reactions. When the species under test is a small molecule, however, both the product of interest and those produced in side reactions may be similar in nature and the separation procedure could be difficult and tedious.

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