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Cationic Modification of Polystyrene

Synthesis and Characterization of Poly(*p*-Methylthio)Carbonylstyrene and Poly(*p*-Carboxystyrene)

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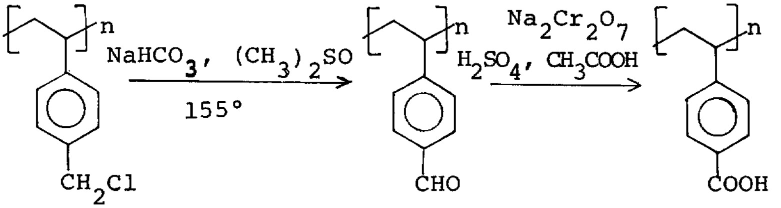
Abstract

This paper concerns the cationic modification of polystyrene by the electophilic substitution of polystyrene with S-methylthiocarboxonium. The substitution is quantitative and gives poly p-(methylthio)carbonylstyrene . After hydrolysis and purification poly(p-carboxystyrene is obtained. The polymers are formed without degradation after this cationic modification.

Introduction

Poly(p-carboxystyrene) is usually prepared from chloromethylated polystyrene (I). (I) is obtained by Pepper's method (1). (I) is oxidized to aldehyde (II) with $NaHCO_3$ in dimethylsulfoxide and thence to poly(p-carboxystyrene) (III) with chromic acetic acid (2).



(I) (II) (III)

We report here a new method for the synthesis of (III), which is obtained in high yield by the hydrolysis of a poly p-(methylthio)carbonylstyrene (IV). (IV) is prepared by electrophilic substitution of polystyrene with S-methylthiocarboxonium. This reaction was first studied by Olah and al. (3) on aromatic hydrocarbons, and we have adapted it to polystyrene. Methylfluoride and Antimony pentafluoride in SO_2 solution form the complex (A) which is capable of alkylating COS.

At -25°C S-methyltiocarboxonium fluoroantimonate (B) is quantitatively obtained.

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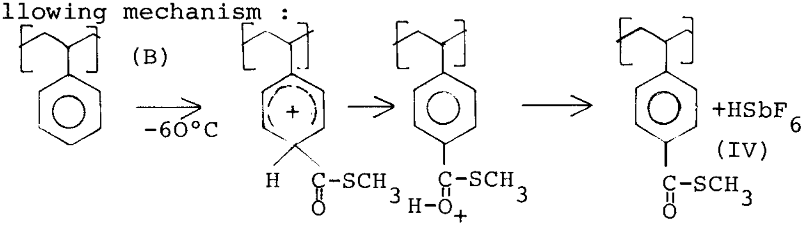
$$CH_3F + SbF_5 \xrightarrow[SO_2]{-70°} \left[CH_3 - O = S = O\right]^+ SbF_6^- \qquad (A)$$

$$A + COS \xrightarrow[SO_2]{-25°} \left[CH_3 - S - C = O\right]^+ SbF_6^- \qquad (B)$$

(B) reacts on the polystyrene (I') according to the following mechanism :



We have studied the experimental conditions to improve functionalization.

Experimental

I - Materials

So_2 was distilled and condensed twice on P_2O_5. SbF_5 was distilled under high vacuum and stored in a bulb equipped with break-seals. COS and CH_3F were passed over molecular sieves to remove traces of moisture. The polystyrene was prepared in benzene solution using sec-butyllithium as an initiator. The polymer was precipitated by methanol and dried under vacuum. $\overline{Mn}$=18000.

II - Preparation of the S-methylthiocarboxonium fluoroantimonate solution : (B) solution

In a round flask equipped with an SbF_5 bulb, a magnetic stirrer and a gas inlet tube, 100 ml of sulfur dioxide was condensed at -80°. SbF_5 was transferred into the flask ; CH_3F also condensed, followed by an excess of COS. The (B) solution was warmed up to -25° and held at this temperature for 30 minutes.

III - Thioesterification of polystyrene

For the functionalization of polystyrene we used three different processes :

Process 1 : Polystyrene swells in SO_2 and gives an emulsion. When the solution of "B" is poured rapidly into a well stirred emulsion of polystyrene in SO_2 at -40°, we observed a partial precipitation of polymer. After 30 minutes, the mixture was poured into methanol (Run a,b Table 1) and the polymer was filtered. The fraction soluble in benzene (60%) is the poly p-(methylthio)carbonylstyrene, the other insoluble part is a crosslinked polymer (40%).

Process 2 : The polystyrene emulsion in SO_2 was added slowly to a solution of thiocarboxonium (B) ; the polystyrene becomes soluble in SO_2 as the reaction progresses (Run c, Table 1). After 30 minutes the solution was poured into methanol to precipitate the poly p-(methylthiocarbonylstyrene. After filtration, the polymer was freeze dried in benzene.

Process 3 : A solution of polystyrene in CH_2Cl_2 was cooled to -30° and added dropwise to the solution of "B". After 30 minutes, the solution was poured into methanol (Run d, Table 1).

IV - Hydrolysis of poly p-(methylthio)carbonylstyrene

1,12g of polythioester was refluxed for 5 hours in 20 percent sodium hydroxide solution. The poly(p-sodiumoxycarbonylstyrene) became soluble. The solution was acidified, and the precipitated polymer filtered and dried under vacuum.

Results and discussion

To determine the ratio of functionalization we used ^1H NMR. ^1H NMR spectra were carried out with a 250 MHz Cameca apparatus (Table 2). The aromatic protons of styrene units show broad signals at 7 ppm and 6.4 ppm, while the aromatic protons of functionalized styrene units show two broad signals at 7.6 ppm and 6.4 ppm typical of AA' coupling of substituted aromatic hydrocarbons. At 2.45 ppm we have the signal of the protons of the methylthioester groups. Using integration of the peak areas the percentage of functionalization is calculated.

Elemental analysis confirms the ^1H NMR results. By gel permeation chromatography we could check that the reaction took place without degradation. The polymers kept the same narrow molecular weight distribution after functionalization. When we used process 1, 40% crosslinking is observed. Nevertheless, the soluble fraction is 84% modified (Run b, Table 1) under the best conditions. With process 2 the polymer became soluble as the modification proceeded ; we found no crosslinked polymer, but we observed less modification : 75%.
To obtain a complete functionalization (98% ; Run d, Table 1), without crosslinking, we had to use a good solvent for polystyrene : CH_2Cl_2, and dropwise addition of the polymer solution to the complex solution.

To confirm the para substitution of the polystyrene, ^{13}C NMR spectra were recorded on a Brucker apparatus

Run	SbF_5 [a)] mole	CH_3F [a)] mole	COS [a)] mole	Process [b)]	Polystyrene [c)]	Cat/PS [d)]	% soluble [e)] polymer	% thioester units [f)] in soluble polymer
a	0,046	0,055	0,060	1	0,092 in SO_2	0,5	60	25
b	0,045	0,050	0,070	1	0,045 in SO_2	1	60	84
c	0,032	0,040	0,050	2	0,025 in SO_2	1,28	100	75
d	0,049	0,054	0,056	3	0,035 in CH_2Cl_2	1,4	100	98

a) in 100 cc SO_2
b) different processes used (see text)
c) in 100 cc SO_2 or in 100 cc CH_2Cl_2. $\overline{M_n}$ of polystyrene = 18 100.
d) ratio of thiocarboxonium and polymer unit concentrations
e) percentage of soluble polymer in benzene after reaction
f) percentage of functionalized units in soluble polymer.

Table 1 : Thioesterification of polystyrene

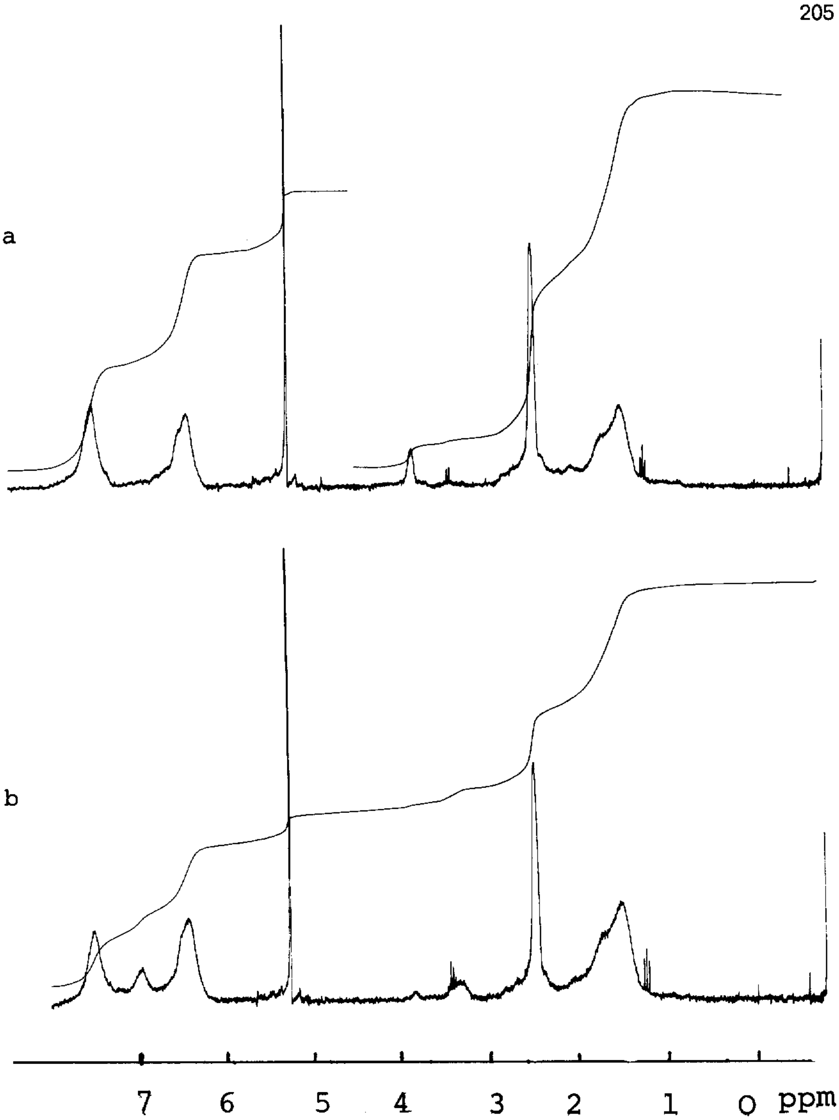


Table 2 : ^{1}H NMR spectrum of poly (p-methylthio)carbonylstyrene

a) 98% functionalyzed

b) 84% functionalyzed

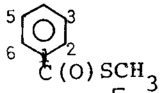
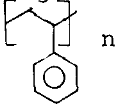
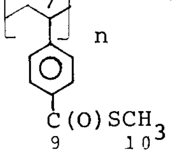
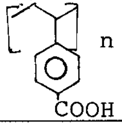
structures	carbon atoms	1	2	3	4	5	6	7	8	9	10
	δ_{exp}	137	128,6	127	133,2	127	128,6				
	$\Delta\delta^{a}$	+8,5	+0,1	-1,4	+4,7	-1,4	+0,1				
	δ_{2exp}	125,7	128	128	145	128	128	40,4	40-48		
	δ^{b}_{cal}	134,2	128,1	126,6	149,7	126,6	128,1				
	δ_{exp}	135,2	127,3	127,3	149,7	127,3	127,3	40,7	40-48	191,6	11,7
	δ^{c}_{cal}	127,8	129,5	127,8	150,2	127,8	129,5				
	δ_{exp}	128,7	129,3	127,6	150,4	127,6	129,3			167,2	

Table 3 : ^{13}C NMR chemical shifts of the modified polymers, in $CDCl_3$ are given in ppm with TMS as internal reference.

a : $\Delta\delta = \delta_{exp} - \delta_{benzene}$ $\delta_{benzene} = 128,5$ ppm

b : calculated chemical shifts $\delta^{b}_{cal} = \delta_{2\ polystyrene} + \Delta\delta_{C_6H_5COSCH_3}$

c : calculated chemical shifts $\delta^{c}_{cal} = \delta_{polystyrene} + \Delta\delta_{C_6H_5COOH}$ given in ref. 4

at 90 MHz. The chemical shifts of different units are given in Table 1. To confirm the assignments of the chemical shifts of the thioester polymer, we prepared methyl benzene thiocarboxylate $C_6H_5-C(O)-SCH_3$. We have calculated the $-C(O)SCH_3$ substitution effects and -COOH effects on the chemical shifts of polystyrene benzene carbon. Theoretical and experimental values are in good agreement (Table 3).

To conclude, the synthesis of a poly p-(methylthio)carbonylstyrene and a poly(p-carboxystyrene) were achieved by an original modification of polystyrene. The electrophilic substitution with S-methylthiocarboxonium is easily carried out in one step (process 3) and the substitution took place solely in the para position. The poly(p-carboxystyrene) is soluble in methanol ; its sodium salt is soluble in water.

References

(1) K.W. Pepper, H.M. Paisley, M.A. Young
J. Chem. Soc., 4097 (1953)

(2) J.T. Ayres, C.K. Mann
Polymer letters vol. 3 p. 505 (1965)

(3) G.A. Olah, M.R. Bruce, F. Clouet
J. Org. Chem. 46, 438 (1981)

(4) D.F. Ewing
Organic Magnetic Resonance, Vol. 12 n°9 p. 499 (1979)

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