SYNTHESIS OF PHOSPHOR CONTAINING MONOMERS AND THEIR ATRP

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Introduction

Phosphorus-containing polymers are involved in a large range of applications. For example, they have been used as adhesion promoters for paints, lacquers, and adhesives, flame-retardant additives, complexing agents to recover metal ions from the environment and industrial liquids, and agents for controlling crystallization of $CaCO_3$ and also have been proposed for use in tissue engineering and drug controlled release because of their biocompatibility and biodegradability. Phosphorous-containing polymers have been prepared through various approaches. One of the methods of incorporating phosphorus functionality into polymers is the polymerization or copolymerization of phosphorus containing vinyl monomers such as vinyl and allyl phosphonates [1]. Polymers with phosphorus in the backbone are usually synthesized by either polycondensation or ring-opening methods [2]. Atom transfer radical polymerization (ATRP) [3], one of the most robust controlled/living radical polymerization (CRP) techniques which allows for the controlled polymerization of various monomers.

Experimental

Monomer 1 (DMMP) Synthesis. In this study, phosphonate monomer was synthesized and polymerized via ATRP. In the first step, diethyl (methacryloyloxy)methyl phosphonate (DMMP), was synthesized with methacryloyl chloride and triethylamine at -5 ^oC and under nitrogen (Figure 1). In the second step, diethyl (methacryloyloxy) methyl phosphonate was polymerized with CuBr/PMDETA catalytic system by using toluene as solvent at 70 ^oC.

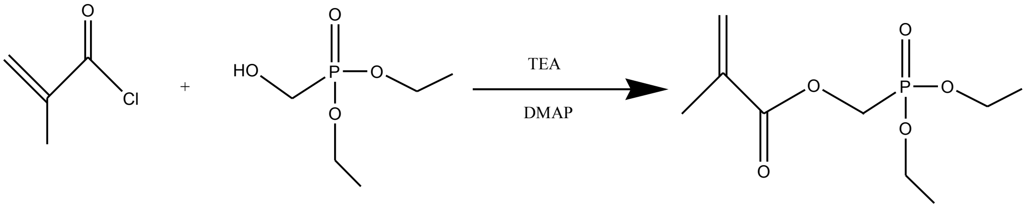

Figure 1. Reaction of diethyl(hydroxymethyl) phosphonate with methacryloyl chloride

Monomer 2(PGMA) Synthesis. Diethylhydroxy methyl phosphonate and GMA were added to a round-bottom flask with a nitrogen inlet. The mixture was stirred at 50 ^oC for 5 h. (Figure 2).

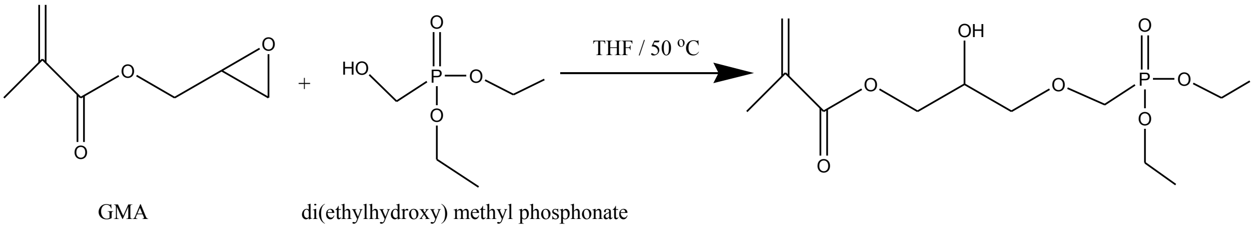

Figure 2. Phosphorylation of GMA

Result and Discussion

We were reported the synthesis of novel phosphonate polymers with a narrow molecular weight via DMMP monomer. This polymer was characterized by using gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). DMMP was synthesized by esterification of diethyl(hydroxymethyl) phosphonate with methacryloyl chloride. Purified product was analyzed by FTIR, ^{1}H NMR and ^{31}P NMR. Monomer 2 showed C=O peak at 1717 cm^{-1} and also showed P=O and P-OEt peaks at 1249 cm^{-1} and 1017 cm^{-1}. Its ^{1}H NMR spectrum is compatible with the spectrum given in the literature [4].

The ring-opening reaction of GMA with a phosphoric acid derivative was used for the preparation of new functional monomer (PGMA). The product was analyzed by FTIR, ^{1}H NMR and ^{31}P NMR. FTIR of monomer 2 showed C=O band at 1717 cm^{-1}, OH band at ~3400 cm^{-1}, P=O and P-OEt bands at 1249 cm^{-1} and 1017 cm^{-1}.

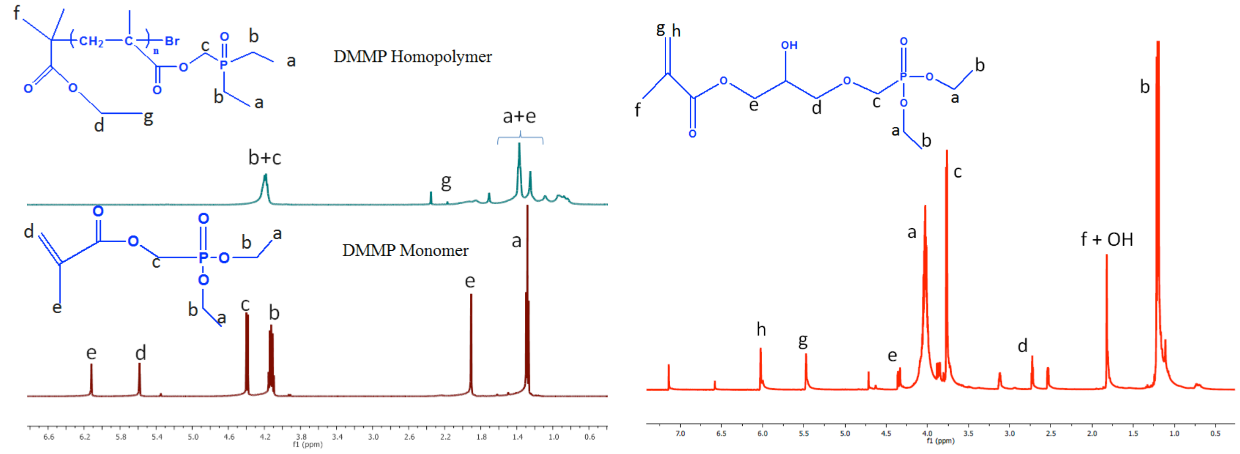

Figure 3. ^{1}H NMR spectra in $CDCl_3$: a) DMMP monomer and homopolymer, b) PGMA Monomer.

Conclusions

In summary, DMMP and PGMA monomers were synthesized respectively by esterification and ring opening reaction. PDMMP homopolymers were obtained having a narrow PDIs (<1.1) via controlled polymerization technical.

References

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