

## Reaction of Diethyl Vinylphosphonate with 2-Aminobenzimidazole

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Phosphorus-containing polymers are particularly attractive for their extensive application in fuel cells, flame retardant, and the biomedical field. Phosphorus-containing polymers include genetic materials DNA and RNA, and synthetic polymers functionalized at the main chain and those functionalized at the side chain. Vinylphosphonate is one of the simplest vinyl monomers with the phosphonate groups at the side chain. Since the late 1940s, different routes for vinylphosphonate synthesis have been reported. Among these techniques, coordinative-anionic polymerization and living rare earth metal-mediated group transfer polymerization are efficient to generate poly(vinylphosphonates) with higher molecular weight and higher conversions. Except for poly(vinylphosphonic acid) (which can be obtained in high yield and moderate molecular weight by free radical polymerization), relatively few investigations into the homo and copolymerization of vinylphosphonate monomers via radical polymerization have been reported. The few reports show that vinylphosphonate monomers fail to homopolymerize to high molecular weight products by the method of radical polymerization (especially for diethyl vinylphosphonate (DEVP)), which usually lead to low yields and provide polymers of low molecular weight. In the case of radical copolymerization, the final results were either unsuccessful or afforded insufficient characterization. Arcus reported the copolymerization of DEVP with styrene initiated by tert-butyl hydroperoxide and determined the reactivity ratios of this monomer pair. For relatively low DEVP contents in the copolymers, DEVP is reluctant to enter the growing polymer chain as compared to styrene. Except for styrene, radical copolymerizations of DEVP with ethylene glycol dimethacrylate, methyl methacrylate, acrylonitrile, and trimethoxyvinylsilane are achieved, but afford inadequate characterization. Therefore, radical copolymerizations of DEVP with other monomers to get relatively high DEVP-containing copolymers with clearly characterized structure are still a significant and challenging issue.

Poly(diethyl vinylphosphonate-co-2-chloroethyl methacrylate) (P(DEVP-co-CEMA)) copolymers are synthesized by free radical copolymerization initiated by benzoyl peroxide. The reactivity ratios for the free radical copolymerization of CEMA (M1) and DEVP (M2) are  $r_1 = 19.45$  and  $r_2 = 0.11$ , respectively. The desired amphiphilic copolymers with relatively low polydispersity index (PDI) and different DEVP contents are isolated and purified from the reaction mixtures through precipitation fractionation. The structures and molecular characteristics of the obtained products are characterized by  $^1\text{H}$  NMR, FTIR, and SEC analysis. All of these fractionated copolymers have a unimodal distribution and moderate PDI. The thermal properties of the P(DEVP-co-CEMA) copolymers are investigated by TGA and differential scanning calorimetry

(DSC) measurements. Single glass transition temperature ( $T_g$ ) appears in the DSC profiles differing from the existence of two  $T_g$ s in the blend of poly (diethyl vinylphosphonate) and poly (2-chloroethyl methacrylate), which indicates the random structure of the copolymers. The MALDI-ToF mass analysis further reveals that DEVP and CEMA units are randomly distributed in the copolymer chains. The self-assembly behavior of the P(DEVP-co-CEMA) copolymers in aqueous solution is preliminarily investigated.

The monomer 2-chloroethyl methacrylate (CEMA) is of special interest as halogen-functionalized comonomer for easy modification and post cross-linking. With initiating haloalkyl groups, graft copolymers can be prepared via atom transfer radical polymerization (ATRP). The chlorine atoms can be readily substituted by nucleophiles, for instance, azide groups, and then followed by click coupling of alkyne end-functionalized polymers to gain new properties. Therefore, CEMA is a potential comonomer for DEVP to broaden the applications of phosphorus-containing polymers. To date, to the best of our knowledge, there is no report on the copolymerization of DEVP with CEMA. What is more, due to the existence of both hydrophobic units (CEMA) and hydrophilic units (DEVP), the copolymers are able to self-assemble into nanoparticles in aqueous solution, which are promising in the fields such as microreactors and encapsulation of guest molecules. The modified copolymers show great potential in biomedical fields for polyphosphonates and proved to be high biocompatibility and adjustable degradability. Meanwhile, the chemical incorporation of a phosphorus-containing flame retardant into a methacrylate polymer via copolymerization may eliminate the leaching and heterogeneous problems associated with the additive approach.

Herein, we synthesize a series of amphiphilic random copolymers, namely poly (diethyl vinylphosphonate-co-2-chloroethyl methacrylate) (P(DEVP-co-CEMA)), through free radical copolymerization using benzoyl peroxide (BPO) as initiator. Copolymers with relatively narrow molecular weight distribution are isolated through precipitation fractionation for the detailed investigation. The structures of the copolymers are confirmed by  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, Fourier transform infrared (FTIR), and MALDI-ToF mass analysis. The thermal properties of P(DEVP-co-CEMA) copolymers are determined by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) measurements. Preliminary investigations on self-assembly behaviors of the copolymers in water are also performed, and the nanoparticles formed in water are observed by TEM. Experimental Materials Triethyl phosphite (98.0%, Aladdin Reagent, China), ethylene bromide (99.0%, Aladdin Reagent, China), triethylamine (Sinopharm Chemical Reagent, China), benzene (Sinopharm Chemical Reagent, China), methacryloyl chloride (J&K Chemical Reagent, China), and 2-

chloroethanol (Shanghai Nanxiang Reagent, China) were used as received. BPO (Shanghai Lingfeng Chemical Reagent, China) was recrystallized from methanol twice before use. THF was refluxed over potassium/benzophenone ketyl before use. All the other chemicals were used as received unless otherwise specified. Synthesis of CEMA 2-chloroethanol (10 mL) and triethylamine (22 mL) were dissolved in THF (50 mL), then methacryloyl chloride (15 mL) was added slowly under argon atmosphere while cooling the solution in an ice bath. The reaction mixture was stirred for 48 h at room temperature and then filtered.