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Highly functionalized polystyrene by direct metalation – carboxylation

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Summary

Polystyrene was directly metalated using 1:1 mixture of n-butyllithium (n-BuLi) and potassium-t-butoxide (t-BuOK) in cyclohexane/hexanes at ambient temperature. The metalated polymer on reaction with solid carbon dioxide followed by a metal-proton exchange gave a carboxylated polymer containing 6.38-6.57 mmol acid/g polymer which corresponds to the introduction of carboxyl groups on 94-97 % of the repeat units of polystyrene.

Based on ^{13}C NMR spectra meta, para and ortho aromatic ring substitution was proposed. No detectable backbone carboxylation occurs. The distribution of carboxylated sites on the aromatic ring: 9 % ortho, 58 % meta and 33 % para. Quantitative ^{13}C NMR analyses indicates essentially quantitative functionalization.

I. Introduction

The reaction of dissolved polystyrene with the 1:1 complex of n-butyllithium (n-BuLi) and N,N,N',N'-tetramethylethylenediamine (TMEDA) has been the subject of several previous studies proving the formation of metalated polystyrene by derivatization (1-3, 5), studying kinetics (4) and the position of derivatization site (5). This reaction route and subsequent functionalization has been used for the synthesis of insoluble, functionalized polymer supports from crosslinked divinylbenzene-styrene copolymer (6-7).

The later recognized phenomenon, the unprecedented reactivity of the 1:1 mixtures of alkyllithium and bulky potassium alcoholates in proton abstraction from low acidity hydrocarbons, has been extensively studied (8-11).

We have investigated the direct metalation of a preformed polystyrene (M_n=23900; M_w/M_n=1.24 by GPC) using the superbasic n-BuLi and potassium-t-butoxide (t-BuOK) mixture (8-10) with the aim of improving the degree of functionalization and confirming the position of the derivatization site. This communication describes metalation following the reaction by quenching with solid carbon dioxide (as shown in Scheme 1) and examining the product by acid-base titration and ^{13}C NMR spectroscopy.

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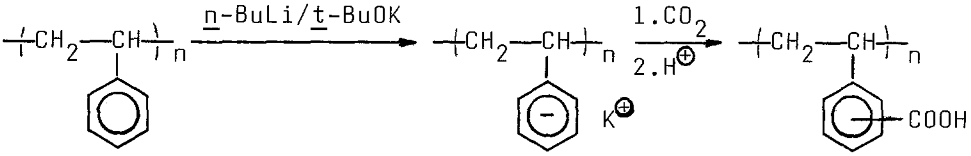
Scheme 1



II. Experimental

The inert atmosphere - syringe techniques were used in all synthetic experiments (12).

Styrene (99 %, Riedel-de Haën) and cyclohexane were purified following standard procedures. _n_-Butyllithium (1.6 M solution in hexanes, Aldrich), potassium-_t_-butoxide (Aldrich) and solid carbon dioxide were used as received.

Polystyrene was prepared in cyclohexane at 25°C using _n_-butyllithium as initiator.

Direct Metalation - Carboxylation of Polystyrene

Polystyrene (5.2 g; $\overline{M}_n$=23900, $\overline{M}_w/\overline{M}_n$=1.24) in 100 g cyclohexane, _t_-BuOK (14.2 g, 125 mmol), and _n_-BuLi (80.0 mL of 1.6 M solution in hexanes, 125 mmol) were agitated for 5 hrs at room temperature. The charge containing metalated polystyrene was transferred onto a large amount of solid carbon dioxide. After standing overnight the carboxylic acid salt was converted to the carboxylated polymer by mixing the charges with 1M aqueous HCl for several hours. The product was further purified by treating it in a large amount of boiling water followed by reprecipitation from 1M aqueous NaOH into 5M aqueous HCl. The polymer was filtered, dried under vacuum at 60 °C. Yield: $\gtrsim$95 % (based on three experiments).

The purified carboxylated polymer was analysed by acid-base titration and ^{13}C NMR spectroscopy.

Acid-Base Titration

The polymer was titrated with 0.1 N aqueous NaOH in the presence of phenolphtalein (13).

Characterization Methods

^{13}C NMR spectra of the polystyrene (in $CDCl_3$ at 50 °C) and the carboxylated polystyrene (in DMSO-d_6 at 50 °C), were recorded on a Bruker 200 SY spectrometer operating in the Fourier transform mode. The pH of the DMSO-d_6 solutions were adjusted to 1.0 or less by addition of a few drops of concentrated HCl.

Quantitative ^{13}C NMR spectra were obtained using the inverse gated decoupling technique (to suppress nuclear Overhauser enhancement).

The line simulation of overlapped carboxylic carbon peaks has been carried out on an Aspect-2000 computer using Linesim program.

The subspectra of quaternary carbon atoms were generated by using the "Quaternary-Only Pulse Sequence" (14).

Molecular weight ($\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) were determined by a Shimadzu C-R3A high pressure GPC instrument equipped with RI detector and five LiChrogel columns. The calibration curve was constructed using polystyrene standards.

III. Results and Discussion

Polystyrene can be metalated rapidly at ambient temperature in a nearly quantitative fashion using n-BuLi/t-BuOK in cyclohexane/hexanes. During the metalation the metalated polymer gradually precipitates into a chocolate brown precipitate. Subsequent introduction onto a large amount of powdered solid carbon dioxide followed by a metal-proton exchange gave carboxylated polymer. Determination of the carboxyl content of the polymer by acid-base titration enables the extent of metalation to be determined. These results showed that it contained 6.38-6.57 mmol-COOH/g polymer which corresponds to the introduction of carboxyl groups on 94-97 % of the repeat units of polystyrene. These results indicate, that the metalation is essentially quantitative by the use of an excess of metalating reagent.

Due to the high extent of carboxylation the resulting carboxylated polymer can be dissolved in aqueous NaOH. The solubility is about 16.5 g/100 g 1M NaOH at 25 °C.

Figure 1a shows the aromatic region of the ^{13}C NMR spectrum of the polystyrene prepared by n-butyllithium. The aromatic C-1 carbon resonances indicate essentially atactic structures (15).

Figure 1b shows ^{13}C NMR spectrum of the aromatic and carboxyl carbons of a carboxylated polystyrene sample with assignments. The assignment of the peaks was aided by substituted benzoic acid chemical shifts (16-17) and by the additivity of substituent effects on the ^{13}C NMR chemical shifts in polysubstituted aryl compounds. The relative intensities of the peaks were used as a further aid in the indentification of carbons.

An examination of the carboxyl carbon chemical shifts of the relevant substituted benzoic acids shows that the carboxyl carbon atom resonances can be found in the range from ~166 to ~170 ppm (16-17). The spectrum, in Figure 1b, consists of three peaks at 166.5, 167,3 and 168,7 ppm in this region which are obviously resonances of carboxylic carbon atoms attached to phenyl ring. Any type of aliphatic carboxyl carbon atom resonances (18-19) which would arise due to the backbone carboxylation would have appeared in the range from ~180 to ~185 ppm. Thus we can conclude that no detectable backbone metalation occurs.

Assuming additivity of substituent effects, the chemical shifts of aromatic carbons in a polysubstituted benzene can be predicted (16-17). Based on these calculations the assignments are as follow. The peak due to C-1 in 1p appears at 150.2 ppm. C-1 carbons in 1m and 1o absorb to give an unresolved peak at 145.3 ppm. The resonances due to C-2, C-3, C-4, C-5 and C-6 in

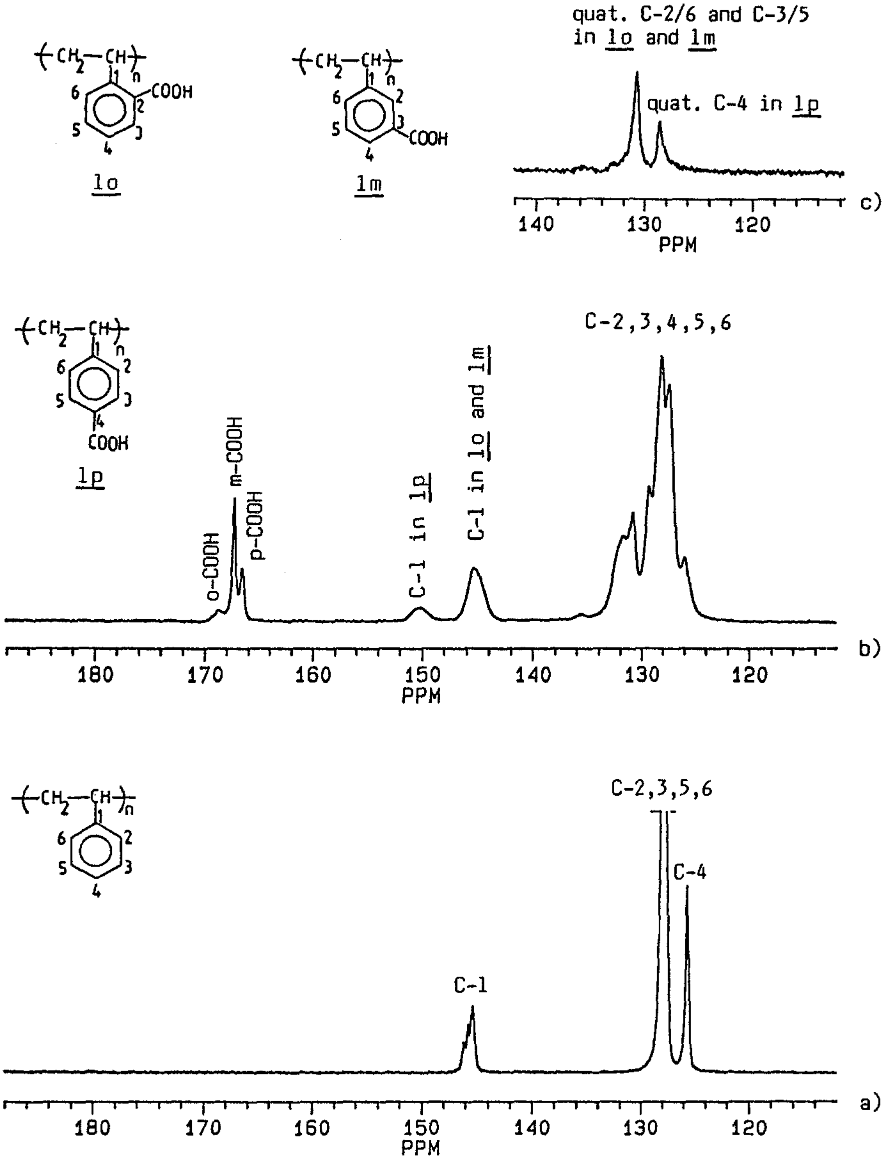


Figure 1. a) Aromatic region of the ^{13}C NMR spectrum of poly styrene (in CDCl$_3$). b) ^{13}C NMR spectrum of the aromatic and carboxyl carbons of a carboxylated polystyrene sample (in DMSO-d$_6$). c) Subspectrum of quaternary C-2/6, C-3/5 and C-4 carbons of a carboxylated polystyrene sample obtained from "Quaternary-Only Pulse Sequence".

lo, lm and lp are highly overlapped in the range from 125.4 to 135.9 ppm.

Figure 1c shows quaternary C-2/6, C-3/5 and C-4 carbon resonances (the resonances of carbon atoms attached to the carboxyl group in lo, lm and lp), separated by using the "Quaternary-Only Pulse Sequence" (14).

The available data for the influence of the alkyl substituents on carboxyl carbon chemical shifts in benzoic acids are very scanty (20-21). The order for the carboxyl carbon chemical shifts in 2-, 3- and 4-methyl benzoic acid: δ (o-COOH) > δ (m-COOH) > δ (p-COOH) (20-21). It seems reasonable that similar steric and electronic effects are working in this carboxylated polymer, which lead to the same peak order. The interaction of ortho-carboxyl substituent with the backbone chain causes the -COOH plane to deviate from coplanarity with the ring, which leads to a decrease in conjugation. As a consequence, the charge density at the carboxyl carbon decreases, which implies a shift to the lowest field among the peaks of the carboxyl carbons.

By the use of curve resolution, the overlapped carboxylic carbon peaks were resolved into three component peaks. These calculations gave the distribution of carboxylated sites on the aromatic ring as follows: 9 % ortho, 58 % meta and 33 % para. The relative intensites of the peaks at 167.3 and 166.5 ppm which were assigned to m-COOH and p-COOH respectively are approximately 2:1. Similar results were reported in ref. (5). Most likely the negativ charge is delocalized over the phenyl ring in the metalated polystyrene and the electrophilic attack of CO_2 is controlled statistically in the ratio 2:1 regarding to meta and para position, and controlled by steric hindrance in the case of the ortho position.

The identity of integrated relative intensites of the peaks at 166.5 (p-COOH) and 150.2 ppm (C-1 in lp) also confirms that the assignment is correct.

Determination of the degree of functionalization based on the ratio of integrated relative intensites of C-1 and -COOH carbons indicates quantitative functionalization within experimental error.

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