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Synthesis of $\alpha-\omega$ unsaturated oligomers by chemical modification of dihydroxylated compounds

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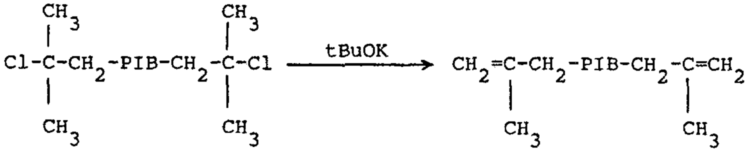
α - ω telechelic diacrylates or dimethacrylates are known and sold as low molecular weight monodisperse oligomers. But for α - ω distyrenic, and diallylic compounds, the object of this study, the situation is not the same.

Essentially only KENNEDY's team introduced unsaturations on extremities of polyisobutylenes (PIB) obtained with cationic catalysts. At first, the chloro isopropane extremity is selectively converted intom ethallyle structure in accordance with (1-2) :

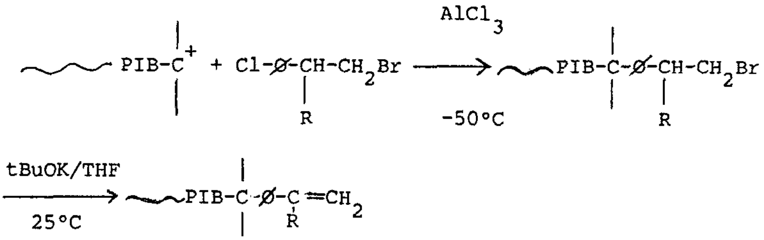


$$Cl-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-PIB-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-Cl \xrightarrow{tBuOK} CH_2=\underset{CH_3}{C}-CH_2-PIB-CH_2-\underset{CH_3}{C}=CH_2$$

With this dienes, the authors obtained diepoxydes (3) and diols (4). More recently, the same authors discovered a new method which consists in reacting living PIB with trimethylallylsilane (5), initiator of polymerization being the mixture :

$$CH_3CO_2-C(CH_3)_2-C_6H_4-C(CH_3)_2-O_2C-CH_3/TiCl_4$$

At last, KENNEDY et al. (6) realized Freidel and Craft reactions from living PIB and precursors based on styrene in accordance with :



$$\sim PIB-C^+ + Cl-\emptyset-\underset{R}{CH}-CH_2Br \xrightarrow[-50°C]{AlCl_3} \sim PIB-C-\emptyset-\underset{R}{CH}-CH_2Br \xrightarrow[25°C]{tBuOK/THF} \sim PIB-C-\emptyset-\underset{R}{C}=CH_2$$

These α - ω distyryl PIB are used to prepare multiblock copolymers with vinyl acetate or networks with N-vinylpyrrolidone, the PIB segments being hydrophobic and the others hydrophilic (7).

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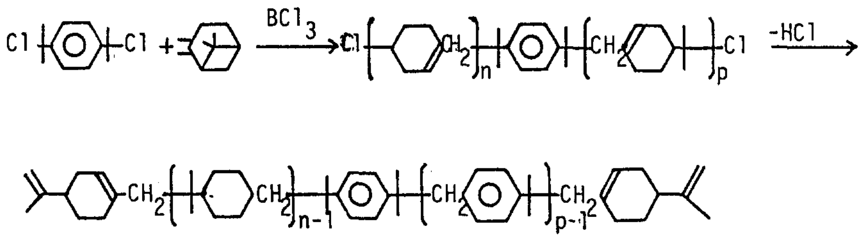
PERCEC and KENNEDY (8) used the phase transfert catalysis (PTC) reaction in order to introduce o.allyl groups like :

$$\sim\text{P-IB}\sim\text{OH} \xrightarrow[\text{Br allyl}]{\text{CTP}} \text{PIB-O-CH}_2\text{-CH=CH}_2$$

Other kinds of chains have been functionalised, like β pinedes (9) :



But silicone chains can also be converted (10) :

$$\text{CH}_2\text{=CH-C}_6\text{H}_4\text{-MgCl} + \text{Cl-}\overset{|}{\underset{|}{\text{Si}}}\text{-(O-}\overset{|}{\underset{|}{\text{Si}}}\text{)}_n\text{-Cl} \longrightarrow$$

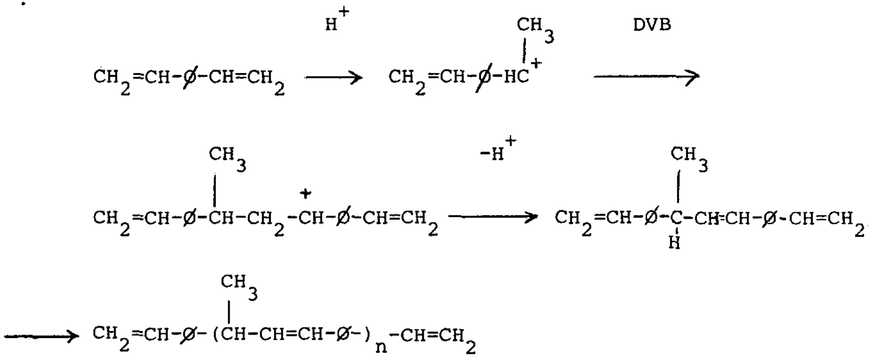
$$\text{CH}_2\text{=CH-C}_6\text{H}_4\text{-}\overset{|}{\underset{|}{\text{Si}}}\text{-(O-}\overset{|}{\underset{|}{\text{Si}}}\text{)}_n\text{-C}_6\text{H}_4\text{-CH=CH}_2$$

Likewise, polystyrene or polyisoprene obtained by anionic polymerization have been functionalised (11) :

$$2\ \text{R-}\overset{|}{\underset{|}{\text{Si}}}\text{-Cl} + \text{Na}^{+-}\ (\text{M})_n\ \text{Na}^{+} \longrightarrow \text{R-}\overset{|}{\underset{|}{\text{Si}}}\text{-(M)}_n\text{-}\overset{|}{\underset{|}{\text{Si}}}\text{-R}$$

$\text{R} = \text{CH}_2\text{=CH-CH}_2\text{-}$ et $\text{CH}_2\text{=CH-O-}$

At last, we note the case of polymerization of divinylbenzene induced by CF_3-SO_3H which leads to α - ω unsatured compounds and which has been described by HIGASHIMURA et al.(12) :



$$\text{CH}_2\text{=CH-Ø-CH=CH}_2 \xrightarrow{\text{H}^+} \text{CH}_2\text{=CH-Ø-}\overset{\text{CH}_3}{\overset{|}{\text{HC}^+}} \xrightarrow{\text{DVB}}$$

$$\text{CH}_2\text{=CH-Ø-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-CH}_2\text{-}\overset{+}{\text{CH}}\text{-Ø-CH=CH}_2 \xrightarrow{-\text{H}^+} \text{CH}_2\text{=CH-Ø-}\overset{\text{CH}_3}{\overset{|}{\underset{\text{H}}{\text{C}}}}\text{-CH=CH-Ø-CH=CH}_2$$

$$\longrightarrow \text{CH}_2\text{=CH-Ø-(}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-CH=CH-Ø-)}_n\text{-CH=CH}_2$$

Beside these particular functionalizations, we can note the use of chloromethylstyrene on α - ω bisphenols :

$$HO\text{-}\emptyset\text{-}p\text{-}\emptyset\text{-}OH \xrightarrow{Cl\text{-}CH_2\text{-}\emptyset\text{-}CH=CH_2} CH_2=CH\text{-}\emptyset\text{-}CH_2\text{-}O\text{-}\emptyset\text{-}p\text{-}\emptyset\text{-}O\text{-}CH_2\text{-}\emptyset\text{-}CH=CH_2$$

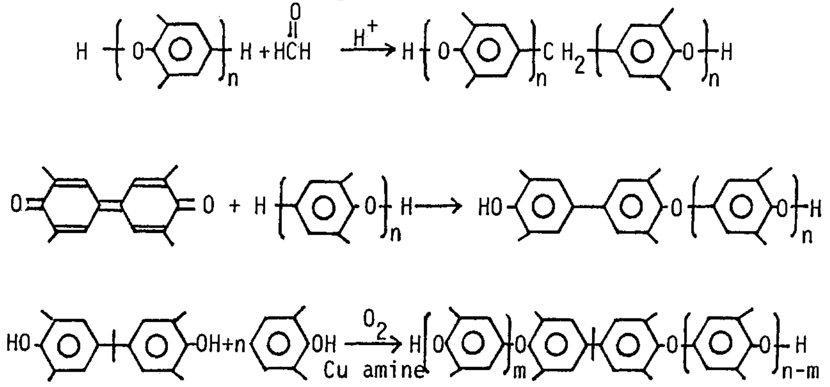
$P = SO_2, (CH_3)_2\text{-}C$

These bisphenols are prepared by many ways that we sum up briefly here :

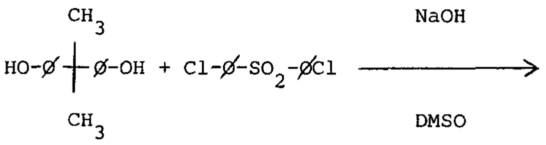
The polyformals (13,14)

$$HO\text{-}\emptyset\text{-}R\text{-}\emptyset\text{-}OH + CH_2Cl_2 \longrightarrow HO\text{-}\emptyset\text{-}R\text{-}\emptyset\text{-}O\text{-}(CH_2\text{-}O\text{-}\emptyset\text{-}R\text{-}\emptyset\text{-}O)_n\text{-}H$$

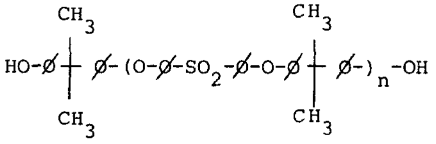
The poly 2-6 dimethyl 1-4 phenylene oxydes (15,16) :



The polysulfones (13) :



$$HO\text{-}\emptyset\text{-}\underset{CH_3}{\overset{CH_3}{\mid}}\text{-}\emptyset\text{-}OH + Cl\text{-}\emptyset\text{-}SO_2\text{-}\emptyset Cl \xrightarrow[DMSO]{NaOH}$$



$$HO\text{-}\emptyset\text{-}\underset{CH_3}{\overset{CH_3}{\mid}}\text{-}\emptyset\text{-}(O\text{-}\emptyset\text{-}SO_2\text{-}\emptyset\text{-}O\text{-}\emptyset\text{-}\underset{CH_3}{\overset{CH_3}{\mid}}\text{-}\emptyset\text{-})_n\text{-}OH$$

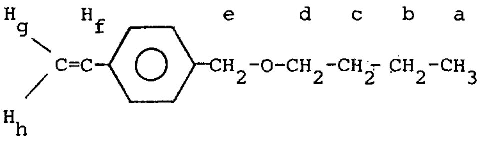
We note that essentially hard segments (aromatics) and PIB have been modified in order to introduce styryl groups into chain extremities SO, we focused on this type of functionalization applied to polyethers (polyethylene glycol and polybutylene glycol) and realized by PTC.

RESULTS AND DISCUSSION

At first, we started on model molecules in order to perfect the synthesis and determine precisely the spectrographic caracteristics of compounds. In this way, several experiments have been run with n-butanol, chloromethylstyrene (CMS) and a tetrabutylammonium hydrogenosulfate catalyst. Different solvents were used : benezene, chloroforme and dichloromethane.

With benzene the yield is low and the use of chloroforme leads to the formation of carbenes. The best conditions are obtained with CH_2Cl_2 and we note that the yield increases with the decrease in solvent concentration. So, we decided to operate without any solvent, the CMS being liquid.

The obtained product has the following structure :



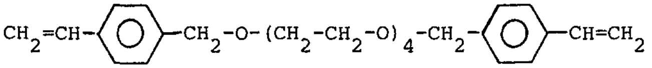
1

By ^1H NMR, the different protons are easily identified.

CH_3 (a)	$0,9.10^{-6}$ (triplet)
CH_2 (b)	$1,4.10^{-6}$ (multiplet)
CH_2 (c)	$1,6.10^{-6}$ (multiplet
CH_2 (d)	$3,5.10^{-6}$ (triplet)
CH_2 (e)	$4,5.10^{-6}$ (singlet)

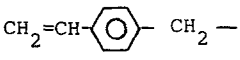
The three vinylic protons absorb at 5,2-5,7 and $6,7.10^{-6}$ in a classic manner for a styrenic group and the four aromatic protons take the form of a complex multiplet because the starting CMS is a mixture of 1-4 and 1-2 isomers.

We applied this synthesis to tetraethylene glycol (TEG) and we obtained a very good yield of product II :



2

In ^1H NMR, we find again rigorously the following segment at the same field :

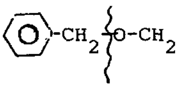


and the 16 H of TEG (large singlet at $3,6.10^{-6}$).

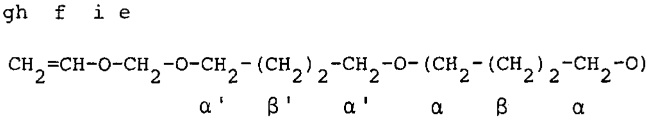
After, we used a polyethylene glycol (PEG) ($\bar{M}n=10^3$) in the same conditions. During 24 heures at 40°C and 600 r.p.m., we obtained product 3 with a yield of 50% of - distyrenic PEG.

$$CH_2=CH-C_6H_4-CH_2-O-(CH_2-CH_2-O)_n-CH_2-C_6H_4-CH=CH_3 \qquad \underline{3}$$

By GPC, we observe non reacted CMS (peak at 22,22 min.) while the product is identified at 18,62 min. and unreacted PEG at 18,42 min. It's difficult to explain this fall in yield but we think that the water solubility of the PEG makes it more vulnerable to basic attack (NaOH 50%) and that breaking of the following link occurs :



We ran the same reaction on a polybutylene glycol (PBG) ($\overline{Mn}$=650). In this case, we obtained the product **4** in greater than 90% yield.



$$\overset{gh}{CH_2}=\overset{f}{CH}-\overset{i}{O}-\overset{e}{CH_2}-O-\underset{\alpha'}{CH_2}-\underset{\beta'}{(CH_2)_2}-\underset{\alpha'}{CH_2}-O-(\underset{\alpha}{CH_2}-\underset{\beta}{(CH_2)_2}-\underset{\alpha}{CH_2}-O)$$

4

We can only observe the protons of the butylenic groups near the extremeties ($3,65.10^{-6}$ for α ' and $1,6.10^{-6}$ for β ', and those inside the chain. Polybutylene glycols are hydrophobic and we can conclude that nature of the chain has a large effect on yield.

CONCLUSION

α - ω unsaturated oligomers are obtained in a biphasic system using a phase transfert agent (tetrabutyl ammonium hydrogenosulfate), vigorous shaking and no heating. In accordance with this process, polyethylene and polybutylenes glycols have been modified and better yields are obtained with the second product. In fact, the partial solubility of oxyethylenic chain in water and the use of a strongly basic environment make possible the inverse reaction.

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