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Synthesis and Characterization of Copolymers Grafted with Oxirane

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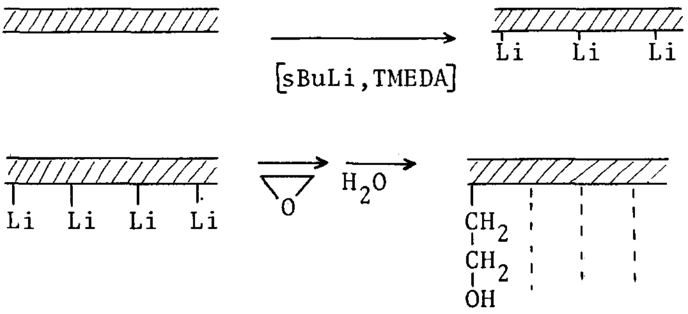
Introduction

The modification of a homopolystyrene, or of a styrene-isoprene copolymer, to introduce -OH groups is possible by several ways:

- metalation of the poly-p-bromostyrene, or metalation of the chloromethylated polystyrene (1 to 5) and grafting of a polyoxyethylene chain.
- oxydation of the metalated polystyrene with oxygen (6).

In this paper, we have used the metalation of the hydrocarbons by the Langer's complexes (7 to 15), but we have chosen the secondary buthyllithium to prevent the breaking of the chains which is observed with n.butyllithium. The use of sec.BuLi/TMEDA on the polystyrene at room temperature does not induce the degradation of the backbone. The deactivation of the polylithiated polymers and copolymers with oxirane produces polyalcoholates and polyols after hydrolysis. A study on a model molecule confirms the binding only one oxirane unit on the metalated sites:



Experimental

- Most of the experiments have been carried out under a purified argon atmosphere.
- Reagents: all solvents used have been purified by usual methods.

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the styrene-isoprene block copolymer has been prepared using sec.BuLi as the initiator, in cyclohexane. (styrene)/(isoprene) ≃ 2 at room temperature. r = (TMEDA/(secBuLi) = 0,7 , R = (TMEDA)/(monomer unit) = 1,4, metalation yield : 40%.

the polylithiated block copolymer precipitates in the cyclohexane solution, which is thermostated at 18°C. Oxirane is distilled in the mixture after cooling. (addition time : 30 minutes to 1 hour). The alcoholate grafts are treated wiht methanol. After decantation the alcoholic phase is poured into a large quantity of acidified water. The polymer is taken off the surface of the solution, purified by the usual procedure, and freeze dried. The results are summarized in Table 1.

Ref.	Backbone A/B	M_n	Monomers A+B=M	sBuLi M	TMEDA M	Metalation yield
Y 7	PI	2 000	0,16	0,17	0,4	13,5
Y 28	PI/PS 93/7 sta	10 000	0,4	0,9	0,6	40
Y 41	PI/PS 75/25 sta	15 000	0,4	0,77	0,53	40
Y 50	PI/PS 75/25 seq	15 000	0,4	0,75	0,53	40
Y 56	PI/PS 50/50 seq	15 000	0,4	0,8	0,56	30
Y 66	PS	2 000	0,4	0,75	0,53	30
Y 115	PS	15 000	0,19	0,38	0,27	36
Y 69	PBu/PS 80/20	180 000	0,4	0,75	0,53	43
Y 75	PS/PI 60/40 seq	20 000	0,4	1,2	0,6	52
Y 106	PS/PI/PS 40/120/40	220 000	0,4	0,55	0,38	47,5
Y 118	phenyl-butane	134,22	0,012	0,006	0,006	30

Table 1

The plot of the competitive metalation between styrene and isoprene units versus time in a styrene-isoprene copolymer is showed in Figure 1.

The structure of the modified copolymer have been determined by ^{1}H-NMR (Figure 2) and IR spectroscopy. The integration of the protons signals in α position to the oxygen (δ = 3,6) gives the yield in the hydroxyethyl unit; the integration of the signals of the protons (δ = 2,7) in the α position to the aromatic nucleus gives the yield of the functional unit bond to the nucleus. The difference between these values represents the yield of the functional unit bonded to the isoprene unit.

Results and discussion

It is possible with the complex secBuLi/TMEDA to metalate the copolymers and to have a high yield of functionalization better than those obtained previously by many authors (52%, ex. Y 75 in Table 1).

During 7 to 10 minutes, the metalation is carried out in homogeneous phase, but latter the polylithiated polymer precipitates and the lithiation then takes place in heterogeneous solution.

We have plotted the lithiation degree versus the total monomer units of a styrene-isoprene block copolymer (50/50, ex. Y 56 in Table 1). The lithiation degree of styrene block (curve A),and the lithiation degree of the copolymer (curve B)(Figure 1). We observe that during the beginning of the metalation, and that after this time, the metalation of the polyisoprene block proceeds. For exemple after 2 hours the yield of the copolymer metalation is about 22%. The degree of lithiation of the styrene block is 13% in relation to the total monomer units of the copolymer. The lithiation rate is faster in homogeneous phase than after the precipitation, in heterogeneous system. However after 4 hours the ratio of the styrene units metalation and the isoprene units metalation is about 2.

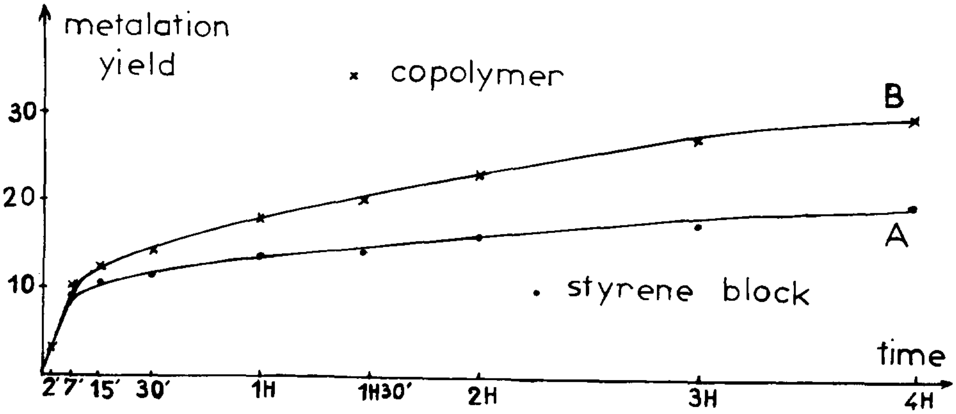

Figure 1 : The plot of the competitive metalation between styrene and isoprene in a styrene-isoprene blockcopolymer

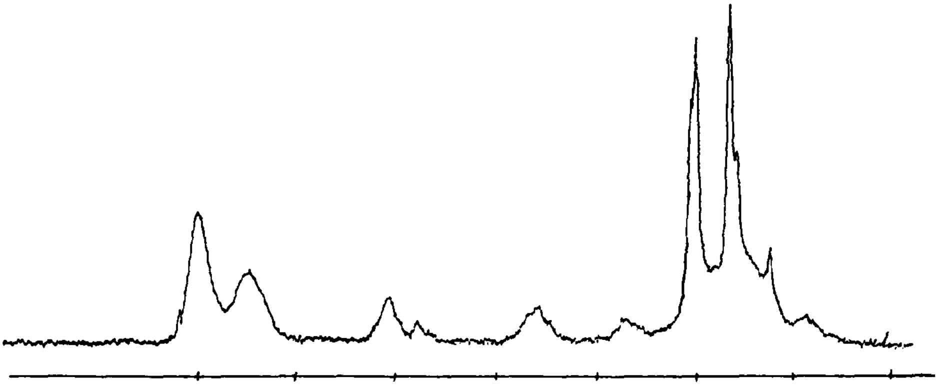

Figure 2 : ^{1}H-NMR spectrum of the modified block copolymer

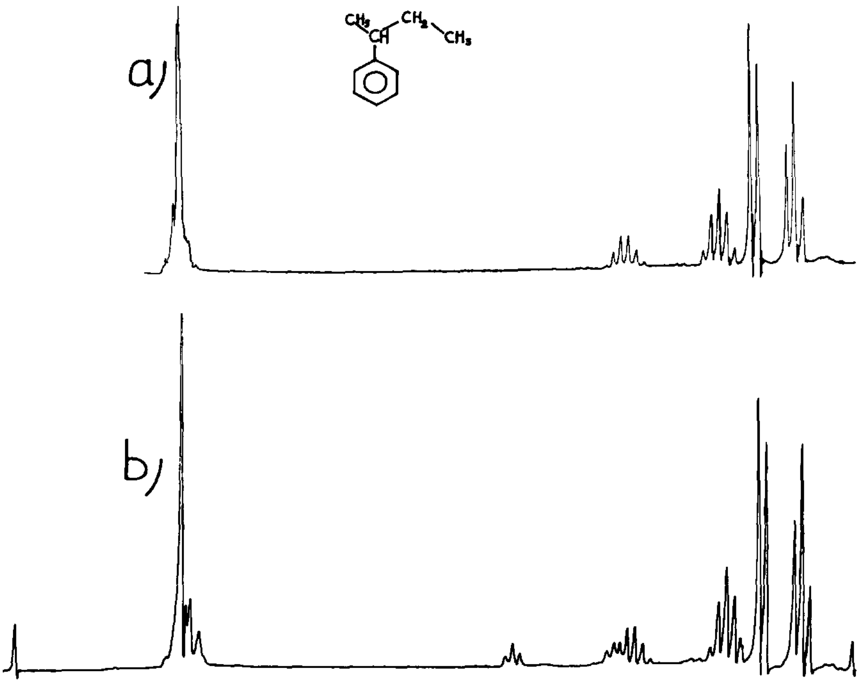

Figure 3 : ^{1}H-NMR spectra of the phenyl-2 butane
a) before reaction
b) after modification

The most important point, in this metalation reaction is that, for the low metalation times ($\simeq$7 minutes) only the styrene block is metalated. This is an exemple of a selective metalation between two metalation sites.

The study of the deactivation by the oxirane has been carried out on model molecule (Figure 3) the phenyl-2 butane preliminary metalated at 30%. The deactivation is quantitative. When the counter-ion is the lithium cation, there is no propagation, and only one monomer units is grafted per nucleus modified. The NMR spectrum of the grafted molecule, does not show the unsaturated allylic structures which are mentioned in the litterature when complexed (with TMEDA) living ends polyethylene are deactivated with oxirane, or when secBuLi/TMEDA is deactivated in the same way.

To conclude, the metalation of a styrene-isoprene block and the deactivation of the lithiated sites by oxirane, is an efficient way to carry out a selctive functionali zation of the styrene blocks.

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