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New α-acetoxystyrenes with pendant ethylenic groups as crosslinking monomers

Copolymerization with styrene

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SUMMARY :

In order to prepare thin films of cross-linked polymers for non linear optic, the synthesis and copolymerization with styrene of two new styrenic enol esters have been carried out. Due to the difference of the reactivities of double bonds, copolymers with pendant double bonds have been prepared and cross-linked after heating in an oven for several hours.

INTRODUCTION :

In the last few years, a great number of works have been devoted to the syntheses and characterizations of polymeric materials exhibiting non linear optical properties (NLO) 1-4). These products are guest-host systems where the NLO dye is dispersed in a polymer matrix or polymers resulting either from the grafting of a NLO species or from the copolymerization of a functionalized monomer bearing the NLO dye. But, even when second-order linearity can be achieved through poling treatment of polymer films containing NLO chromophores, decay of the induced non linearity due to the local thermal motion of the oriented chromophores is observed. Various solutions have been studied by using cross-linking of the copolymers : thermally cross-linked epoxy system 5-6) or photo chemically cross-linked copolymer system with photoreactive NLO chromophores have been synthezised 7-8). New dienes have been recently described in order to prepare cross-linked polymers. 1,4-di isopropenyl benzene reacts slowly with styrene and twelve molar percents of this diene are used giving with styrene, a gel of a copolymer after twelve hours of heating at 65°C 9). Vinylbenzylchloride reacts in basic medium with potassium hydroxide 10) or with sodium sulfide 11) and provides a bis vinylbenzylether or a bis vinyl benzylsulfide. These two dienes have been homopolymerized and copolymerized. Di functional ethers, bis(4 isopropenyl phenoxy) alkanes have also been studied and photopolymerized 12).

But with all these dienes, except for 1,4 di isopropenyl benzene, the cross-linking reaction is generally fast and these dienes cannot be used in the NLO field which needs soluble polymers to prepare thin films of products. Therefore, we suggest using copolymerization reactions with dienes bearing low reactivity double bonds, able to give cross-linked copolymers after thermal reaction. The polymerization of α acetoxystyrene **2a** (R=H) has been previously studied 13-14). By using azobisisobutyronitrile (AIBN) as initiator, the

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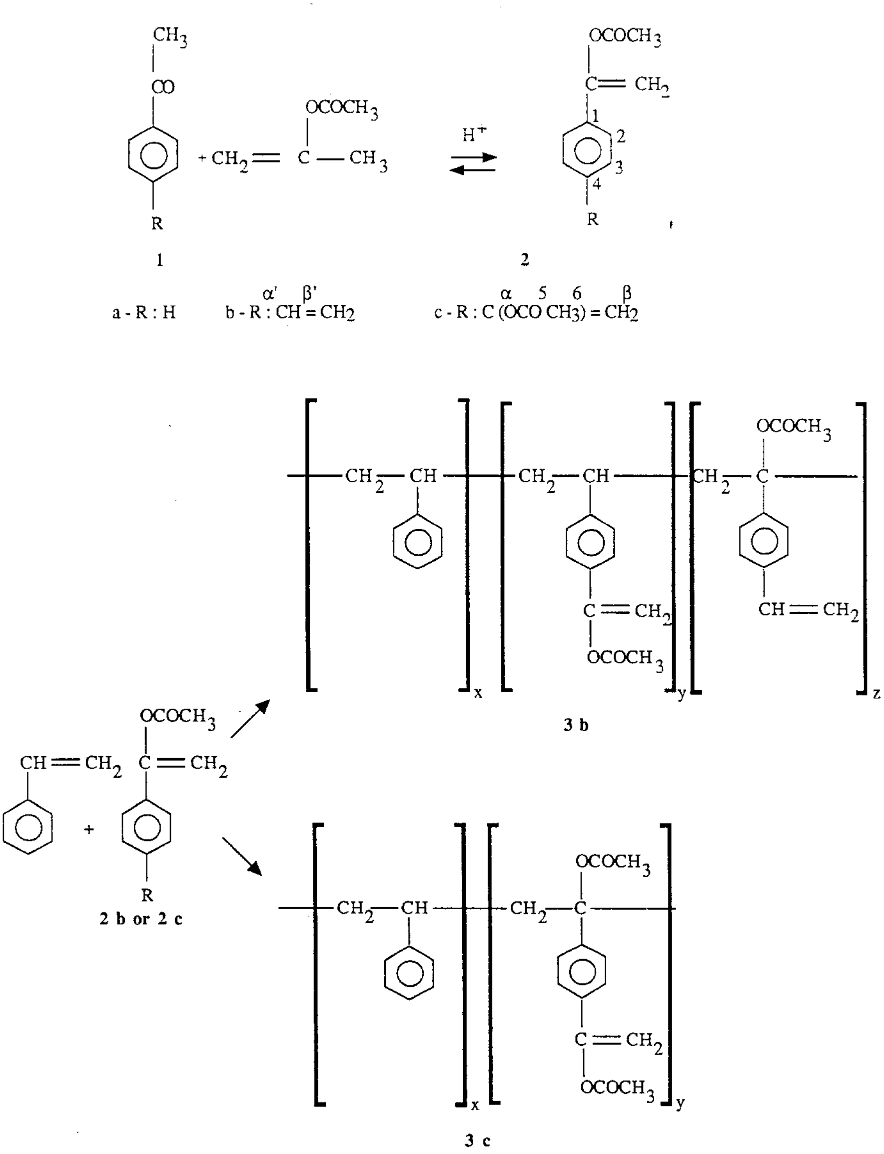
duration of the reaction is long (three weeks at 65°C) before obtaining an accurate yield and high molecular masses. The mechanism of the polymerization is in fact an equilibrium polymerization-depolymerization [15)]. Therefore, we have synthesized the two new derivatives **2b** and **2c** of α acetoxystyrene and studied their copolymerizations with styrene in order to prepare thin-films of cross-linked copolymers.



Scheme of the preparation of the monomers 2b and 2c and of the copolymers 3b and 3c.

EXPERIMENTAL :

Molecular masses of the copolymers have been measured with a Knauer apparatus and Ultra Styragel columns (10^3 Å, 10^4 Å, 10^5 Å) using tetrahydrofuran (THF) as solvent and monodisperse polystyrenes as standard. The glass transition temperatures have been recorded with a D.S.C. 92 Setaram using a sample mass of 10-15 mg and a heating rate of 10°C min^{-1}. The NMR ^{13}C spectra of monomers have been obtained in 15% (w/v) CD Cl_3 solutions (100 mg in 0,7 ml) using a Bruker AM 300 at 75, 469 MHz and at a temperature of 301° K. The IR spectra have been recorded with a FTIR 7PC Biorad apparatus. Thermogravimetric analyses have been performed with a Thermobalance G70 Setaram in programming heating runs at 10° C/min under helium flow, sample Mass 20 mg.

SYNTHESES OF THE MONOMERS :

Enol esters **2b** and **2c** have been synthesized by heating the corresponding ketones **1b** and **1c** with isopropenyl acetate in acidic medium according to a previously described procedure for the synthesis of α acetoxystyrene **2a** from acetophenone16) **1a**. Vinylacetophenone, has been prepared in two steps by a Friedel-Crafts acylation of 2 bromoethylbenzene 17), followed by dehydrobromination in basic medium 18). 1-4 diacetylbenzene **1c** is commercially available (Janssen Chemica). The global yields of the syntheses of enol esters **2b** and **2c** are close to 50%. The products have been purified by liquid-chromatography and characterized by IR spectroscopy and their ^{13}C NMR spectra (Tab. 1).

2b (liquid) ; 1759 cm^{-1} (C=O) ; **2c** (mp = 125°C) ; 1755 cm^{-1} (C=O)
1636 cm^{-1} (C=C) 1639 cm^{-1} (C=C)

Table 1 : ^{13}C chemical shifts assignments for the enol esters **2b** and **2c**

	2b	**2c**
C_1	133,51	134,72
C_2	126,35	125,03
C_3	124,99	125,03
C_4	138,12	134,72
C_5	168,90	168,94
C_6	20,84	20,89
C_α	152,63	154,28
C_β	101,98	104,28
$C_{\alpha'}$	114,58	
$C_{\beta'}$	136,12	

SYNTHESES OF COPOLYMERS :

The copolymers of styrene and enol esters **2b** or **2c** have been prepared by heating in bulk at 70°C under nitrogen atmosphere, 1g of styrene with **2b** or **2c** in molar proportions 99/1 with 1% in weight of AIBN as initiator. The durations of these reactions are given in Table 2. The copolymers have been purified by solubilization with chloroform and fractionation with methanol.

RESULTS AND DISCUSSION :

The structures of the copolymers **3b** and **3c** have been first studied by IR spectroscopy. The copolymer **3b** shows in IR spectroscopy two weak peaks at 1730 and 1759 cm^{-1} in fairly equal proportions. These peaks are referred to a satured carbonyl of ester (1730 cm^{-1}) and to a carbonyl of enol ester 1759 cm^{-1}. A further study by means of ^{13}C NMR could give the exact proportions of these two carbonyls. Similar observations for the copolymer **3c** show equal carbonyl absorptions in the range 1730 cm^{-1} (satured ester) and 1755 cm^{-1} (enol ester).

The Table 2 gives the characteristics of a polystyrene (PS) prepared during short periods (between 75 and 140 minutes with AIBN as initiator) and of copolymers of styrene with **2b** or **2c** during the same periods. An increasing of the molecular masses and of the ratio $\overline{Mw}/\overline{Mn}$ is observed for the copolymers **3b** and **3c**. After 105 minutes, the decreasing of this ratio is due to the high proportions of insoluble copolymer.

The glass transition temperatures of the witness polystyrene are normally in the range 95-100° C but those of the copolymers **3b** and **3c** are higher and respectively in the range 105-110 and 110-115 ° C. It may be explained by the ratio of cross-linking and by the relatively high masses of the copolymers. The Fig.1 shows the variation of the distribution of the molar masses for the copolymer **3c** versus the duration of the copolymerization. For the two copolymers, the cross-linking reaction is observed after 110 minutes of reaction.

Thermogravimetric analyses (TGA) have showed a weight loss at 125° C of 3% and 7% (weight percentage) respectively for the copolymer **3b** and **3c**. If the mechanism of degradation of these copolymers is similar to that of poly α acetoxystyrene, the weight losses are due to the elimination of acetic acid of the ester functions 16). These observations are in good agreement with a proportion of 5% and 6% (molar proportions) of incorporated enol esters **2b** and **2c**.

Thin films of copolymers **3b** and **3c** have been prepared from a solution in THF. After 12 hours of heating at 120° C in an oven, the copolymer **3b** is insoluble, but 48 hours at 120° C are necessary to obtain the insolubility of the film of **3c**. This insolubility results from the cross-linking reaction due to the pendant double bonds. The low percentages of incorporated dienes **2b** or **2c** explain that a cross-linking exothermic phenomenom is not observed in the D.S.C. runs. These runs have been preliminarily carried out to check that at the NLO polarization temperature (some degrees above Tg), the cross-linking reaction could not occur during the polarization. Studies of the terpolymerization of styrene, styrenic dye and **2b** or **2c** are now in progress.

Table 2 : Polymerization of styrene (S) and copolymerization of styrene with **2b** and **2c**. Measurements of the molecular masses ($\overline{Mw}$ and $\overline{Mn}$) and of the glass Transition Temperature Tg.

	Time (min)	$\overline{Mn}$ x 10^{-3}	$\overline{Mw}$ x 10^{-3}	$\overline{Mw}$ / $\overline{Mn}$	Tg° C
	75	28	43	1,53	95
	90	31	46	1,48	105
PS	105	33	50	1,51	98
	120	34	51	1,50	102
	140	35	54	1,50	94
	75	49	209	4,26	105
	90	43	222	5,16	111
3 b	105	64	246	3,84	105
	120	58	235	4,05	105
	140	54	170	3,15	111
	75	56	130	2,32	111
	90	77	211	2,74	95
3 c	105	80	309	3,86	113
	120	125	398	3,18	114
	140	71	226	3,18	114

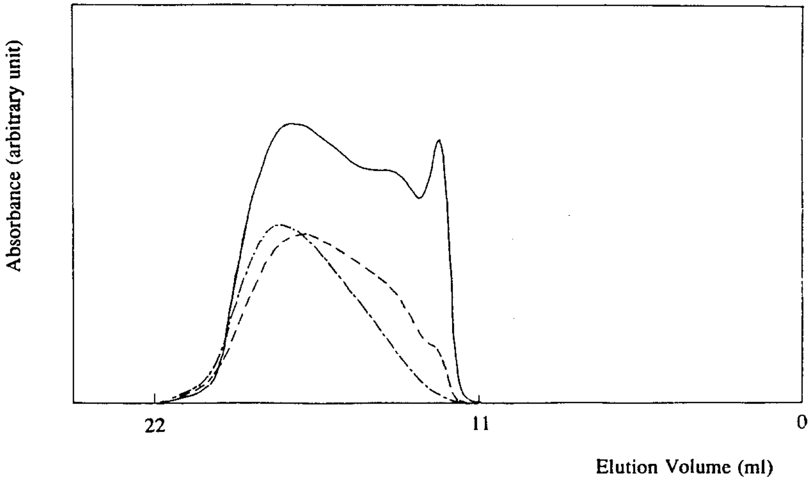


Fig. 1 : Elution curves of copolymer **3c** after 75 min (– . – . –), 90 (– – – –) and 105 min (——) of copolymerization time.

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