

Polymeization of 1, 3- dioxolane by activated monomer mechanism in presence of 2- hydroxypropylmethacrylate (2-HPMA)

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ABSTRACT

Macromonomers of poly -1,3 (dioxolan) were synthesized, using the activated monomer method, which consists to polymerize 1,3-dioxolan in the presence of an unsaturated alcohol such as the 2 - hydroxypropylméthacrylate (2-hpma) (co- catalyst) and sulphuric acid (H₂SO₄) as catalyst. The reaction was carried out under atmosphere, the macromonomer obtained was characterized by NMR ¹H, UV, GPC and FTIR. The product yielded is useful, thereafter, as precursor, to the preparation of grafted copolymers. In order to obtain grafted copolymers, we have prepared series of macromonomer samples having each one a different number.-average molecular weight.

Key words: Polymeization of 1, 3- dioxolane and 2- hydroxypropylmethacrylate (2-HPMA).

INTRODUCTION

Contrary to the traditional starting of the heterocycles polymerization which occurs according to a tertiary oxonium mechanism¹ (ACE mechanism)¹⁻⁴ and which leads in a majority way, to the formation of macrocycles, method of starting by activated monomer mechanism (AM)⁷ leads, in great part, to the formation of linear polymers. By starting polymerization, of epoxides in the presence of diol (ethylene glycol) Okomoto and Penczek^{5,6} observed, indeed, a very small quantity of macrocycles when the molecular weight of awaited polymer is lower than 3000. Beyond this value, the concentration in macrocycles becomes important. Some authors³ observed a linear increase in the molecular weight with conversion. A poly (1,3-dioxolane) macromonomer was, thus, prepared by the method of the activated monomer, by starting the polymerization of the 1,3 - dioxolan in the presence of acid triflic (CF₃SO₃H) and an alcohol carrying a polymerizable unsaturation fonction as p- isopropenybenzlique⁷ alcohol.

In the present article, we extended the activated monomer mechanism to the synthesis of poly (1,3 - dioxolan) macromonomers by starting the cationic polymerization of 1,3-dioxolan in the presence of sulphuric acid as catalyst and, 2-hydroxypropylmethacrylate as co initiator, the yielded macromonomers were than characterized of by NMR ¹H, FTIR and UV.

EXPERIMENTAL

Materials

1,3 dioxolan Monomer - (Merck) is distilled and beforehand preserved cold. Before use, initiator (H₂SO₄), as well as, Co- initiator (2-hydroxypropylméthacrylate) are commercial products.

The reaction was carried out in solution in chloroform, under atmosphere during 5 hours. The poly (1,3 - dioxolane) is dried after precipitation in a solvent- no solvent mixture (chloroform- hexane). Spectra RMN¹H were recorded, at ambient

Table 1: The chemical shifts relating to the various protons of poly(1,3-dioxolane) and the group of oxypropylmethacrylate

groupement	a et b	c	D (d)	e	f	G (s)	h et h' (d)
δ ppm	5.6-6.14	1.24	4.11	3.75	1.90	4.90	3.37

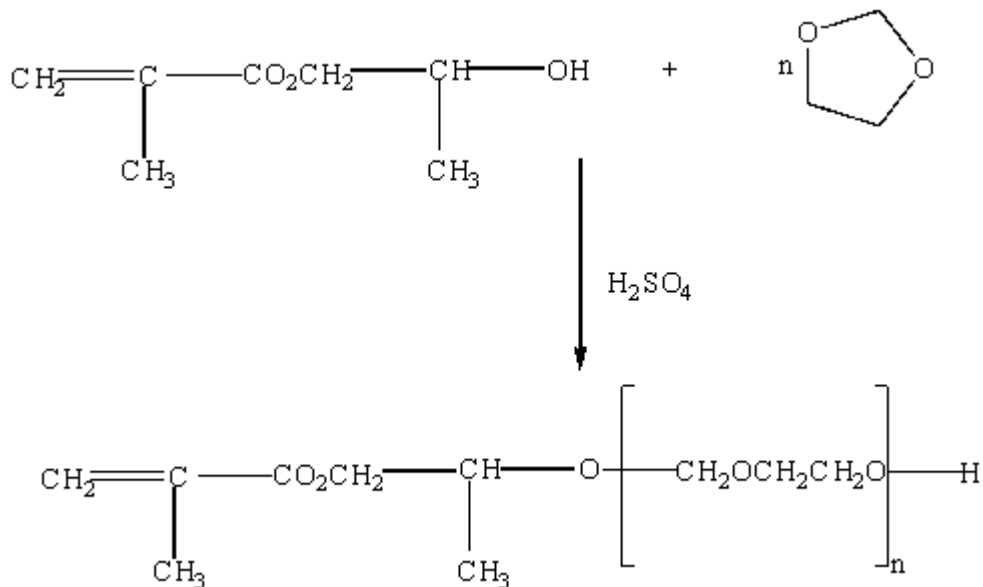


Fig. 1: Reaction scheme illustrating the routes for synthesizing 1,3 dioxolane macromonomer w-oxypropylmethacrylate

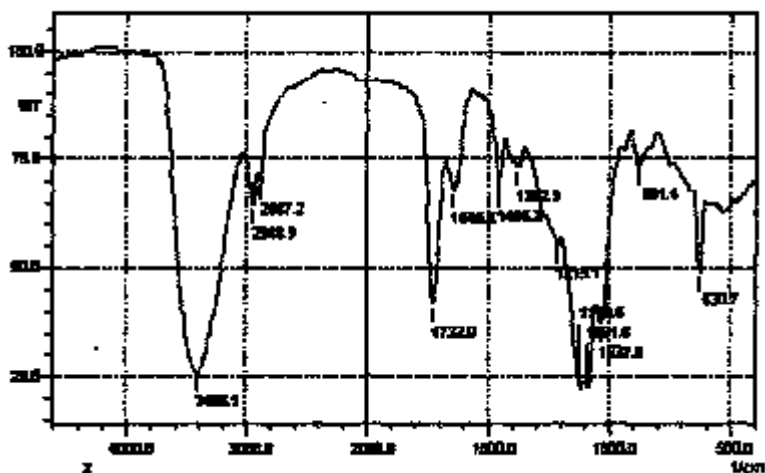
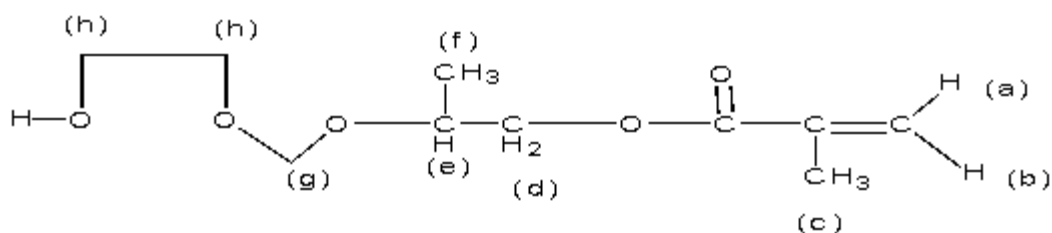


Fig. 2: The ir spectrum of a macromonomer of 1,3- dioxolanne ω- oxypropylmetacrylate

temperature, on an apparatus Bruker ARX 300. Spectra UV and FTIR were obtained respectively from SPECTRO- NIC. GENESYS 5 and SHIMADZU 2406 apparatuses. The coefficient of molecular extinction of the 2-hydroxypropylméthacrylate was given by calibration curve representing the variation of the optical density against to the concentration according to LAMBERT BEER's law using, the acetonitril as solvent ($\epsilon = 8463$, $\lambda_{\max} = 220$ nm).

RESULTS AND DISCUSSION

Starting the polymerization of the 1,3 - dioxolane by the sulphuric acid in the presence of 2 -hydroxypropylmethacrylate we obtained macromonomers bearing an ω oxypropylméthacryloyl end according to the reaction scheme:



Scheme 1

The products obtained, which must be used as precursors for the preparation of grafted copolymers, were characterized by some physical methods of analysis such as spectroscopy UV, nuclear magnetic resonance (RMN¹H) and FTIR spectroscopy.

Analysis by RMN¹H

After precipitation in a solvent - no solvent couple (chloroform- hexan), the product obtained was submitted to the RMN¹H analysis (200MHZ). The latter indicates the presence of the principal signals relating to the hydrogen atoms corresponding to the structure:

The analysis by RMN¹H of the sample M₁ thus shows, that they correspond well, each one, with a macromonomer of poly (1,3 -dioxolane) ω -oxypropylméthacryloyl.

Analysis by UV

Determination of the molecular weight of the macromonomer samples of (1,3-dioxolane) (M_n): With an aim of proportioning the quantity of 2-hpma represented by the double bond methacrylic connection being with the one of the ends of the chain, polymer of each macromonomer, we initially determined the molecular extinction coefficients, of compounds taken as models connected at the unsaturated ends, on the basis of the assumption that the absorption of chromophoric is independent of the nature and the length of chain. Starting from a calibration curve representing the variation of the optical density according to the concentration one thus obtains a curve which Suit the law of Beer Lambert and which enabled us to calculate the molecular extinction coefficient of the 2-

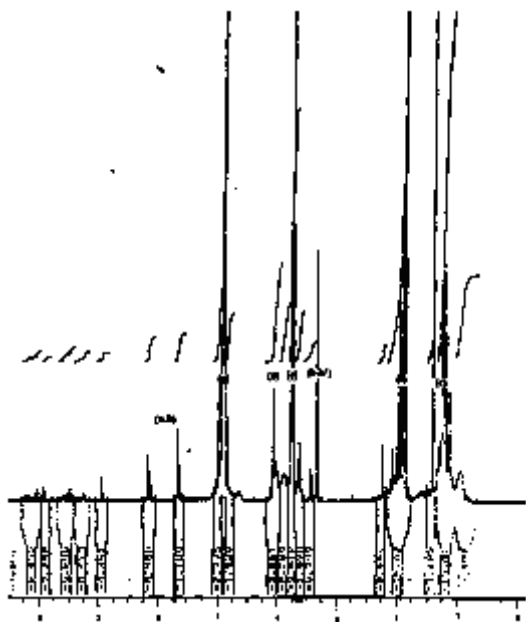


Fig. 2: H¹-NMR spectrum macromonomer poly(1,3-dioxolane) ω -oxypropylméthacryloyl. (solvent CDCl₃)

Table 2: The values of the average molecular weight of the samples of macromonomers determined by UV, by RMN ¹H and the average molecular weight determined theoretically

sample	Mn (UV)	Mn (RMN)	Mn (theoretically)
M ₁	384,68	401	389
M ₃	940,33	799	652
M ₄	1336,26	1258	1179
M ₅	3761,33	3090	3156

hydroxypropylmethacrylate taken as model ($\epsilon = 8463$ with $\lambda_{\text{max}} = 220$ nm in acetonitril). The coefficient of extinction molecular thus determined was used as a basis of calculation for the average molecular weight (Mn) of different macromonomers prepared, by admitting the assumption of one chromophoric per polymeric chain.

We observed that average molecular weight determined by UV is very close to those which were theoretically given or those determined by RMN¹H. These results enable us to suggest that the samples are linear, in addition, that this method can lead with efficiency to the fixation of a chromophoric group on the polymeric chain end. However, some authors⁸ showed that the starting of the dioxolane-1,3 polymerization, under these conditions, also leads to the formation of other linear species carrying, either two unsaturated end groups (bis- macromonomers), or α, ω hydroxyl final end (transacetalization reactions).

In the present study, following characteristic bands were observed: - an absorption band located between 3406,1 cm⁻¹ corresponding to a vibration of valence of grouping (- OH). - an absorption band located between 2948,9 and 2887,2 cm⁻¹ representing a valence vibration of the grouping (CH₃-CH₂). - an absorption band located between 1732 cm⁻¹ and 1645,2 cm⁻¹ correspondent to a valence vibration of the of grouping (C=O). - an absorption band located at 1456,2 cm⁻¹ representative a deformation vibration of of the grouping (- OH). - an absorption band located at 1382,9 cm⁻¹ corresponding to of deformation vibration of grouping (CH₃, CH₂). - an absorption band located at 1215,1 cm⁻¹ representing valence vibration of of grouping (C-O-C). - an absorption band located at 1118,6 cm⁻¹ corresponding to valence vibration of grouping (CO). - an absorption band located at 1091,6 cm⁻¹ representing with a valence vibration of grouping (C-O-C). - an absorption band located between 881,4 cm⁻¹ and 630,7 cm⁻¹ corresponding to a vibration of deformation of grouping (=C-H).

CONCLUSION

The analysis by RMN¹H, IR and UV of the various synthesized samples thus showed us that the starting of the polymerization of 1,3 - dioxolane by the sulphuric acid in the presence of the 2 - hydroxypropylmethacrylate led, according to a mechanism by activated monomer (AM), with the formation of a macromonomer at oxypropylmethacrylate end. The average weights of the macromonomers obtained were determined by the UV analyzes.

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