

Preparations of 4-(2-chloroethyl)styrene, 4-(2-chloroethyl) α -acetoxystyrene and 4-(3-bromopropyl) α -acetoxystyrene

Preliminary studies of their corresponding polymers and copolymers

Jean-Pierre Monthéard*, Marcel Camps, and Belabbas Benayad

Laboratory of Organic and Macromolecular Chemistry, Faculty of Sciences and Techniques, 23, rue du Docteur Paul Michelon, F-42023 Saint-Etienne Cédex 2, France

Summary

Functionalized styrenes such as 4-(2-chloroethyl)styrene, 4-(2-chloroethyl) α -acetoxystyrene and 4-(3-bromopropyl) α -acetoxystyrene have been synthesized in two steps from commercial products and a preliminary study of their polymerization and copolymerization has been carried out.

Introduction

Chloromethylated polystyrene resins are used for the preparation of polymer-support reagents¹⁾²⁾ but the activity of catalysts is often less than that of soluble catalysts and also they are not always stable in acidic or basic medium³⁾⁴⁾ because of the presence of benzylic linkages. To improve on these disadvantages, some new polystyrenes, with a spacer between the active site and the polymer backbone have been synthesized by chemical modifications of polystyrene³⁾⁵⁾⁶⁾⁷⁾ or by polymerization or copolymerization of a functionalized styrene: Tomoi and al⁸⁾ have prepared a mixture of meta and para isomers of 4-bromobutyl or 7-bromoheptylstyrene. from commercial chloromethylstyrene. To study the influence of the chain length on the reactivity or on the stability of functionalized polymers, we need pure isomers in para position and therefore we have investigated easy methods of preparation of functionalized monomers and polymers. Some bromoalkylated styrenes: 4-(2-bromoethyl)styrene⁹⁾ and 4-(4-bromobutyl)styrene¹⁰⁾, have been previously described but their syntheses were quite difficult. We propose a two-steps method of synthesis for 4-(2-chloroethyl)styrene, 4-(2-chloroethyl) α -acetoxystyrene, 4-(3-bromopropyl) α -acetoxystyrene. A preliminary study of their polymerizations and copolymerizations is also given.

* To whom offprint requests should be sent

Experimental

Molecular masses of polymers were measured with a Knauer apparatus and Ultra Styragel column 10⁴ Waters (0,7 ml/min). Polystyrene standards were used for the calibration. The glass transition temperatures were measured with a D.S.C. 101 Setaram : Mass sample 10-15 mg heating rate 10°C/min. ¹H NMR and ¹³C NMR spectra were recorded using respectively a Perkin-Elmer Hitachi R-24 (60 MHz) and a Brücker (75 MHz) apparatus. Samples of monomers or polymers were dissolved in CDCl₃ (5 % and 15 % weight/volume for ¹H and ¹³C).

Preparation of 4-(2-chloroethyl)styrene

Condensation of ethylene oxide with the Grignard compound of 4-chloromagnesium styrene I, using a process previously described¹¹⁾ gives 4-ethanolstyrene II which was transformed in 4-(2-chloroethyl)styrene IIIa with carbon tetrachloride and triphenylphosphine¹²⁾.

The global yield, from 4-chlorostyrene is close to 40 %. By reaction of carbon tetrabromide, triphenylphosphine in acetonitrile¹³⁾ as a solvent 4-(2-bromoethyl)styrene IIIb is also synthesized with a over-all yield of 47 % from 4-chlorostyrene.

Preparation of 4-(2-chloroethyl)α-acetoxystyrene VIIa and 4-(3-bromoethyl)α-acetoxystyrene VIIb.

Friedel-Crafts acylations of commercially available 2-chloroethylbenzene Va and 3-bromopropylbenzene Vb with acetyl chloride and AlCl₃ as a catalyst have been carried out in carbon disulfide¹⁰⁾. Yields are close to 75 % and ketones VIa and VIb have been characterized by IR and ¹H NMR spectroscopy : ν C=O = 1675 cm⁻¹ ; resonances (ppm) of CH₃CO at 2,5 (s). Enol esters VII a and VIIb have been prepared by heating ketones, isopropylacetate with p.toluensulfonic acid as a catalyst using the process described for the preparation of α-acetoxystyrene VIIc from acetophenone¹⁴⁾. Enol esters and ketones have similar boiling points (VIa : Bp°C 106-110 at 0,07 mbar ; VIb : Bp°C 138-140 at 0,07 mbar) and in spite of a careful bidistillation they contain less than 10 % of the starting ketones. Overall yields from Va,b for VIIa,b are respectively 35 and 25 %. NMR spectra (¹H) of monomers IIIa, VIIa,b are given in the table 1.

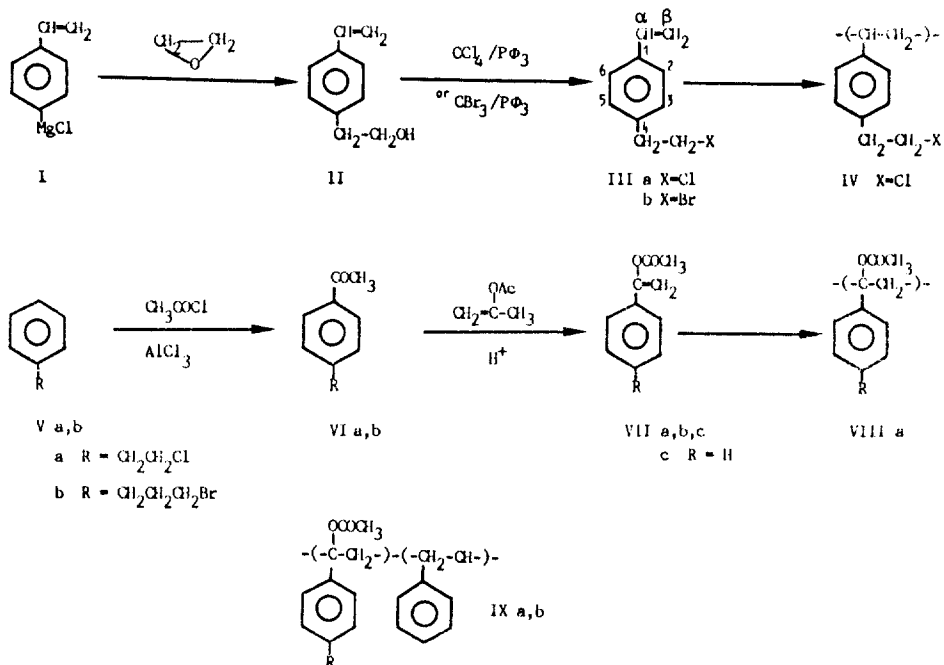


Fig 1 : Preparation of monomers and (co) polymers

Table 1 : Chemical shifts in the ^1H NMR Spectra of IIIa, VIIa and VIIb

	III	VIIa	VIIb
$-\text{CH}_2-\text{CH}_2\text{X}^*$	3,05 (t)	3,1 (t)	1,9 (t)
$-\text{CH}_2\text{X}^*$	3,7 (t)	3,9 (t)	3,4 (t)
$\text{CH}_2-\text{CH}_2-\text{CH}_2\text{X}^*$			2,7 (t)
$-\text{C}=\text{CH}_2$	5,2 and 5,75 (2d)	5,1 and 5,6 (2d)	4,8 and 5,4 (2d)
$\text{CH}=\text{CH}_2$	6,62 and 6,72 (2d)		
OOCCH_3		2,2 (s)	2,2 (s)
Ar^{**}	7,2-7,8 (m)	7,1-7,6 (m)	7-7,4 (m)

$\text{X}^* = \text{Cl}$ for III and VIIa and Br for VIIb $\text{Ar} = \text{aromatic protons}$

s = singlet, 2d = pair of doublets, t = triplet, m = multiplet

NMR spectra (^{13}C) of III, VIIa,b,c are given in the table 2.

Table 2 : Chemical shifts in the ^{13}C NMR spectrum of III and VII a,b,c

	IIIa	VIIa	VIIb	VIIc
α	136,42	152,72	152,83	153,09
β	113,55	101,86	101,46	102,01
C_1	137,64	138,98	141,48	134,46
$\text{C}_2 + \text{C}_6$	129,95	125,04	124,97	124,90
$\text{C}_3 + \text{C}_5$	126,36	129,05	128,68	128,68
C_4	136,19	132,91	132,21	128,98
$\text{C}_4 - \text{CH}_2 -$	39,79	38,76	33,64	-
$-\text{CH}_2\text{X}^*$	44,79	44,64	33,86	-
$\text{CH}_2 - \text{CH}_2\text{X}^*$	-	-	32,94	-
OCOCH_3	-	20,86	20,85	20,61
OCOCH_3	-	168,93	168,83	168,75

* X = Cl for III and VIIa, Br for VIIb

Preparation of polymers and copolymers

The syntheses of polymers or copolymers were performed in a sealed tube, in bulk using a free radical initiator (Azo bis isobutyronitrile, AIBN, 2 % in weight) but the duration of the reaction is different for polymerization of IIIa and for polymerization of VIIa and VIIb.

a) preparation of poly 4-(2- chloroethyl)styrene

After 24 hours of heating at 70°C, the content of the tube (90 % of yields) is poured in chloroform and separated by filtration of insoluble polymers (55 %). The soluble part is precipitated by methanol and dried (35 % of yield).

b) polymerization and copolymerization of VIIa

The monomers, with initiator, is heated during two weeks at 65°C. The solidified product is dissolved in chloroform and precipitated by pentane and dried (yield 38 %).

The same method was used for copolymerization of VIIa with styrene (yield 52 %).

c) copolymerization of VIIb

VIIb could not be homopolymerized but copolymerized with styrene (1/2,7) by heating with AIBN during two weeks at 65°C. Yields, molecular masses, polymolecularity and glass transition temperature are given in table 3.

Table 3 : Yields, Molecular Masses, Polymolecularity and glass
Transition temperature of IV, VIIIa, IX a, b

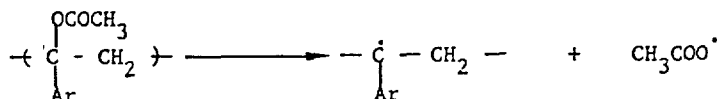
(Co) Polymers	Yields %	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	Tg °C
IV *	35	63000	85000	1,35	84
VIIIa	38	59000	115000	1,95	91
IXa	52	30000	102000	3,4	no visible Tg
IXb	53	9000	46000	5,1	130

* soluble part

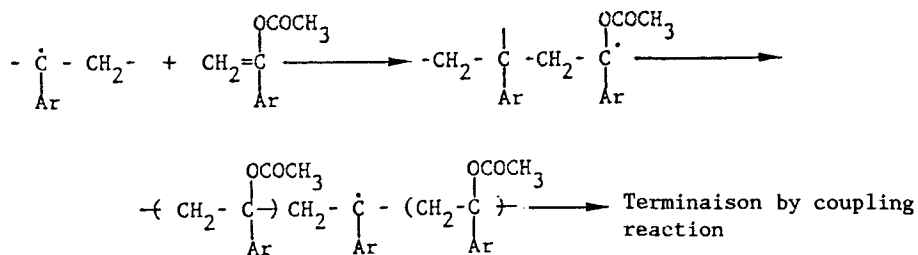
Infra-red spectra, microanalyses of polymers and copolymers are in good agreement with the attempted structures.

Results and Discussion

Polymerization of 4-(2-chloroethyl)styrene, 4-(2-bromoethyl)styrene¹⁵⁾ gives chiefly insoluble products unless the reaction is of short duration. It is probably due to a chain transfer to the benzylic hydrogen followed by a cross-linking reaction. To avoid this problem with the two enol esters (VIIa and VIIb) we have employed a long time polymerization as for α -acetoxystyrene VIIc, two weeks at 65°C¹⁶⁾. The structure of corresponding polymer has been studied¹⁷⁾; the main structure of the product result from a normal reaction but examination of ^1H and ^{13}C NMR spectra have suggested transfer reaction as described below (Ar = aromatic nucleus).



The two new radicals can initiate a propagation reaction and the probable mechanism is given with a polystyryl radical.



These transfer reactions are minor but can explain why, after some days, all the initiator being consumed, the molecular masses were increasing. By using this procedure with enol esters (VIIa,b) we obtained soluble products (polymers and copolymers) without losses of halogen atoms and cross-linking reactions. However, the reactivity of monomer VIIb is low and we have obtained only copolymers with styrene. In spite of the fact that the bromine atom is more mobile than chlorine it would be better, in the future, to use only aliphatic chains with chlorine.

These products can have some applications : (co) polymers, VIIa, IXa,b are bifunctional compounds which could be used for various organic reactions such as support of catalysts and produce polyols by reaction of a strong base as it was done for a copolymer of styrene and α -acetoxystyrene¹⁸⁾.

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