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Synthesis and Characterization of Bioactive Amphiphilic Graft Copolymers with Hydrophilic Poly (1, 3-dioxolane) Side Chains

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ABSTRACT

2-oxypropylmethacrylat termined poly (1, 3 dioxolane) macromonomers having various chain lengths, were prepared by cationic polymerization using H_2SO_4 as initiator. The end group is introduced via the termination (end capping) using 2-hydroxypropylmethacrylate (2-HPMA). The amphiphilic graft copolymer is formed by the hydrophilic poly (1, 3- dioxolane) side chain and hydrophobic poly 2-hyèdroxypropylmethacrylate backbone with various chain lengths, were synthesized by free radical copolymerization of poly (1, 3 dioxolane) ω- oxypropylmethacrylate in the presence of 2-hydroxypropylmethacrylate using benzyle peroxide as initiator.

Key words: Cationic polymerization; macromonomer; radical free copolymerization; Amphiphatic, Graft copolymers, Surface tension, poly (1, 3 dioxolane).

INTRODUCTION

The graft copolymers have received attention recently[1-3], they have many important application[4-10] in the polymer industry, mainly as surface modifiers for uses as coating, adhesives and dispersants; as compatbilizing agents in polymers blends, but also biomedical use. The amphiphilic graft copolymers are investigated widely because of their special physical and chemical properties and self assembly morphologies[11] in order to obtain amphiphilic graft copolymers with hydrophilic side chains of defined size, we have chosen a method using a precursory polymer[12-17].

EXPERIMENTAL

Materials

The monomers 1, 3 dioxolane (DXL prolabo) were purified by vacuum distillation, sulfuric acid (H_2SO_4, prolabo). The free radical initiator employed for the polymerization was benzyl peroxide

(Fluka) all solvents chloroform, diclorométhan, tetrahydrofurane and cyclohyxane, were purified by standard procedures.

Measurements

UV spectra were record on a Spectronic Gensys 5 spectrometry using chloroform as a solvent. FT, IR spectra were performed on a nocolet 520 by 4000- 400 cm^{-1}range spectrophotometer, the 1H-NMR and 13C NMR spectra of the polymers were recorded using Brucker DPX 300 MHZ spectrometer at room temperature, tetramethylsilane (TMS) is the internal standard. Viscosities of the polymer solutions (0,1- 1g/dl were measured with a capillary viscosimeter (ubbelhode viscosimeter).

Synthesis of poly (1, 3- dioxolan) macromonomers

1, 3- dioxolane is dissolved in 10 ml of freshly distilled chloroforme and placed under nitrogen atmosphere in a three- necked flask equipped with a condenser and magnetic stirring. The 2-hydoxypropylmehacrylate is added to the reaction mixture, the polymerization is terminated by introducing dimethylamine. The precipate is filtered off, washed with ether and dried in vacuum. The synthesis of a macromonomer of 1, 3-dioxolane is shown in scheme below.

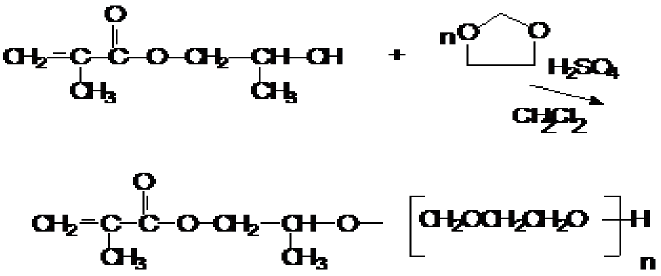

Table 1 list the experiment conditions of the reaction

Table 1: Experimental conditions and yields of cationic polymerization of 1, 3- dioxolane initiated by H_2SO_4

Product	[DXL] (mol/l)	[2HPMA] (mol/l)	[H_2SO_4] (mol/l)	[DXL]/ [2HPMA]	Rendement
BMD$_1$	12,550	0,658	0.025	19,07	86%
BMD $_2$	13,127	0,327	0.688	40,14	73%
BMD$_3$	12,550	0,344	0,125	36,48	78%
BMD$_4$	12,550	0,172	0,3546	72,96	82%
BMD$_5$	13,127	0,1635	0,456	80,28	88%

Preparation of the 1, 3- dioxolan graft copolymer

The polymerization is initiated by benzoyl peroxide. After 24 hours, the copolymer were precipitated into excess of cyclohexane in order to eliminate the poly(methylmethacrylate) homopolymer, dried under vacuum and dissolved in chloroform and precipitated again in water for eliminating the 1, 3-dioxolan monomer. The experimental condition is reported in Table 2.

RESULTS AND DISCUSSION

UV analysis of oxypropylmethacryloyle end chain

UV analysis is used; on one band (λ= 220 nm) to observe the fixation of chromophoric group oxypropylmethacrylate on the 1, 3- dioxolane end chain on the other hand to calculate number- average molecular weight Mn of the macromonomer.

Table 2: The experimental conditions of formation the copolymer 1, 3-dioxolane- g- 2- hydrpropylmethacrylate

$[P]_0$ Mole/l	$[M]_0$ mole/ l	[PB] mole/l	$[M]_0$ / $[P]_0$
0,124	0,07	$1,3.10^{-1}$	9,66
0,124	0,401	$0,061.10^{-1}$	3,23

Notes: [P]0: initial concentration of poly (1, 3- dioxolane) macromonomer calculated by UV analysis; [M]0: initial molar concentration of 2hydrxypropylmethacrylate comonomer; [PB]0: initial molar concentration on benzoyl peroxide initiator; Poly(DXL-g- 2HPMA); poly (1, 3-dioxolan graft poly methylmethacrylat), P(DXL- g-2-HPMA): poly 1, 3 dioxolane-g- 2-hydroxypropylmethacrylate.

Table 3: Numbers of average molecular weights of 1, 3-dioxolane macromonomers calculate from UV analysis (ε= 8643, λ=220 nm, solvent: dichloromethane)[17]

Product	$Mn_{\text{théorical}}$	Mn_{UV}
$M_{1,}$	1500	1500
M_2	2000	2000
M_3	2500	2500
M_4	3000	3000

Table 4: Number average molecular weight Mn of 1, 3- dioxolane macromonomers determined by viscosity ($K= 2,3\ 10^{-2}$, α=0,65, T= 25°C solvent: dicloromethane)

Macromonomer	Mn(viscosity)
M_1	1600
M_2	2100

By assuming, that only one of the chromophoric groups is attached to end polymeric chain and by using molecular extinction coefficient of molecular model, in this case, the 2-hydrxypropylmethacrylate (2-HPMA), we can calculate the molecular weight of our samples.

Thus, starting from a calibration curve representing the variation of the optical density according to the concentration of 2-HPMA in chloroforme. We have obtained a curve which follows BEER LMABERT's low, which can calculate the molecular extinction coefficient of 2-HPMA taken as model (ε=8463 at λ= 220 nm) in chloroforme.

The number average molecular weights calculated from UV analysis are listed in Table 3.

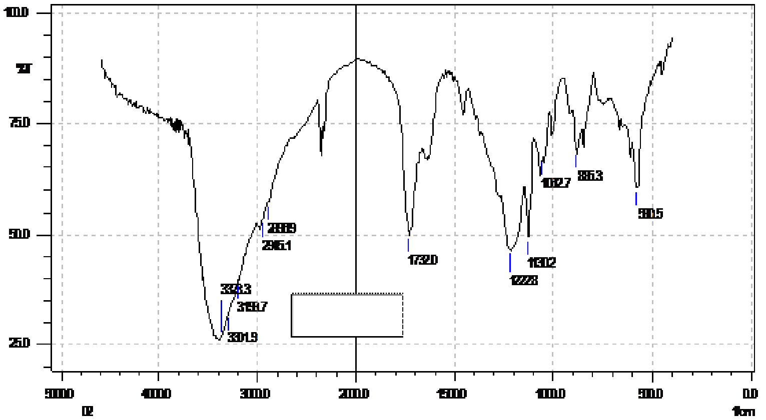

Fig. 1: FT- IR of the ω-oxypropylmethacrylate 1,3 dioxolane in chloroforme

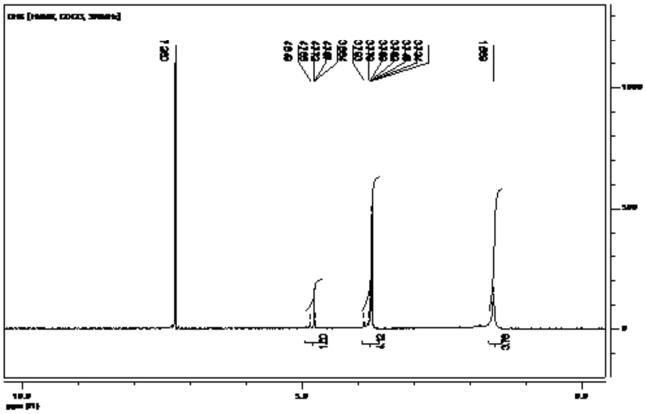

Fig. 2: ^{1}H- NMR spectrum of the ω-oxypropylmethacrylate 1,3 dioxolane in $CDCl_3$

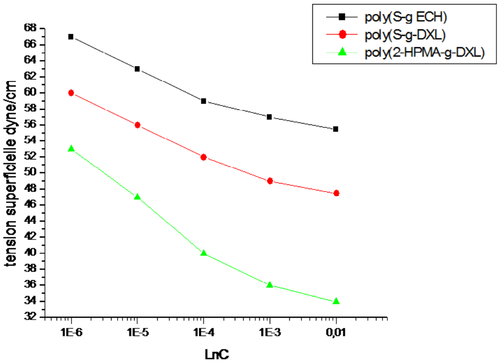

Fig. 3: The logarithmic plot of superficial tension of the graft copolymer solution vs, concentration

Viscosity measurements used to obtain the average molecular weights of polymers produced the Mark- Houwink equation was used to calculate the viscosity average molecular weight[18-19]. The values of Mn are presented in Table 4.

We notice that the values of the number-average molecular weight determined by UV analysis and by viscosimetry are relatively in accordance with those calculated theoretically. This results suggest that the contribution of transfer reactions could by much less important, which could mean that the reaction occurs, according to a “living form”.

Analysis FT-IR

The FT-IR spectra of 1, 3-dioxolane macromonomers (Fig. 1) shows the most characteristic absorption at 1732 cm^{-1} corresponds to the carbonyl group, the peak at 2945 cm^{-1} due to the stretching vibration of methyl group in the end of chain, the peak at 1222 cm^{-1} is attributed to stretching vibration band of the double bond. The bands at 1082 cm^{-1}are assigned to ester faction. The peak at 886 cm^{-1} and 580 cm^{-1}corespond to bonding vibration, we notice the disappearance of characteristic band at 1630 cm^{-1} and 981 cm^{-1}related to the double bond of the monomer and a new characteristic peak appears at 1384 cm^{-1} due to the oxypropylmethacrylate double bond.

The ^{1}H-NMR spectra of 1, 3- dioxolane macromonomer was record in $CDCl_3$ solution using a DPX 300 Brucker spectrometer; the ^{1}H-NMR spectra of macromonomer is shown in Figure 2.

Characterization of copolymer by ^{13}C-RMN

The poy (1, 3- dioxolan)-g-PMMA was characterized by ^{13}C-RMN, ^{13}C-RMN analysis of poly (1, 3-dioxolan)-g-2HPMA confirms that the chain are copped with poly (2-HPMA) backbone. The ^{13}C-RMN spectrum of the copolymer shows the signal with chemical shifts of about 38-42 ppm, 36- 30 ppm correspond to the $–CH_2$ – carbon atms and those observed at 170- 178 ppm and 57 ppm are attributed respectively to carbonyl carbon and CH- carbon of oxypropylmethacrylate.

Determination of the surface tension of the copolymer poly (1, 3-dioxolan)-g-PMMA

Interestingly, the amphiphilic character of the poly (1, 3-dioxolan) in the graft copolymer, has been evidenced by the superficial tension measurements.

Purposely; solution of poly(1, 3-dioxolan)-g-PMMA, in water, Fig. 3 shows the logarithmic plot of superficial tension of the graft copolymer solution vs, concentration (expressed in g/l at 25°C, the superficial tension goes down from 63;3 N/m to 53,9 N/m, demonstrating the tensioactive proprieties of the new type of amphiphilic graft copolymer. The critical micelle concentration (CMC) has been determined from the intersection between the tangents drawn from higher concentration portion of the sigmoid plot and calculated as 10^{-4}g/l.

CONCLUSIONS

The graft copolymer of poly (1, 3dioxolan)-g-MAA were prepared by radical copolymerization. Amphiphilic graft copolymers containing hydrophobic poly (2-hydroxypropylmethacrylate) backbone and hydrophilic poly (1, 3-dioxolan) side chain were synthesized by free radical copolymerization, using benzoylperoxide as initiator. The analysis by ^{1}H NMR, ^{13}C NMR, FTir and UV confirmed the sequence copolymer of poly (1,3- dioxolane)-g-P-2HPMA. These materials have potential applications in various fields and in particular with the aim of pharmacy and medicine.

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