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Preparations of methoxymethyl α methylstyrenes and 4-(2-chloroethyl) α methylstyrene

Preliminary studies of their cationic polymerizations and copolymerizations

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Summary

Three isomeric methoxymethyl α methylstyrenes have been synthesized from commercial products in two steps and the para isomer has been polymerized with a cationic catalyst. 4-(2-chloroethyl) α methyl styrene has been prepared from 4-chloro α methyl styrene in two steps. This substituted styrene can be polymerized and copolymerized with styrene by using a cationic catalyst.

Introduction

The applications of polymers to the field of microelectronics have been growing for the past few years. Many substituted polystyrenes such as polychloromethylstyrenes(1) and chloromethylated polystyrene(2) have been studied. More recently some poly para substituted α methylstyrenes such as poly 4-acetoxy α methylstyrene(3), poly 4-t-butoxy α methylstyrene(4) and poly halomethyl α methylstyrene(5) have been synthezised for such purposes. These polymers must have a good sensitivity to UV irradiation and phenolic or hydroxy groups which are blocked by acidic labile groups or halomethyl groups with a narrow polymolecularity. Two types of polymers can easily be synthesized from commercial products in three steps : poly methoxymethyl α methylstyrene and poly 4-(2-chloroethyl)α methylstyrene. Preparations of monomers and a preliminary study of their cationic polymerization are now going to be described.

Experimental

Molecular masses were measured with a Knauer apparatus and Ultra-Styragel columns 10^3-10^4 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°/min. ^1H and ^{13}C NMR spectra were recorded with a Brucker apparatus, with frequencies of 300 MHZ (^1H) and 75 MHZ (^{13}C). Vapor phase chromatography was performed with a Girdel 30 apparatus (capillary column 15 m long), N_2 as a vector gas.

Preparations of monomers

a) Methoxy methyl α methylstyrenes III a, b, c.

A typical run is described for the preparation of IIIc. To 3,8 g (0,166 A/g) of magnesium powder with an iodine crystal in 15 ml of anhydrous tetrahydrofuran (THF) are slowly added 29,5 g (0,147 M) of ether IIc with 50 ml of THF, prepared according to the procedure described by R. Arshady et al(6) from commercial 4 bromobenzylbromide Ic, under a stream of nitrogen. After addition is completed, the mixture is refluxed

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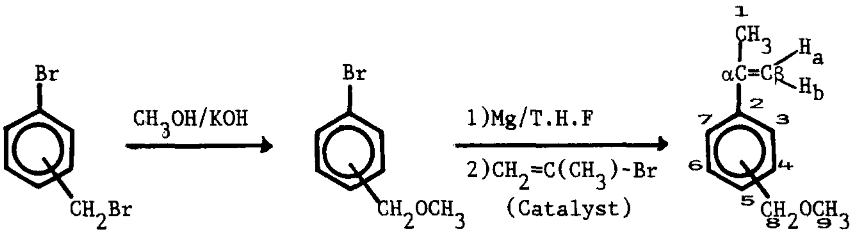
*To whom offprint requests should be sent while stirred for 30 min. then cooled in an ice bath and 20 ml of THF are introduced with 200 mg of Nickel Diphenylphosphinoethane Dichloride (Ni DPPE) as a catalyst for the coupling of Grignard compound and halogenated derivative. Isopropenyl bromide (17,79 ; 0,147 M) is slowly added in 30 ml of cold anhydrous THF. The mixture is stirred at room temperature for 20 hours and filtered on a Büchner, 70 ml of THF are evapored then the residual mixture is poured in a satured ammonium chloride solution (100 ml) and extracted with 3 x 50 ml of diethyl ether. After the drying and the evaporation of solvents, the 4-methoxymethyl α methylstyrene is distillated (bp 78-84°C at 1mbar). The same experimental procedures are applied to the preparations of IIIa and IIIb. Over-all yields from commercial bromobenzylbromides are close to 50 %. Vapor phase chromatography show less than 5 % of impurities.



Ia,b,c IIa,b,c IIIa,b,c

IV c

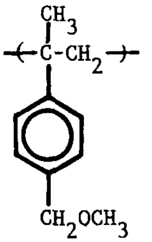


Fig.1:Syntheses of monomers methoxymethyl α methyl styrene and poly + methoxymethyl α methyl styrene IVc (a:ortho; b:meta; c:para).

b) 4-(2-chloroethyl) α methylstyrene

The 4-(2-hydroxyethyl) α methylstyrene has been prepared according to the previously described procedure(7)from the Grignard compound of 4-chloro α methylstyrene. To 6,48 g (0,042 m) of alcohol in 70 ml of anhydrous carbon tetrachloride are added 14,7 g (0,056 M) of triphenylphosphine. After 8 hours of heating at 75°C then cooled in an ice bath, triphenyl phosphine oxyde is precipitated by addition of 70 ml of petroleum ether. After the filtration and the evaporating of solvants the monomer is distillated at 85-90°C (1mbar) (Yield : 50%). These substituted styrenes IIIa, b, c andVII have been characterized by means of infra-red spectroscopy ; the frequencies of isopropenyl groups are close to 1630 cm^{-1} for the C=C bond, and 900 cm^{-1} for the = CH_2 bond in agreement with those observed by R.A Niquyst for various α methylstyrenes(8).

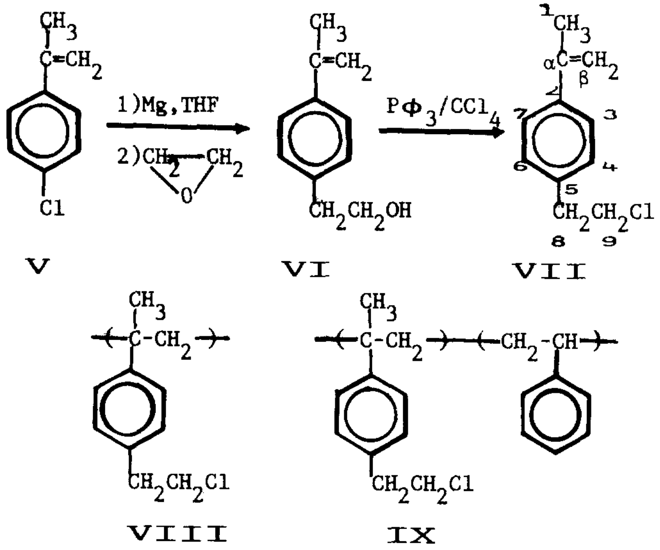


Fig.2 : Preparations of 4-(2-chloroethyl) α methyl styrene and corresponding polymers and copolymers.

The chemical shifts in ^{1}H NMR of monomers IIIa, b, c and VII are given table 1.

Table 1 : Chemical shifts in ^{1}H NMR spectra of monomers IIIa, b, c and VII.

	IIIa	IIIb	IIIc	VII
$\underline{CH_3}$-C=CH_2	2,02 (s)	2,08 (s)	2,07 (s)	1,71 (s)
-$\underline{CH_2}$ CH_2Cl				2,57 (t)
-CH_2-$\underline{CH_2}Cl$				3,21 (t)
CH_3O-	3,37 (s)	3,29 (s)	3,28 (s)	
-$\underline{CH_2}$-OCH_3	4,42 (s)	4,36 (s)	4,34 (s)	
H_a	5,38 (d)	5,02 (d)	5,02 (d)	4,66 (d)
H_b	5,78 (d)	5,34 (d)	5,33	4,98 (d)
Ar*	7,15-7,45 (m)	7,15-7,54 (m)	7,20-7,57 (m)	7-7,3 (m)

s = singulet d = doublet t = triplet Ar*= Aromatic protons
m = multiplet

The assignments of chemical shifts of monomers IIIa, b, c and V have been established by correlation with ^{13}C spectra of various substituted styrenes(3)(4)(9). The chemical shifts are given in table 2.

Table 2 : Chemical shifts in the ^{13}C NMR of IIIa, b, c and VII.

	IIIa	IIIb	IIIc	VII
C_1	25,12	21,34	21,27	21,35
C_2	144,52	140,94	137,04	139,24
C_3	134,72	126,34	127,16	128,32
C_4	128,78	137,75	125,05	125,27
C_5	127,42	124,37	140,07	136,91
C_6	127,83	127,85	125,05	125,27
C_7	126,94	124,39	127,16	128,32
C_8	72,32	74,23	73,84	38,37
C_9	57,92	57,49	53,37	44,50
C_α	143,44	142,68	142,47	142,33
C_β	115,12	112,11	111,84	111,83

Preparations of polymers IVc, VIII and copolymer IX.

a) Polymer IVc

To a solution of 1,34 g of monomer IIIc in 5 ml of dichloromethane at -78°C are added 0,8 ml of a 1 m solution of Boron trichloride in dichloromethane. After three hours the solution is poured in 30 ml of methanol and a white powder (0,45 g) is obtained after drying (Yield : 35 %).

b) Polymer VIII and copolymer IX

Polymer VIII is prepared by a similar method with the same proportions of catalyst. The product is wholly insoluble in organic solvents (Yield : 30 %). Copolymer IX is prepared after mixing equimolar proportions of styrene and monomer VII with Boron trichloride 1 M in dichloromethane. After three hours at -78°C, the yield is close to 60 %. The characteristics of polymers and copolymer IX are given in table 3.

Table 3 : Molecular masses, polymolecularity and Glass Transition Temperature.

	Mn	Mw	Mw/Mn	Tg °C
IVc	2600	6100	2,3	50
VIII	Insoluble	-	-	no visible
IX	3400	11500	3,38	no visible

Results and Discussion

If studies about substituted styrenes are not lacking methoxy methyl α methylstyrenes have only just described by Russian authors(10) : a mixture of para isomer and meta (90/10) was prepared through a chloromethylation reaction of 2-methyl 1-bromo ethylbenzene with carcinogenic chloromethyl methyl ether. They also studied the radical copolymerization of the mixture of isomers (11) (12) with methyl methacrylate, because the pure monomers could not be homopolymerized. By using a coupling reaction(13) between a Grignard compound and isopropenyl bromide our method enables us to obtain, in two steps from commercial products, pure monomers. The first essays of homopolymerization with Boron trichloride as a catalyst give new polymer with low molecular masses. 4-(-2 chloroethyl) α methylstyrene has also been synthesized in two steps, from 4 chloro α methylstyrene. By using a cationic catalyst, this new monomer gives an insoluble product because of the cross-linking reaction due to the formed carbocation of CH_2Cl groups with Boron trichloride. The cationic copolymerization with styrene enabled us to prepare a soluble product in which the percentage of incorporated monomer VIII is close to 70 % by calculation of the relative area of CH_2Cl in the ^1H NMR spectrum of copolymer IX. The copolymerization of these monomers with other cationic catalysts are now under study.

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