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Action of Oxygen on Polylithiated Polystyrene A New Route to a Styrene-Hydroxystyrene Copolymer

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Summary

The synthesis of the copolymer styrene m,p-hydroxystyrene has been carried out by chemical modification of polystyrene. The initial polystyrene has been lithiated by the complex of sec.butyllithium with N,N,N',N'-tetramethylethylenediamine in cyclohexane and hexane. The lithiated sites have been quenched with oxygen. From the physicochemical characterization we have observed that the initial polystyrene is not degraded and that the oxidation reaction is quantitative. This reaction yields a styrene m,p-hydroxystyrene copolymer. The hydroxy groups are located in the meta-(2/3) and para-positions of the aromatic ring.

INTRODUCTION

The literature describes few ways to obtain polyhydroxystyrene samples and styrene-hydroxystyrene copolymers. These polymers are generally obtained by a free radical polymerization (1,2,3). This method requires the synthesis and the purification of monomers and generally gives a polymer of low molecular weight. The method chosen which has already been mentioned (4) offers three advantages:

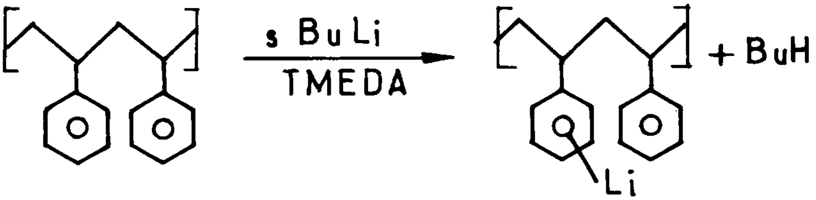
The use of a well-known material: polystyrene;

The modification occurs in a one-shot process.

The polystyrene is lithiated and the oxygen reacts with the carbanionic sites to give the functional groups;

Variation of the degree of lithiation yields styrene m,p-hydrostyrene copolymers, the proportion of the phenolic groups being directly correlated.

At the beginning of the one-shot modification the polystyrene is lithiated by the complex of sec.butyllithium with N,N,N',N'-tetramethylethylenediamine (TMEDA). During our investigations on model molecules, we have determined the positions of lithiated sites (5). For polystyrene, there is no metallation in the benzylic position, and the lithiation occurs mainly in the meta (2/3) and para (1/3) positions of the aromatic ring.



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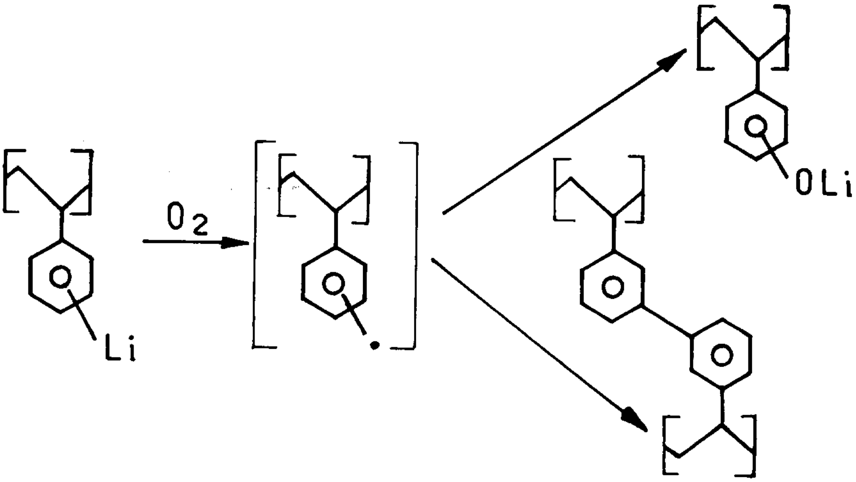
At the end of the reaction the lithiated sites are deactivated with oxygen. The general conditions of the oxidation reaction of ω-carbanionic ends are described in a previous article (6). We have observed that this reaction gives hydroperoxide end groups (92%) and coupled molecules (6%). The action of oxygen on organolithium compounds in organic chemistry leads to phenol and gives high yields of coupled hydrocarbon compounds (7). The oxidation reaction is not directly applicable to the lithiated polymer, and in this paper we present our results concerning the study of parameters to check the functionalization and the coupling reaction.

The reaction scheme is shown below:



EXPERIMENTAL

1) Purification

Cyclohexane-heptane were purified by refluxing over and distillation from sodium wire and distilled from living anions immediately before use.

N,N,N',N'-tetramethylethylenediamine was passed over molecular sieves and distillated under vacuum from sec.butyllithium.

Styrene: distillation (twice) from sodium.

2) Polystyrene

Polystyrene was prepared in benzene solution using sec.butyllithium as an initiator. The polymer was precipitated by methanol and dried under vacuum.

PS I : $\bar{M}_n$: 2 200   PS IV : $\bar{M}_n$: 24 000

3) Metallation of polystyrene

Under argon 2.5 g of polystyrene (PS 21) were dissolved in 300 ml of cyclohexane. Sec.butyllithium (1.8×10^{-2} mole) and TMEDA (1.8×10^{-2} mole) were added and the medium was stirred at 20°C for 2 hours.

After decantation of the lithiated precipitated polymer, the solvent was sucked off. 400 cm^3 of heptane were added and the mixture was cooled at - 60°C. This experimental method is necessary to prevent dangerous explosions during the oxidation process. An aliquot sample was taken and deactivated by trimethylchlorosilane.

4) Oxidation

Inverse oxidation: the anionic polymer was deactivated by adding it dropwise to a solution of heptane (200 cm^3),cooled at - 60°C and saturated with oxygen.

Direct oxidation: oxygen was bubbled directly through the solution of living polymers.

Methanol was added to the mixture to dissolve the modified polymer. After decantation, the methanolic solution was separated from hexane and the methanol evaporated. The polymer is dissolved in chloroform, treated with dilute hydrochloric acid and washed with water. After decantation, the solvent was evaporated and the polymer isolated and freeze dried in benzene.

Analysis :							
	I_a : %	C	87.33	H	7.28	O	5.38
	I_b : %	C	87.23	H	7.27	O	5.50

Analytical methods

Molecular weights have been determined by gel permeation chromatography (GPC) (Water apparatus) using styragel columns and THF as a solvent.

Spectral measurements: ^{1}H-NMR spectra of polymers have been carried out with either a Brucker (90 MHz) or a Hitachi Perkin Elmer (50 MHz) spectrometer.A Perkin Elmer 225 spectrometer was used to obtain IR spectra.

Determination of the lithiation yield from the silylated sample : T_1

The ratio of the integration of one proton of the methyl group to one proton of the aromatic group allows to calculated the yield of the lithiated styrene units.

Determination of the yield of hydrostyrene units

T_2 (NMR I) : the protons of the phenolic groups whose shifts are located in the aromatic region are exchanged with the deuterium of deuterated trifluoroacetic acid. The ratio of the integration of one proton of the generated trifluoroacetic acid to one aromatic proton gives the yield of hydrostyrene units.

T_2 (NMR II) : the polymers are treated with N,O-bis-(trimethylsilyl)trifluoroacetamide, which provokes the silylation of the phenol group. The ratio of the integration of one proton of the methyl group to one aromatic proton allows to determine the ratio of hydroxystyrene unit.

Determination of the coupling yield C

N_o .... : number of the initial macromolecules $\bar{M}_{n,o}$

N_1 .... : number of the initial macromolecules which have been functionalized and have not been coupled. Their molecular weight is $\bar{M}_{n,1}$

N_2 .... : number of the coupled macromolecules of molecular weight $\bar{M}_{n,2}$

$\bar{M}_n$ .... : molecular weight of polyfunctional polymer

$\bar{x}\, N_2$ ... : number of the initial macromolecules which have been coupled $(\bar{x}-1)$ times

$(\bar{x} = \bar{M}_{n,2}/\bar{M}_{n,1})$

We have defined the coupling ratio C for the polycarbanions from :

$$C = \frac{\bar{x}\, N_2}{\bar{N}_1 + \bar{x}\, N_2} = \frac{\bar{x}}{\bar{x}-1}\left(1 - \frac{\bar{M}_{n,1}}{\bar{M}_n}\right) \qquad N_o = N_1 + \bar{x}\, N_2$$

We have computed C by deconvolution of the GPC curves.

Yield of carbanionic sites which have given C-C bonds by the coupling reaction: T_3

Total number of carbanionic sites : $N_o \,.\, \overline{DPn} \,.\, T_1$

Total number of carbanionic sites which have given the coupling reaction: $2(\bar{x}-1)N_2$

$$T_3 = \frac{2(\bar{x}-1)N_2}{N_o . \overline{DP}_n . T_1} = \frac{2(\bar{x}-1)C}{\bar{x} \,.\, \overline{DP}_N . T_1}$$

Theoretical yield of hydroxystyrene units: T_4

This yield is computed by taking account of the coupling reactions: $T_4 = T_1 - T_1 \,.\, T_3$

RESULTS AND DISCUSSION

The action of the oxygen on the polylithiated polystyrene ($\bar{M}_n$ = 2 200) gives a polymer which is soluble in methanol : this observation is the first proof that we have carried out an important chemical modification of the polymer.

The results of the NMR spectroscopy and elemental analysis are shown in Table 1:

Table 1 Functionalization ratio of several polystyrenes ($\bar{M}_{n,o}$ = 2 200)

Samples	T_1 (%)	T_2 (%) NMR I	NMR II	Elemental analysis	C (%)	T_3 (%)	T_4 (%)
I_a	29	28	27	28	16	2.5	28
I_b	29	26	24	24	18	3	28
II_a	36	30	30	31	17	2	35
II_b	36	30	30	31	18	2.5	35
III_a	43	38	37	37	27	3	42
III_b	43	38	37	38	23	2.5	42

a : inverse oxidation b : direct oxidation

Table 1 shows that there is a good correlation between the values of T_2 obtained by NMR and those obtained by elemental analysis. Moreover, the lithiation yield of T_1, measured by NMR spectroscopy, for an aliquot sample deactivated with trimethylchlorosilane slighty differs from the functionalization ratio (T_2). This difference arises from the coupling reaction: the carbanionic sites which have given carbon-carbon bonds after the deactivation reactions are not functionalized and these coupling reactions decrease the functionalization ratio. On the GPC chromatogram the number average molecular weight ($\bar{M}_{n,2}$) of the coupled compounds corresponds to twice the molecular weight of the non-coupled macromolecules ($\bar{x}$=2). The ratio T_3 of the carbanions which have participated in the coupling of the different samples varies between 2 and 3%.

This result cannot explained the fact that the T_2 values are always lower than those of T_4. This difference, which is due to a radical hydrogen transfer, increases with the lithiation yield. The oxygen is in more and more stoichiometric deficiency relative to the carbanions when the proportion of carbanions increases; consequently the phenyl radicals formed abstract a hydrogen atom more easily. The solid state of the lithiated compound is also very important for the coupling reaction. The low values of T_3 are apparently in opposition to the following results:

The oxidation of phenyllithium or tolyllithium (7) gives a high yield in coupling reactions (17 to 35%);

During the oxidation of ω-carbanionic polystyrene (10^{-2} M) we had observed in polar solvent 20% of coupling reactions.

From these observations, it was possible to expect a gel formation during our oxidation; in fact,we do observe either a gel or a polymer of high molecular weight. At - 60°C the lithiated polymer is precipitated and the movements of the chains are practically stopped. When the oxygen reacts with the carbanionic sites the reaction gives phenyl radicals and the probability of these radicals to react with one another is very low which explains the low values of T_3.

To check this claim we have carried out the oxidation of a polylithiated polystyrene, the molecular weight of which was 24 000. The results are listed in Table 2.

Table 2 Functionalization ratio of polystyrene ($\bar{M}_{n,o}$ = 24 000)

Samples	T_1 (%)	T_2 (%)	Observation
IV_a	33	28	gel
IV_b	33	27	"
V_a	30	26	"
V_b	30	26	"
VI_a	35	31	"
VI_b	35	31	"

a : inverse oxidation
b : direct oxidation

All the experiments carried out on this polymer give a gel after oxidation. T_2 has been determinated only by elemental analysis. We had observed for the samples of Table 1 that in the solid state 3% of the carbanions (T_3) give a coupling reaction. If we use this percentage for all the samples of Table 2 we find on the average a number of bridges up to 2; this explains the gel formation.

On the other hand, for all the experiments (Table 1 and 2) we find no difference in the yield of functionalization T_2 between the two deactivation methods; direct and inverse oxidation. This fact corroborates the low rate of migration of oxygen in the precipitated polymer.

For the characterization of the structure of the polymers we have used in the first step IR analysis. At 3515 cm^{-1} the IR spectra show the stretching vibration of the non-associated OH groups. The large band at 3350 cm^{-1} corresponds to the stretching vibration of the associated OH groups. The aromatic substitution with the OH functions is shown by the expansion and the increase in the intensity of the band at 1600 cm^{-1}. This band corresponds to the skeletal in-plane vibration of C=C of the aromatic nucleus. The OH deformation mode occurs near 1380-1310 cm^{-1}. Between 1265 and 1210 cm^{-1} the absorption corresponds to the C-O stretching mode. The most interesting region of the spectra is located between 900 and 650 cm^{-1}. The meta substitution is characterized by two absorption bands:

1) at 875 cm^{-1} which is due to the out-of-plane deformation vibrations of the hydrogen atoms remaining on the ring between the two substitutions and

2) at 780 cm^{-1} for the position of the out-of-plane C-H bonding vibration of the three other aromatic hydrogen atoms.

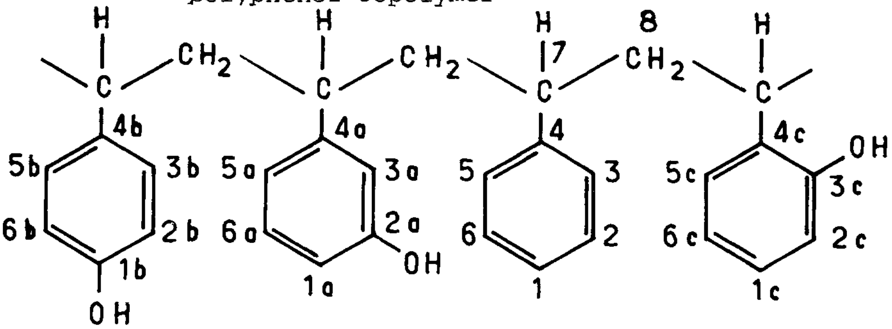
The para substitution is shown at 825 cm^{-1} which is the absorption frequency of the out-of-plane C-H vibrations of two adjacent ring hydrogen atoms.

The ^1H-NMR spectra of the copolymer styrene/hydroxystyrene do not show a well-defined peak for the phenolic proton. We only observe a broadening of the peak between 5 and 6.5 opm (TMS as a reference).

The ^{13}C-NMR gives the chemical shifts of the different carbons of the copolymer (Table 3).

LAUTERBUR suggest that variations in the local π electron densities govern the ^{13}C shieldings in the aromatic ring and he has tested this suggestion by examining the variation in shielding of carbon nuclei for a variety of aromatic systems and for a series of phenols (8). If we use the substitution effects found

Table 3 Aryl carbon shielding of the polystyrene-polyphenol copolymer



polystyrene	δ_C ppm from TMS	$\Delta\delta_1$ from C_6H_6		
C_1	125.7	- 3	C_7	43.8 multiplet
C_2 C_3 C_5 C_6	128.1	- 0.6	C_8	40.5 multiplet
C_4	145.6	+ 16.9		

polystyrene/ polyphenol		$\Delta\delta_1$	$\Delta\delta_2$	$\Sigma\ \Delta\delta$	δ_3	δ found
meta OH	1a	- 3	- 12.6	- 15.6	113.1	112.7
	2a	- 0.6	+ 26.9	+ 26.3	155	155.3
	3a	- 0.6	- 12.6	- 13.2	115.5	115-115.3
	4a	+ 16.9	+ 1.8	+ 18.7	147.4	147.4
	5a	- 0.6	- 7.9	- 8.5	120.2	120.2-121.1
	6a	- 0.6	+ 1.8	+ 1.2	129.9	129.3
para OH	1b	- 3	+ 26.9	+ 23.9	152.6	153
	(2b (6b	- 0.6	- 12.6	- 13.2	115.5	115-115.3
	(3b (5b	- 0.6	+ 1.8	+ 1.2	129.9	129.3
	4b	+ 16.9	- 7.9	+ 9	137.7	137.5
ortho OH	1c	- 3.01	+ 1.8	- 1.21	127.49	hidden
	2c	- 0.6	- 12.6	- 13.2	115.5	115-115.3
	3c	- 0.6	+ 26.9	+ 26.3	155	155.3
	4c	+ 16.9	- 12.6	+ 4.3	133	not observed
	5c	- 0.6	+ 1.8	+ 1.2	129.9	129.3
	6c	- 0.6	- 7.9	- 8.5	120.2	120.2-121.1

$\Delta\delta_1 = \Delta\delta_{PS}$ $\Delta\delta_2 = \Delta\delta_{C_6H_5OH}$ $\delta_3 = \delta_{C_6H_6} + \Sigma\ \Delta\delta$

$\delta_C C_6H_6$ from TMS = 128.7 ppm

for the polystyrene and for the phenol in comparison with the benzene we can estimate the $\Delta\delta$ for each benzenic substitution. The effects of substituents (alkyl or OH group) on the aryl carbon shielding follow an additive relationship:

$$\Sigma\Delta\delta = \Delta\delta_{PS} + \Delta\delta_{OH}$$

If we add this total shielding to the chemical shift of the benzene we obtain a theoretical estimation of the chemical shifts for all the carbons of the polyphenol in meta, para and ortho positions. These theoretical values are in good agreement with the experimental shifts (Table 3). The observation of the specific peaks of the meta (δ_c = 147.4; 113 ppm) and the para (δ_c = 153; 137.7 ppm) hydroxystyrene units shows that the oxygen atom is linked with the very same carbon that carried the lithium atom; in first approximation, the para and the meta substitution are in the ratio 1/2. The very low amount of the ortho metallation sites ($<$ 9%) has not allowed us to observe the peak of the C-4 atom (δ_c = 133 ppm), the chemical shift of which only points out this substitution type.

In conclusion, the synthesis of the copolymer polystyrene-polyhydroxystyrene has been conducted by chemical modification of the polystyrene. The sequence of the reactions that we have chosen, lithiation and oxidation, is easily carried out, because it is not necessary to apply inverse oxidation. The direct oxidation gives good yields of phenolic groups. The solid state of the polylithiated polystyrene allows to reduce the coupling reaction which is dominant in organic chemistry. These phenolic groups are especially fixed in the meta and para position (2/1).

The oxidation of the high molecular weight polymer gives crosslinked functionalized polystyrene, the phenolic groups of which are extremely useful, because they can generate nucleophilic substrates.

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