# Functionalization of Polystyrene Resins by Chemical Modification: Characterization of Halogenated Polystyrenes by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: The halogenation of polystyrene using ferric chloride and thallic acetate as catalysts for the bromination, and thallic trifluoroacetate with iodine in stoichiometric amounts for the iodination, has been studied by $^{13}$C-NMR spectroscopy using standard polymers obtained by polymerization of *o*-, *m*-, and *p*-bromostyrene. In all cases, the halogenated polymers were found to be substituted exclusively in the para position. Similarly, a brominated polymer prepared by reaction of polystyrene with *n*-butyllithium–TMEDA complex followed by bromine quenching was found to be substituted exclusively in the para position, while a similar lithiation followed by quenching with methyl iodide gave a methylated polymer substituted both in the meta and para positions in a 2:1 ratio. Lithiations carried out with *tert*-butyllithium–TMEDA resulted in higher degrees of functionalization than those carried out with *n*-butyllithium–TMEDA.

In a previous communication from this laboratory,[1] we reported on several useful procedures for the bromination and lithiation of cross-linked polystyrene. A problem which is always encountered when working with cross-linked polymers is the difficult characterization of the products after reaction, since a number of analytical methods are not well suited for the study of insoluble materials. In particular, it is difficult to evaluate the aromatic substitution pattern in a reaction such as the bromination of cross-linked polystyrene. Since it is reasonable to expect that cross-linked polymers with a low degree of cross-linking will react in a fashion similar to their soluble counterparts, we decided to study the halogenation of soluble polystyrene to determine the position of substitution by $^{13}$C-NMR spectroscopy.

Among the procedures which have been used for the bromination of polystyrene resins,[2] three have received most attention: the catalytic bromination with ferric chloride as catalyst,[3] the thallation–bromination procedure involving a stoichiometric amount of thallic acetate,[4,5] and the thallium(III)-catalyzed bromination reaction[1] which we developed. Although the ferric chloride catalyzed reaction has been used successfully in a number of instances, its use leads to a product which is less satisfactory than that obtained by the two other procedures.[1,6] The thallation–bromination procedure gives excellent results, but the method is very costly and removal of the thallium salts from the brominated polymer may be a tedious and difficult operation. In contrast, the thallium(III)-catalyzed bromination offers the advantage of simplicity, as was the case with the ferric chloride catalyzed reaction, and of cleanliness and homogeneity of the brominated polymer as was the case with the thallation–bromination.

All three methods yield polymers which have not been fully characterized and for which the exact position of substitution on the aromatic rings is not known. The present study involves the preparation of brominated and iodinated polystyrene by chemical modification of soluble polystyrene and the study of the position of aromatic substitution by NMR spectroscopy using authentic samples of *o*-, *m*-, and *p*-bromopolystyrene for comparison. The position of substitution in the case of the iodination reaction will be ascertained by comparison of the chemical shifts with those obtained by calculation.[7]

## Results and Discussion

Polymer standards were prepared by free-radical polymerization of *o*-bromostyrene, *m*-bromostyrene, and *p*-bromostyrene, respectively. The polymers were then studied by $^{13}$C-NMR spectroscopy. The effects of the position of substitution of bromine on the chemical shifts of the various carbon atoms of the aromatic rings of polystyrene were measured (Table I). These were found to be generally consistent with the chemical shifts calculated using data available for bromine-substituted benzenes.[7]

Soluble polystyrene resins of molecular weight 20 000 were brominated using two different procedures: with ferric chloride catalyst, and with thallium triacetate as catalyst. In both cases the reaction conditions were chosen to yield partially brominated polymers with degrees of functionalization comparable to those of cross-linked polystyrene resins commonly used in solid-phase reactions. The $^{13}$C-NMR spectra of the polymers prepared by these methods contained both lines corresponding to the unsubstituted styrene residues and lines for the brominated rings (Table II). The spectra of the polymers prepared by the two methods were very similar, with differences in line intensities resulting from the different degrees of functionalization of the polymers. In both cases, however, only signals corresponding to para substitution were observed indicating that both catalytic brominations yield para-substituted polystyrene. A typical spectrum is shown in Figure 1.

We have also studied the iodination of soluble polystyrene using a method similar to that which was used in the case of the cross-linked polymer.[1] The reaction involves the use of a stoichiometric amount of thallic trifluoroacetate. Unlike the bromination reaction this process cannot be made catalytic as thallous iodide is formed during the reaction. The reaction is therefore very costly and of little practical value since, when applied to cross-linked resins, removal of the thallous iodide from the solid polymer is a very difficult process. The $^{13}$C-NMR spectrum of the iodinated polymer showed exclusively para substitution, a result which was expected in view of the results which have been obtained in the thallation–halogenation of various aromatic compounds.[8]

In an attempt to prepare polymers brominated in the meta position a third bromination procedure was studied. It involved the direct lithiation of polystyrene using the *n*-butyllithium–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) complex followed by quenching with an excess of bromine in the dark. Using this method a partially brominated polymer containing 3.72 mequiv of Br/g, for a degree of functionalization of 0.55, was obtained.[9] The

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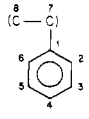
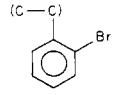
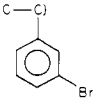
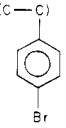
Table I
Chemical Shifts in $^{13}$C-NMR Spectra of Polystyrene and Standard *o*-, *m*-, and *p*-Bromopolystyrenes

| carbon atom no. | polystyrene | *o*-bromopolystyrene | *m*-bromopolystyrene | *p*-bromopolystyrene |
|---|---|---|---|---|
| |  |  |  |  |
| 1 | 145.3 | 143.6 | 146.9, 146.6 | 143.3 |
| 2 | 128.0-127.8[a] | 132.7 | 130.0, 129.5 | 129.4 |
| 3 | 128.0-127.8[a] | 127.4 | 122.4 | 131.4 |
| 4 | 125.7 | 127.4 | 130.0, 129.5 | 119.8 |
| 5 | 128.0-127.8[a] | 125.5 | 130.0, 129.5 | 131.4 |
| 6 | 128.0-127.8[a] | 127.4 | 126.2 | 129.4 |
| 7 | 42.4-45.5[a] | 41.1-45.2[a] | 41.8-44.9[a] | 41.0-44.3[a] |
| 8 | 40.7 | 38.4 | 40.5 | 40.3 |

[a] Broad band.

Table II
Chemical Shifts[a] in $^{13}$C NMR of Partially Halogenated Polystyrenes

| | $FeCl_3$ cat. bromination | $Tl(OAC)_3$ cat. bromination | $Tl(OC(O)CF_3)_3$ cat. iodination[b] | *n*-BuLi-TMEDA reaction with bromine |
|---|---|---|---|---|
| DF | 0.65 | 0.40 | 0.30 | 0.55 |
| carbon atom no. | | | | |
| 1 | 143.6-144.2[c] | 144.6-145.1[c] | 144.6-145.1[c][146.3] | 143.7-145.2[c] |
| 2,6 | 127.6, 128.3 (129.3) | 127.6, 128.1 (129.3) | 127.6, 128.2 (129.6[130.8]) | 127.6, 128.1 (129.2) |
| 3,5 | 127.6, 128.3 (131.3) | 127.6, 128.1 (131.1) | 127.6, 128.2 (137.1[138.1]) | 127.6, 128.1 (131.3) |
| 4 | 126.1 (119.6) | 125.9 (119.4) | 125.8 (90.8[93.7]) | 125.8 (119.8) |
| 7 | 41.1-44.9[c] | 42.4-45.4[c] | 41.5-45.9[c] | 41.5-46.1[c] |
| 8 | 40.2-40.3[c] | 40.4 | 40.4 | 40.3 |

[a] For each method of synthesis the numbers not in parentheses correspond to the unsubstituted units and the numbers in parentheses apply to the halogenated styrene units. Where one line is observed a single entry is made. [b] Numbers in brackets correspond to calculated values for *p*-iodopolystyrene (see ref 7). Calculated values for *m*-iodopolystyrene did not fit with the measured data. [c] Broad line.

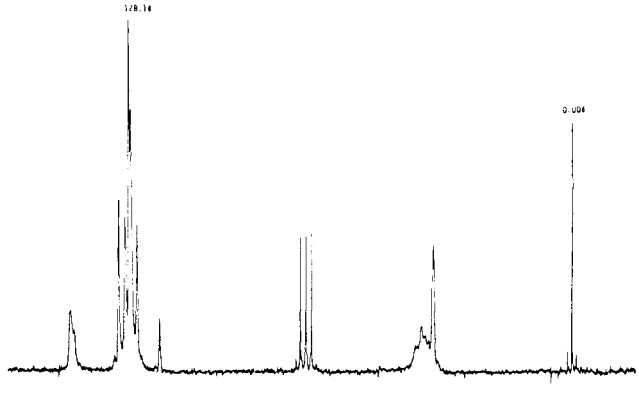


**Figure 1.** $^{13}$C-NMR spectrum of Ⓟ-Br prepared by $Tl(OAc)_3$-catalyzed bromination of polystyrene (DF = 0.40).

$^{13}$C-NMR spectrum of the polymer showed that bromination had occurred exclusively at the para position (Table II). This result is extremely surprising in view of an earlier report by Chalk[10] which claims that substitution occurs in both para and ortho position and a report by Evans et al.[11] in which a similar reaction carried out with methyl iodide quenching yields a product in which substitution occurs in the meta and para positions in a 2:1 ratio. Since the study of Evans et al.[11] was carried out under conditions which gave a very low degree of functionalization (0.05), we decided to reinvestigate this reaction to see if an increase in the degree of functionalization would result in a change in the substitution pattern.

Metalation of polystyrene with *n*-BuLi–TMEDA at room temperature followed by reaction of the lithiated polymer with excess methyl iodide gave a polymer with a degree of functionalization of 0.19;[12] the same reaction carried out with metalation at 65 °C gave a higher but still unsatisfactory degree of functionalization of 0.27. In an attempt to increase further the degree of functionalization, *tert*-butyllithium was substituted for *n*-butyllithium, and the metalation carried out with TMEDA at room temperature proceeded smoothly to give a degree of functionalization of 0.5 comparable to that obtained in the bromination reaction. Another experiment carried out with triethylenediamine (TEDA or DABCO) confirmed the lower reactivity of the complex with butyllithium which we had observed earlier.[1] Study of the methylated polystyrene resins by $^{13}$C-NMR spectroscopy confirmed the results of Evans et al.[11] In every case, regardless of the degree of substitution or metalating complex used, the polymer showed aromatic substitution in meta and para positions. A quantitative evaluation[11] of the meta/para ratio using both ring carbon resonances and methyl carbon resonances confirmed that reaction occurred mainly at the meta position with a meta/para ratio of 2:1.

The different outcome of the *n*-BuLi–TMEDA reactions with bromine vs. methyl iodide quenching is probably due to completely different reaction pathways which might warrant further study on model compounds.

## Experimental Section

$^{13}$C-NMR spectra were recorded using a Varian CFT 80 spectrometer operating at 20 MHz in the Fourier transform mode with $^1$H noise decoupling. The polymers were examined as solutions in deuteriochloroform (ca. 200 mg in 1.5 mL). Halogen analyses were carried out in this laboratory using a Parr peroxide bomb on 200–300-mg samples of the halogenated resins. Polystyrene (mol wt 20 000) and *o*-, *m*-, and *p*-bromostyrene were purchased from Polysciences Inc.

**Preparation of Polymer Standards.** To a solution of 2 g of *o*-bromostyrene in 25 mL of toluene was added 0.05 g of azobis(isobutyronitrile). The mixture was stirred under nitrogen at 90 °C for 2 days. After concentration of the solution, the polymer was precipitated by pouring it into 200 mL of methanol. After filtration the polymer was washed three times with methanol then dried under vacuum to yield 1.5 g of poly(*o*-bromostyrene). The $^{13}$C-NMR spectrum of the polymer is given in Table I.

Poly(*m*-bromostyrene) and poly(*p*-bromostyrene) were also prepared using this procedure; their spectra are given in Table I.

**Bromination of Polystyrene with $FeCl_3$ Catalyst.** To a solution of 2.5 g of polystyrene in 30 mL of $CCl_4$ were added 0.1 g of $FeCl_3$ and 1 mL of bromine. The reaction was allowed to proceed in the dark for 3 days at room temperature with stirring. After filtration, the polymer was precipitated by pouring the reaction mixture into an excess of methanol. After filtration and washing with methanol the polymer was redissolved in methylene chloride, reprecipitated in methanol, collected on filter, and dried under vacuum. The dried polymer weighed 2.13 g and contained 4.18 mequiv of bromine/g for a DF of 0.65; its $^{13}$C-NMR spectrum is given in Table II and shows para substitution.

**Bromination of Polystyrene with Thallic Acetate Catalyst.** To a solution of 7.5 g of polystyrene in 100 mL of carbon tetrachloride was added 0.2 g of thallic acetate. Bromine (1.8 mL) was added dropwise while the polymer was stirred in the dark at reflux temperature. After 2 h the mixture was cooled and the polymer precipitated by pouring it into excess methanol. The polymer was redissolved in dichloromethane and the solution was filtered to remove any solid impurity and finally poured into methanol to reprecipitate the polymer. After drying, 8.08 g of polymer were obtained; analysis indicated 2.96 mequiv of bromine/g for a DF of 0.40. The $^{13}$C-NMR spectrum of the polymer is given in Table II and shows that para substitution occurred.

**Iodination of Polystyrene with Thallic Trifluoroacetate and Iodine.** To a solution of 4 g of polystyrene in 125 mL of carbon tetrachloride was added 15 mL of a 0.8 M solution of thallic trifluoroacetate. The mixture was stirred at room temperature for 1 h and 3 g of iodine were added portionwise while the solution was heated, letting the iodine color disappear between additions. After addition of 3 g, the iodine color remained and the mixture was refluxed for an additional 1 h. After filtration to remove precipitated thallous iodide, the polymer was precipitated by pouring it into methanol. After being washed with methanol and hot water, the polymer was dissolved in dichloromethane then reprecipitated in methanol. After drying the polymer weighed 4.1 g and contained 2.1 mequiv of iodine/g for a DF of 0.30. The $^{13}$C-NMR spectrum of the polymer is given in Table II and shows that the iodination occurred in the para position.

**Bromination of Polystyrene with *n*-BuLi–TMEDA and Bromine** To a solution of 2.5 g of polystyrene in 125 mL of dry cyclohexane containing 3.8 mL of TMEDA was added 15 mL of 1.6 N *n*-BuLi. The mixture was stirred under nitrogen for 6 h at room temperature. After addition of a large excess (8 mL) of bromine the mixture was stirred in the dark overnight. The polymer was precipitated in methanol, washed extensively with methanol, then dissolved in dichloromethane. The solution was filtered to remove insoluble impurities and after reprecipitation in methanol the polymer was dried. The dry product weighed 1.99 g and contained 3.72 mequiv of bromine/g for a DF of 0.55. $^{13}$C-NMR analysis of the polymer (Table II) showed that it was substituted exclusively in the para position.

**Methylation of Polystyrene with *n*-BuLi–TMEDA and Methyl Iodide.** Polystyrene (mol wt 20 000, 2.5 g) was dissolved in 125 mL of cyclohexane, and 4 mL of TMEDA and 10 mL of *n*-BuLi (2.6 N) were added. The reaction was stirred under $N_2$ at room temperature for 4 h and 6 mL of methyl iodide was added and allowed to react for 16 h. The reaction mixture was then poured into excess methanol and the precipitate was collected and redissolved in $CH_2Cl_2$. The solution was filtered and reprecipitated in MeOH. After filtering and drying, 1.87 g of polymer was obtained. $^1$H NMR showed the degree of functionalization to be 0.19.

$^{13}$C NMR showed the substitution pattern to be meta and para in a 2:1 ratio.[11] A similar experiment in which the poly(styryllithium) was formed by heating at 65 °C for 4 h resulted in a polymer with 27% of the rings substituted by Me groups. $^{13}$C NMR showed the same substitution pattern described above.

**Methylation of Polystyrene with *t*-BuLi–TMEDA and Methyl Iodide.** Polystyrene (mol wt 20 000, 2.5 g) was dissolved in 150 mL of cyclohexane, and 4 mL of TMEDA and 23 mL of *t*-BuLi (1.2 N) were added. After 1 h under $N_2$ at room temperature, 6 mL of $CH_3I$ was added and the reaction mixture was stirred 1.5 h. An isolation procedure similar to that described above yielded 1.24 g of a polymer with a degree of functionalization of 0.50. $^{13}$C NMR shows a meta–para ratio of 2:1.[11]

A similar experiment using 2.5 g of polystyrene, 3.1 g of TEDA, 23 mL of *t*-BuLi and heating to 50 °C for 2 h yielded 1.54 g of polymer with a degree of functionalization of 0.19 and a meta–para ratio of 2:1.

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## References and Notes

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