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Structure

Preparation and characterization of polymethoxymethylstyrenes ^1H-^{13}C NMR studies

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Summary

To study the influence of dipolar moments on the permittivity of polymers, three isomeric polymers ortho, meta and para polymethoxystyrenes have been synthesized. Physical properties and NMR studies ^1H and ^{13}C are described.

Introduction

In previous work, it was observed that the ϵ' values of a substituted polystyrene, in the side chain or in aromatic nucleus, could depend on the nature of polar group and on his position in the aromatic nucleus ; with a para substituted poly-α-acetoxystyrene, the variation of the permittivity can be related to the polarity of the substituent 1) and for poly (orthoacetoxymethylstyrene co-para acetoxymethylstyrene) and poly (meta acetoxymethylstyrene co-para acetoxymethylstyrene) the highest values of ϵ' were obtained with the ortho-para copolymer 2). In general, the permittivity of a polymer depends on the chain length and tacticity, but probably also on the nature and the position of the polar substituent.
To understand the variation of ϵ' values with the position of substituent three isomeric polymers, ortho, meta and para methoxymethylstyrenes have been synthesized. Preparations of monomers and polymers, characterizations and NMR studies are described.

Experimental

Molecular masses of polymers were measured with a Knauer apparatus and a ultra styragel column 10^4 Å Waters (0,7 ml/min). Polystyrene standards were used for the calibration. The glass transition temperatures were

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measured with a D.S.C. 101 Setaram : Mass Sample 10–15 mg, heating rate 10°C/min. ^1H (350 MHz) and ^{13}C (88 MHz) N M R spectra were recorded using a CAMECA 350 F.T. Samples of polymethoxymethylstyrenes were dissolved in $CDCl_3$ (5 % and 15 % weight/volume for ^1H and ^{13}C), respectively. Typical analysis conditions were for ^1H : tube diameter = 5 mm, pulse angle = 13°, acquisition time = 1,6 s, number of scans = 300 ; for ^{13}C : tube diameter = 8 mm, pulse angle = 40°, acquisition time = 0,8 s, repetition time = 1,3 s, number of scans = 15 000.

The three, ortho, meta, para, methoxylmethylstyrenes III a, b, c were synthesized as described in Figure 1, from the three commercial bromobenzylbromides I a, b, c. The bromobenzylethers II a, b, c were repared according to the procedure of R. Arshady and al 3). The yields were close to 95 %. The methoxymethylstyrenes III a, b, c were obtained by using the coupling reaction between the Grignard compound of bromoethers II a, b, c and vinylbromide with a transition metal catalyst : dichloro [1,3-bis (diphenylphosphonine) propane] Nickel as previously described 4).

The yields of this coupling reaction were close to 65 %. The three vinyl ethers III a, b, c were identified by means of ^1H N M R ; they exhibit resonances (ppm) of CH_3O at 3,2 (s) , $\underline{CH_2}OCH_3$ (s) at 4,35 , $\underline{CH}=CH_2$ between 7,2 and 7,6 (para isomer was first prepared by R. Arshady and al) 3).

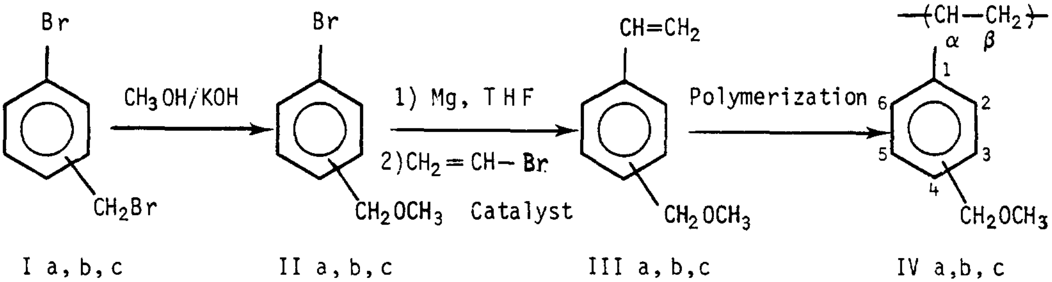

Fig. 1 - Syntheses of monomers methoxymethylstyrene III a, b, c and corresponding polymers. a = ortho b = meta c = para

The syntheses of polymers were performed in a sealed tube, in bulk, using a free radical initiator (Azo bis isobutyronitrile, AIBN) for the meta isomer III b or by thermal way for the para isomer III c ; the meta isomer, with initiator, 2°/₀₀ in weight, was heated during 48 hours at 75°C ;

the contents of the tube were dissolved in chloroform and precipitated with methanol. Each operation was repeated twice and the polymer was dried under vacuum until constant weight was attained. The procedure was the same for the thermal polymerization of para isomer, but the tube was heated during 48 hours at 100°C. For the ortho isomer III a, the rate of polymerization seems to be slow. First the monomer was heated during 48 hours with AIBN (2°/₀₀ in weight) at 75°C, then three days at 100°C to observe a solidification. Polymerization was, in fact, thermal. This phenomenon should be due to the steric hindrance between the vinyl groups and the methoxymethyl group. Yields, molecular masses and glass transition temperature are given in the table 1.

Table 1. Molecular masses, polymolecularity and glass transition temperatures of polymers

Polymers IV	Yields %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Tg °C
a ortho	27	63 000	160 000	2,54	69
b meta	71	60 000	238 000	3,96	29
c para	55	116 000	470 000	4,05	56

Results and discussion

In spite of a long drying under vacuum residual monomers are present in all the three polymers IV a, b, c . In ^1H as well in ^{13}C NMR, the ortho polymer presents the less resolved spectra. The proposed assignments of the ^1H and ^{13}C resonances are reported in tables 2 and 3. The calculation of the ^1H and ^{13}C approximate chemical shifts of the aromatic ring has been performed using the corresponding values of atactic polystyrene and the known substituent parameters of $-CH_2OH$ instead of methoxymethyl 5).

Table 2. Calculated chemical shifts (ppm) of atactic Polystyrene (P S) and Polymers IV a, b, c in ^1H N M R

	H_α	H_β	H_2	H_3	H_4	H_5	H_6
PS	1,95	1,5	6,6	7	7	7	6,6
IV a				6,93	6,93	6,53	6,53
IV b			6,53		6,93	6,93	6,53
IV c			6,53	6,93		6,93	6,53

^1H N M R. Aromatic resonances of para polymer IV c and meta polymer IV b are well resolved (H_2 + H_3) and (H_4 + H_5) while only one wide peak is found for the aromatic protons of the ortho polymer IV a. Methylene oxy and methoxy resonances that are obviously but insufficiently splitted by configurational effects, do not allow any calculation of the different stereosequences concentrations. The widening of all the resonances of polymer IV a should be due to the lack of chain mobility. It is worthy of note that only methoxy resonances emerge from the overlapped ones of $-OCH_2 + H_\alpha$

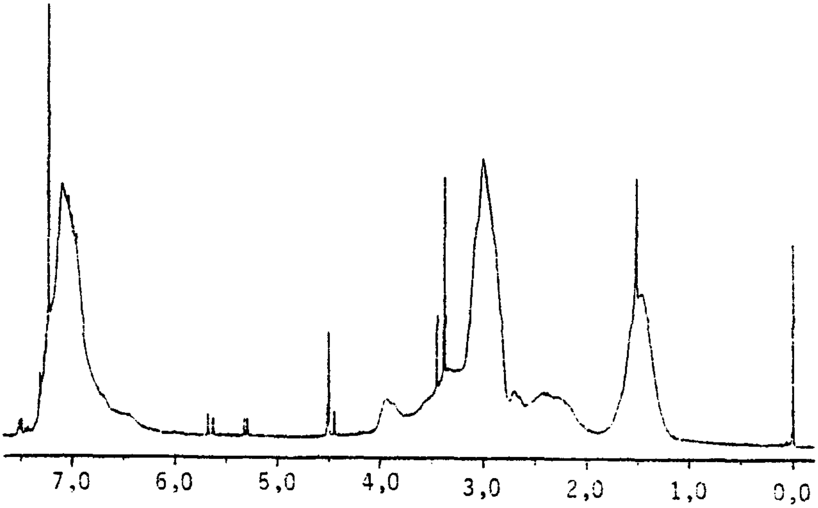

Fig. 2 - ^1H N M R Spectrum of poly ortho methoxymethylstyrene

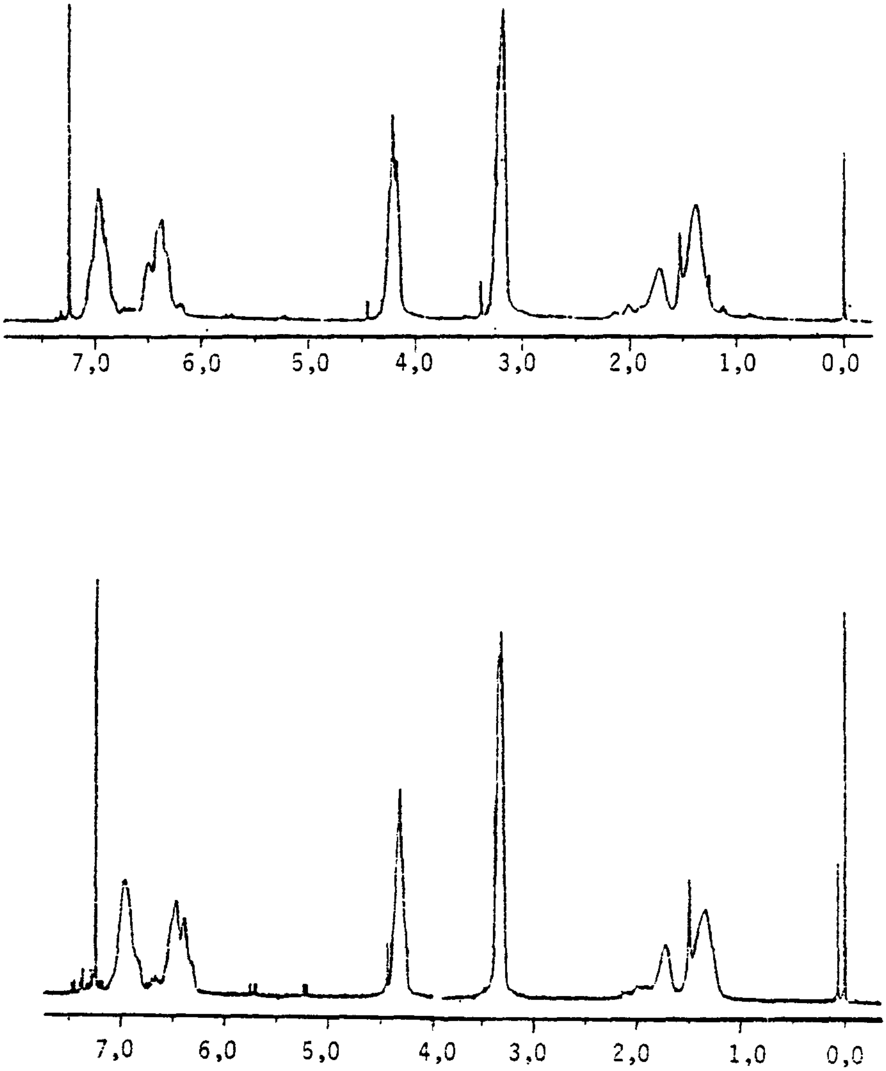

Fig. 3 - ^{1}H NMR Spectra of poly meta and para methoxymethylstyrenes

^{13}C NMR Spectra. Contrary to ^{1}H spectra, the quaternary carbons of the three polymers are sensitive to configurationnal odd sequences, but the tetrad configurations are only observed in the spectra of polymers IV c and IV b. Attentive examination of the two methoxymethyl carbons shows that only in the case of polymer IV a, the resonance of these two carbons are splitted by the odd stereosequences. Although no calculation of the tacticity has been attempted, radical or thermal propagation being bernouillan, it is believed that the three polymers obtained are atactic. Polymers IV b and IV c should be preferentially heterotactic : the strongest, C_1 (IV c) at 144,6 ppm, C_4 (IV c) at 135,6 ppm and C_1 and C_4 region. Polymer IV a should be preferentially syndiotactic ; the most intense line of C_α and C_2 are at the highest (34,3 ppm) and the lowest filed (136,4 ppm), respectively.

Table 3. Calculated chemical shifts (ppm) of atactic polystyrene (P S) and polymers IV a, b, c in ^{13}C N M R

	C_α	C_β	C_1	C_2	C_3	C_4	C_5	C_6
P S	40,8	40,5	146	128	128	125,9	128	128
IV a			144,6	141	126,6	125,9	126,8	128
IV b			146	126,6	141	124,5	128	126,8
IV c			145	128	126,6	138,9	126,6	128

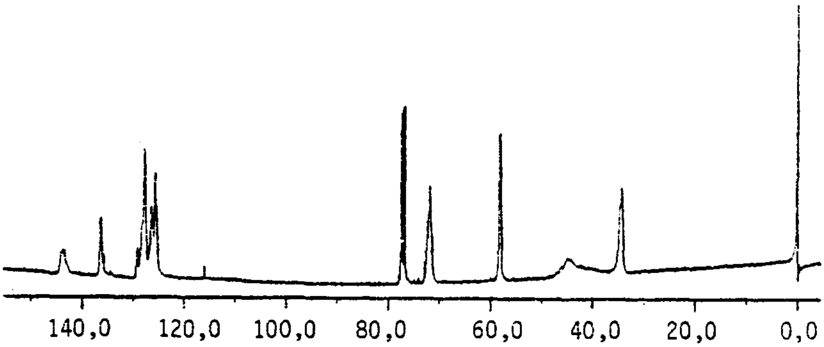

Fig. 4 - ^{13}C N M R Spectrum poly ortho methoxymethylstyrene

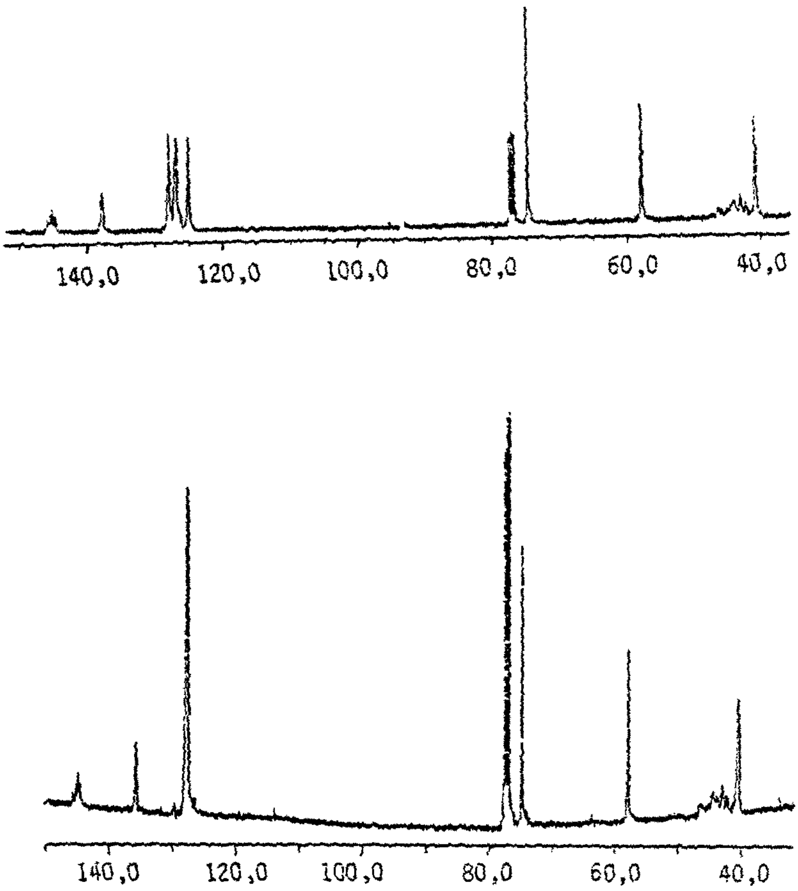

Fig. 5 - ^{13}C NMR Spectra of poly meta and paramethoxymethylstyrenes

In summary, the chemical shifts (^{1}H and ^{13}C) are given in table 4.

Table 4. Chemical shifts (^{1}H and ^{13}C) of polymers

		α	β	1	2	3	4	5	6	$-CH_2$	$-OCH_3$
IV a	^{1}H	2-2,6	1,5	-	-	6,5 ——	——	——	——7,5	3-4	3
	^{13}C	34	36-48	142-145	136	125			130	72,3	58
IV b	^{1}H	1,7	1,4	-	6,53	-	7	7	6,53	4,21	3,2
	^{13}C	40,8	42-47	144-147	126,8	137,9	125	128	126,8	74,7	57
IV c	^{1}H	1,73	1,34	-	6,4	7	-	7	6,4	4,34	3,32
	^{13}C	40,4	41,5-47	144-146	127,6	127,6	135	127,6	127,6	74,7	57,9

These three polymers have never been described except the para isomer which was copolymerized with styrene and divinylbenzene [3]. Dielectric studies of these compounds are now in course.

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