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Synthesis of new maleimide monomers having a perfluoroaliphatic side chain and study of their copolymerization with vinylethers

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Summary : A fluorinated maleimide has been prepared from fluorinated diol with monofluoronitrobenzene. All the intermediates have been perfectly characterized by N.M.R. The study also describes the synthesis of a copolymer from a commercial vinyl ether and this maleimide. Copolymerization is not perfectly alternated as we could expect but the copolymer exhibits a glass transition equal to 165°C.

INTRODUCTION

The research of new transparent polymers is a field of many investigations ; the most studied polymers are polystyrene (PS) and polymethylmethacrylate (PMMA). But the last one have too lower glass transition temperature so, it is impossible to use them for temperatures higher than 100°C. So, producers tend to modify these polymers by introducing stable functions as, for example, glutaramides [1,2,3,4] or by copolymerization between MMA and maleimides [5,6,7]. More recently, Wagener [8] and Buttler [9,10] developed new copolymers based on vinyl ethers. They studied their copolymerization with maleimides in order to obtain thermostable products. These non fluorinated polymers start to decompose around 270°C.

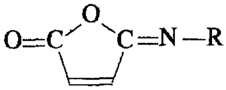
Our research concern the synthesis of new fluorinated maleimides and their copolymerization with common vinyl ethers.

RESULTS AND DISCUSSION

Commercial maleimides are not very numerous and the most often encountered are N phenyl or N methylmaleimide and more easily, maleimide. These products are prepared in a two steps process :

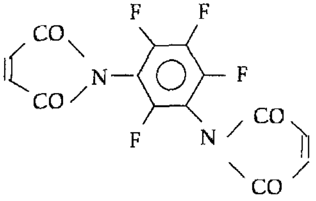
- reaction between an amine and an anhydride acid that leads to an amic acid [11]
- cyclisation of the last with deshydratants like P_2O_5 [12,13] or mixtures like CH_3CO_2H / CH_3CO_2Na [14].

The main problem of this technique is the formation of isoimides :

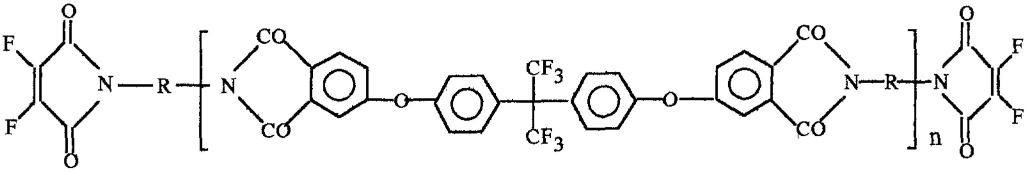


This by-product can be reduced in performing at low temperatures for the first step and moderate for the second one [14].

Concerning fluorinated maleimides, few products are present on the market. Monsanto Chemicals [15] developed :



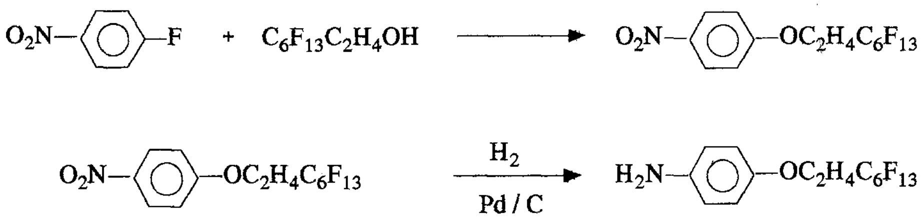
Similary, Green et al. [16] synthesized partially fluorinated bismaleimides with a low fluorine content :



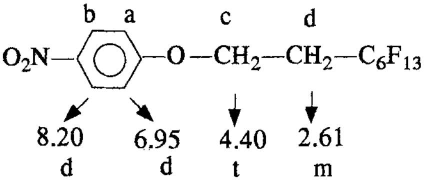
with n > 3

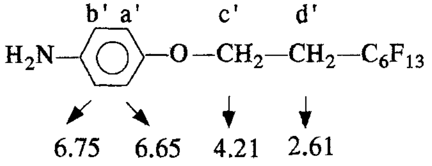
R : aromatic radical

Our work focuses on maleimide with perfluoroalkyl pendent group prepared by the classic process in two steps. In order to do that, we had to prepare a fluorinated amine. Reactional scheme is :



The first reaction is carried out by phase transfert catalysis in a basic medium ($NaOH/H_2O$) ; the reduction is achieved with hydrogen gas catalyzed by palladium supported on coal. Overall yield equals 40 % and product can be easily characterized by ^1H-NMR.

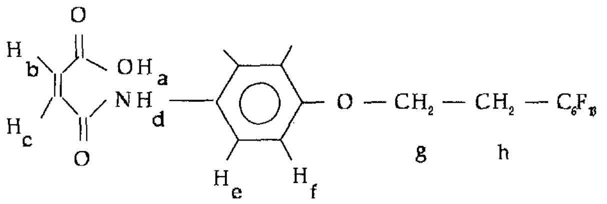




with t = triplet
d = doublet
m = multiplet

We note the aromatic protons are greatly modified when we change the electroattractive group (NO_2) to electrodonnor one (NH_2). In the first case, the NO_2 group deshields protons in ortho position. In the second one, the amine and ether groups are both electrodonnor so, the chemical shifts of the protons a and b are quite similar.

Amic acid is obtained with maleic anhydride in chloroform at -30°C and characterized by ^{1}H-NMR.



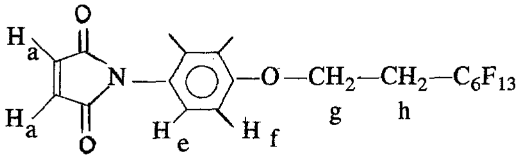
Protons	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h
Chemical shift (10^{-6})	13.00	8.35	8.45	10.50	7.50	7.00	4.30	2.70

Table 1 : NMR data on amic acid obtained with fluorinated amine

The amic acid presents characteristic bands coming from AB system where protons H_b and H_c display a very low difference in chemical shift.

Cyclization is conducted at 90°C in acetic anhydride with sodium acetate. Maleimide is isolated from precipitation in water and recrystallization from cyclohexane.

The ^{1}H-NMR characterization gives the following results :



Protons	H_a	H_e	H_f	H_g	H_h
Chemical shift (10^{-6})	7.00	7.35	7.10	4.45	2.70

Table 2 : NMR data on fluorinated maleimide

The purity of the maleimide can be controlled by chemical shift of typical maleimide protons H_a that appear as a singlet contrarly to the AB system present in amic acid structure. Protons H_e and H_f are weakly affected by cyclization. Furthermore, we note that reaction conducted according to these conditions does not produce by-products

Then, we try to copolymerize this maleimide monomer, (FM), with a commercially available vinyl ether = benzylvinylether (BVE) initiated by AIBN in tetrahydrofurane at 80°C under nitrogen atmosphere. Copolymerization was performed with a initial molar ratio maleimide / BVE of 0,5.

The reaction yield is 66 % and the product was characterized by elementary analysis and ^{1}H-NMR.

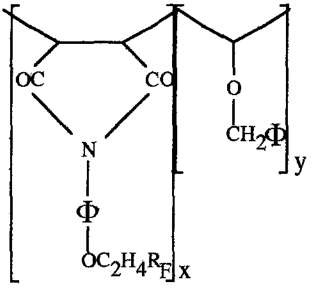
	% C	% H	% N	% F
Experimental data	44.03	2.48	2.42	42.32
Theorical data	48.43	2.98	2.09	36.92

Table 3 : Elementary analysis data on copolymer

We observe no agreement between obtained data and those coming from a theorical 50/50 % composition. Actually, both monomers are not able to polymerize and consequently, must copolymerize. In previous papers, it has been shown that vinyl ethers give a diadduct [17] only while maleimides give under U.V. conditions dimers only [18,19]. Characterization was confirmed by ^{1}H-NMR where the ratio between aromatic protons and protons coming from fluorinated chain permit to calculate the composition of the copolymer by the following equation :

$$\left(\begin{array}{rl} 4x+5y & = KH \\ 2x & = Kh \end{array} \right.$$

where H and h are integrations for maleimid aromatic and vinylic aromatic protons, respectively.



Moreover, we obtain x = 0.75 and y = 0.25 that leads to a copolymer wich contains three times folder fluorinated maleimide than vinyl ether. Thus, we note the important disparity between starting conditions and experimental conditions. That means that copolymerization is not perfectly alternated as we could expect for this kind of monomer.

Finally, we studied heat behaviour of this prepared copolymer. Actually, these products are glassy and could allow to obtain organic glass with interesting heat and surface properties in comparison with PS and PMMA which have too low glass transition and decomposition temperatures. Our copolymers exhibit a glass transition equal 165°C which is higher than those of PS and PMMA.

Concerning the decomposition temperature, we obtain the thermogram represented by the figure 1 :

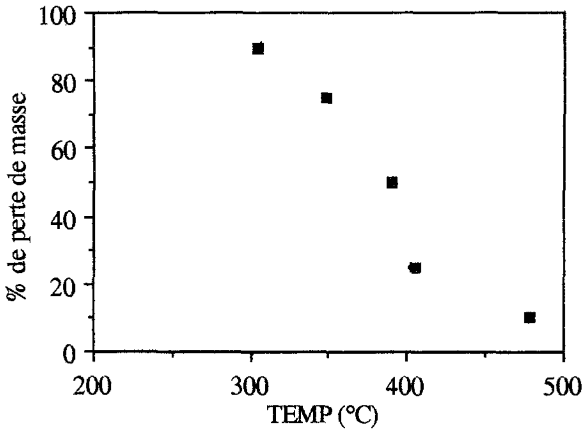


Figure 1 : Heat behaviour of FM/BVE copolymer (conditions = 10°c/mn under N_2).

So, we note that the polymer starts to decompose smoothly from 270°C and the decomposition is complete at 480°C.

CONCLUSION :

This study consists of preparing fluorinated maleimide from fluorinated amine and to copolymerize this monomer with vinyl ether. The amine is obtained in a yield of 40%. After copolymerization with benzyl vinyl ether, we note a desagreement between theorical composition and experimental composition. We can conclude that copolymerization is not alternated as we could expect for this kind of monomers unable to homopolymerize. First thermal study shows a Tg of 165°C and a starting weight loss at 270°C. Future works will consist of modifying the vinyl ether used in copolymerization and of studying the effect on thermal properties.

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