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Structural study by ^{1}H NMR of the first adducts of the telomerization of methylmethacrylate with thiophenol

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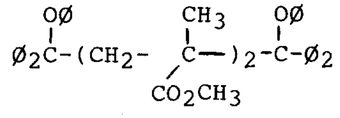
ABSTRACT

The stereoselectivity of the different steps (addition step and transfer step) of the radical telomerization of methylmethacrylate with thiophenol has been determined by preparing and analyzing the first adducts by ^{1}H NMR analysis.

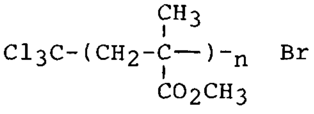
INTRODUCTION

The stereochemistry of radical polymerization of methylmethacrylate (MMA) was studied in several laboratories [1 to 9]. In these studies the ^{1}H NMR gave interesting information about the tacticity of methacrylic chains. However, all these analyses were performed on high $\overline{DP}_n$ materials which were polymolecular in order to enable treatment of the experimental data in terms of statistics. One could think that the individual analysis would be possible with "macromolecules" which only exhibit several methacrylic units. Thus, several laboratories have recently started the preparation and study of dimers and trimers of MMA. Balard et al. [10] obtained the diadducts 1 by radical reaction with tetraphenyl-1,1,2,2 diphenoxy-1,2 ethane and they identified the two diastereoisomers by ^{1}H NMR. However, the isomers ratio was not mentioned. Kimura et al. [11] prepared diadducts 2,n (n = 2) and triadducts 2,n (n = 3) by radical telomerization of MMA using bromotrichloromethane. The stereoisomers were characterized or identified, but the quantitative determinations concerned only the diadducts.



$\emptyset_2\overset{O\emptyset}{C}-(CH_2-\underset{CO_2CH_3}{\overset{CH_3}{C}}-)_2-\overset{O\emptyset}{C}-\emptyset_2$

1



$Cl_3C-(CH_2-\underset{CO_2CH_3}{\overset{CH_3}{C}}-)-_n\ Br$

2,n

These results did not give interesting information about the stereochemistry during the course of the reaction. Thus the objective is to perform a more complete study by preparing and analysing the first adducts of MMA with thiophenol with a radical initiation.

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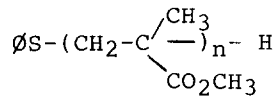
RESULTS AND DISCUSSION

The reaction between thiophenol and methylmethacrylate (MMA), initiated by azobisisobutyronitril (AIBN) was studied in order to analyze low DP_n telomers. This reaction was carried out in acetonitril at 79° C, with the ratios of [thiol] /[MMA] and [AIBN]/[MMA] equal to 0.30 and 0.02 respectively. Such a reaction led to a mixture of 3,n telomers which exhibited a $\overline{DP}_n$ of approximately 3. After evaporation of the solvent and non consumed starting materials, these telomers were obtained with yields higher than 90 %.



$$\text{ØS-}(\text{CH}_2\text{-}\overset{\text{CH}_3}{\underset{\text{CO}_2\text{CH}_3}{\text{C}}}\text{—})_n\text{- H}$$

3,n

The separation of first telomers was performed by chromatography using a column of partially deactivated alumina. The elution with pentan/diethylether of increasing polarity, was followed by GPC analysis. Using these conditions we obtained successively the 3,1 monoadduct and the 3,2, 3,3 and 3,4 telomers purely by chromatography.

Upon examining the structure of (3,n) telomers, it seems that there are as many asymetric carbon atoms as methacrylic units. Thus, a telomer with $\overline{DP}_n$ equal to n will be composed of a blend of $2^n/2$ diastereoisomers. For high n, it is impossible to distinguish the different diastereoisomers. However, for lower n, the number of diastereoisomers is limited (e.g. the number of diastereoisomers equals 8, 4 or 2 for n equal to 4, 3 or 2 respectively). Whether or not it is possible to separate the isomers, determination of spectrographic characteristics of each isomer is possible.

Monoadduct

This 3,1 monoadduct is composed of only one compound which is well characterized by mass and NMR spectra.

Diadducts

These compounds 3,2 exist as two diastereoisomers (threo and erythro) and the ^{1}H NMR spectrum confirmed a blend of two compounds in 2/1 ratio.

In that spectrum, we can notice the proton of the methylene group located between the two asymetric carbon atoms of each diastereoisomer. These protons are not equivalent and give an AB system doubled by terminal proton. As it is very often conducted on diastereoisomers the two asymetric centers of which are separated by a methylene group [12, 13, 14], the ^{1}H NMR analysis allowed us to identify the threo and erythro structures (respectively called r and m diads by polymerists). The difference, in the chemical shifts of the two protons of that methylene group ($\Delta\delta$) is only considered. In a diastereoisomer which exhibits a central symetry (threo), $\Delta\delta$ is smaller than that of the other isomer which has a planar symetry (erythro). In this case, we found $\Delta\delta$ equal to 0.34×10^{-6} and 0.68×10^{-6} for the major and minor diastereoisomers respectively. Thus, we can say that the former isomer exhibits a r structure whereas the latter, a m structure.

Triadducts

Due to the existence of four diastereoisomers a complete analysis of 3,3 telomers was difficult to perform. However it was carried out by separating the blend by chromatography on alumina column. The fractions we obtained were analyzed by ^{1}H NMR and according to the evolution during the separation, it was possible to identify the signal of each isomer. It was found that the protons of the methylene groups of each of the four stereoisomers were not equivalent. The central methylene groups act as AB systems centered at about 2.13×10^{-6} ; but those of the last diad appear as ABX systems, the AB part of which is centered at about 1.80×10^{-6} as was found for the 3,2 adducts.

As in the same case of 3,2 adducts, we identified the four structures by considering the chemical shifts of the protons of the methylene group of the chain. An important difference $\Delta\delta$ between the chemical shifts of the two hydrogen atoms of a methylene group means that this methylene belongs to a m diad. On the other hand the values of $\Delta\delta$ are small for r diads. With this criteria we can identify without ambiguity the mr, rr, rm and mm sequences with a knowledge of the stereochemistry of the diads in order of their molecular formation.

The relative proportions of the different 3,3 telomers were calculated from the mass and composition (deduced from the interpretation of the ^{1}H NMR spectra) of each previous chromatographic fraction. This calculation confirms that obtained directly from the ^{1}H NMR spectrum of the blend of the four isomers. The respective amounts of rm, rr, mr and mm diastereoisomers were 48.7, 25.7, 8.1 and 17.5 %.

Tetraadducts

We could not isolate the eight stereoisomers of the 3,4 adducts. However, each of them was characterized by chromatographic fractioning followed by ^{1}H NMR and 2D ^{1}H NMR analyses.

Therefore, the problem of the identification of the couples of protons of the methylene groups which belong to the second and the third methacrylic repeat units was solved by the ^{4}J coupling between these protons and their neighbouring α-methylene group. These long distance couplings allowed to establish the correct succession of the methylene and the methyl groups bound to the chain.

Similarly to 3,3 adducts, the stereochemistry of each 3,4 isomer was determined by considering the difference of the chemical shifts, $\Delta\delta_{(A-B)}$, between the protons of each methylene group $-CH_AH_B-$ of its structure.

These results permitted an analysis of the stereoselectivity of the different steps of the reaction. However, the two different processes, the addition of the growing radical on the MMA molecule and the transfer (capture of a proton of another thiol molecule by this radical) determine the stereochemistry of the sequence. These phenomena can be observed in table I which lists the different r/m ratios calculated from quantitative values obtained for 3,2 and 3,3 telomers. This table shows that the terminal radical is added on MMA to lead to a r diad preferentially. The r/m ratio which results from this addition does not depend upon the stereochemistry of the penpenultimate diad. Its value is about 3/1 in both cases. This conclusion is related to Kimura's one [11]. This author worked on radical telomerization of MMA with bromotrichloromethane. This statement confirms that which was deduced from the study of the tacticity of the PMMA prepared by radical initiation. The terminal diads obtained from the transfer step (capture of an hydrogen atom of the thiol) by the growing radical, are primarily m diads. The analysis of 3,2 and 3,3 telomers lead to a r/m ratio approximately equal to 1/2, independent from the stereochemistry of the penpenultimate diad.

The constancy of this phenomenon, in the case of 3,4 telomers was qualitatively verified.

The stereoselectivity obtained this way (for the transfer step) is different from that deduced from Kimura [11] who obtained a r/m ratio roughly equal to 3/1. However, in this case, the growing radical caught a bromine atom. Thus it could seem that the stereoselectivity of the last step is related to the nature of the attacked atom.

Table I : Stereochemistry of the formation of triadducts 3,3

Formation step	Stereochemistry of the penpenultimate diad	% r/m
Addition (of the third monomer)	without	74.4/25.6
Transfer	without*	33/67
	r	34.5/65.5
	m	31.6/68.4

* formation of the diadducts 3,2

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