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Synthesis and Characterization of a New Graft Copolymer Based on Poly(1,3-dioxolane)

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This paper reported the synthesis of poly((dioxolane-1,3)-*g*-styrene) and poly(dioxolane-1,3-*g*-AMM) copolymers. It involves the copolymerization of macromonomers of dioxolane-1,3-ω-oxypropyl-methacryloyl with co-monomers such as methacrylic acid, 2-hydroxy-propylmethacrylate (2-HPMA) and styrene, initiated by azobisiso-buteronitrile (ABIN).

Key Words: Amphiphilic, Copolymer, Graft, Block, ^{1}H NMR.

INTRODUCTION

Micelle-like aggregates with amphiphilic copolymers have been recently[1] receiving much attention as carriers for hydrophobic drugs[2-5]. Such as amphiphilic block or graft copolymers have been found to form self-assemblies, nanosized micelle-like aggregates of various morphologies in aqueous solution. The hydrophobic part forms the core of the micelle as preferential incorporation site for lipophilic drugs, while the hydrophobic corona or outer shell limits their uptake by reticuloendothelial systems and thus extents the *in vivo* life time of the drug carrier. Furthermore, this nanosized aggregates have the advantages of displaying a narrow size distribution, a low critical aggregation concentration compared to low molecular weight surfactants, a slow rate of dissociation and high drug loading capacity in biotechnological and pharmaceutical applications. The compatibility between polymeric material and living organism and strict control of degradation and bioassimilation by living systems have led to the demand for new biocompatible and biodegradable materials based on synthetic polymers bearing functional pendant groups[6].

EXPERIMENTAL

Grafts copolymers of dioxolane-1,3 were synthesized with the copoly-merization method and purified by the precipitation in hexane.

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Macromonomers of 1,3-dioxolane were prepared by the direct method. It involves the cationic ring opening polymerization of 1,3-dioxolane in presence of 2-hydroxypropylmethacrylate (2-HPMA) as co-initiator, initiated by sulphuric acid. 1,3-Dioxolane (Merck) distilled under nitrogen. ^{1}H NMR spectra were recorded using a Bruker AMX-300 apparatus at room temperature in $CDCl_3$ molecular weight of all samples ere determined using asize exclusion chromatography (SEC) waters 510 with an RI (waters 410) detector and polymer laboratories columns calibrated with linear polystyrene standards. In all cases $CHCl_3$ was applied as eluant.

Synthesis of the graft copolymer poly(AMM-*g*-1,3-dioxolane (AMMS*g*-DXL))(CG_1): In a round bottom flask, a mixture of methylmetha -crylate (0.401 mol/L) and poly(1,3-dioxolane-ω-oxypropylmethacrylote) (0.124 mol/L) was copolymerized in bulk at 60 °C for 18 h using AIBN as initiator and CH_2Cl_2 as solvent. After dissolution in THF, the copolymer was recovered by selective precipitation in eight-fold excess of hexane, filtration and drying under reduced pressure (conversion 95 %). Yield = 87 %. ^{1}H NMR (200 MHz, $CDCl_3$ δ ppm): 4.75 (s, 2H), 3.72 (t, 2H), 0.84-1.3 (s, 3H), 1,83 (t, 2H), 3.6 (s, 3H) (Fig. 1).

Synthesis of the graft copolymer poly(styrene-*g*-1,3-dioxolane) (S-*g*-DXL)(CG_2): In a round bottom flask with a three way stopcock, 1,3 g (Mn(UV)= 2030) of macromonomer poly(1,3-dioxolane)-ω-oxypropyl-methacrylote was dissolved into 100 mL of THF at 60 °C and added with 0.05 g of styrene of 24 h using azobis isobutyonitrile (AIBN) as initiator.

The solvent was evaporated before recovering the copolymer by extensive drying at 50°C under reduced pressure. Yield = 98 %. ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm : 4.75 (s, 2H), 3.72 (t, 2H), 0.95-2 (d, 2H), 6.5-7 (m, 5H).

RESULTS AND DISCUSSION

In the first step, the macromonomers of 1,3-dioxolane were synthesized then a new graft copolymers including hydrophobic poly(styrene) and poly(methacrylatemethyl) backbones and hydrophilic 1,3-dioxolane branches were prepared. The incorporation of the co-monomer into the polymers was proved by ^{1}H NMR spectra (Fig. 1) for the graft copolymer poly (AMM-*g*-dioxolane-1,3 (AMM6*g*-DXL)) (CG_1) and (Fig. 2) for the graft copolymer poly(styrene-*g*-1,3-dioxolane) (S-*g*-DXL) (CG_2) The clear increase of molar masses observed by size exclusion chromatography (SEC) proves the formation of polymers with high molar masses. The curves of (CG_1) and (CG_2) presented in Figs. 3 and 4.

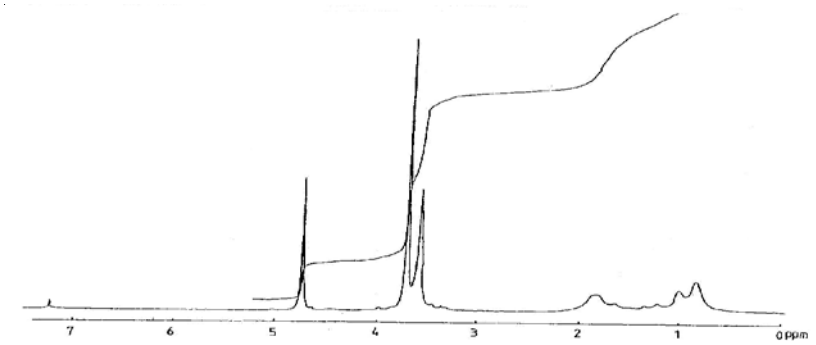

Fig. 1. ^{1}H NMR spectrum of the graft copolymer poly(AMM-*g*-dioxolane) (solvent = $CDCl_3$)

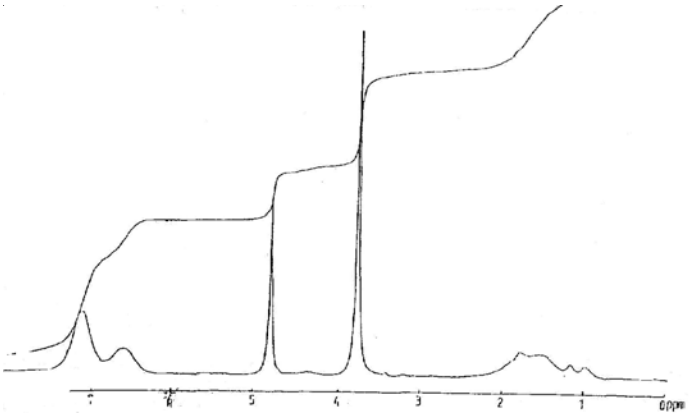

Fig. 2. ^{1}H NMR spectrum of the graft copolymer poly(S-*g*-dioxolane) (solvent = $CDCl_3$)

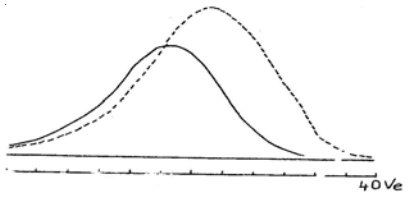

Fig. 3. SEC Traces of macromonomer dioxolanne-1,3 ω-oxypropylmethacryloyl (-------), copolymer poly(AMM-*g*-DXL) (——)

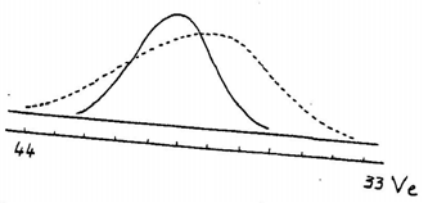

Fig. 4. SEC traces of macromonomer dioxolanne-1,3 ω-oxypropylmethacryloyl (-------), copolymer poly(styrene-*g*-DXL) (——)

The percentage relating to the absorbent part to the hydrophobic part is also determined by NMR and the average molecular mass determined by viscosimetry. An average number of the grafts by grafted copolymer has also been calculated. The absorbent number of grafts varies from 2 to 4 per hydrophobic skeleton. This number of grafts per skeleton owes depended for a great part of the report/ratio of reactivity of macromonomer and co-monomer. The number of the graft of copolymers for $CG_1 = 4$ and $CG_2 = 3$.

Conclusion

In this paper, the preparation of a new graft copolymers based on the macromonomer 1,3-dioxolane-ω-oxypropylmethacryl and methylmethacrylate (AMM) and styrene (S) as comonomers, using radical polymerization method. By this technique, new graft copolymers, poly(styrene-*g*-1,3-dioxolane) (S-*g*- DXL) (CG_2) and poly(AMM-*g*-1,3-dioxolane (AMM6*g*-DXL) (CG_1) were synthesized. The resulting copolymers can by used as a modifier surface. In all cases, the polymerization did not result in the formation of homopolymer. All molar masses calculated by SEC, calibrated by linear standards, are lower than the ones calculated from ^{1}H NMR and the increase of masses strongly suggests the formation of graft copolymers.

REFERENCES

1. O. Coulembier, P. Degée, C. Barbaud, P. Guérin and P. Dubois, *Polym. Bull.*, **52**, 41 (2004).
2. M. Yokoyama, S. Fukushima, R. Uehara, Okamoto Kataoka, Y. Sakari and T. Okana, *J. Control. Rel.*, **50**, 79 (1998).
3. K. Kataoka, A. Harada and T. Katasaki, *Adv. Drug Del.*, **47**, 113 (2001).
4. L. Zhang and A. Eisenberg, *Science*, **268**, 1728 (1995).
5. H.S. Kang, S.R. Yang and J.D. Kim, *Langmuir*, **17**, 7501 (2001).
6. X. Lou, C. Detrembleur and R. Jéröme, *Macromol. Rapid Commun.*, **24**, 161 (2003).
7. S.O. Kada, Ph.D. Thesis, Oran University, Oran, Algeria (1988).
8. M. Boukar, Mémoire de magister, Oran, Algeria (2000).

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