



Thermal decomposition of phosphonate-containing methacrylate-based copolymers

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ARTICLE INFO

Article history:

Received 26 October 2017

Received in revised form

22 March 2018

Accepted 29 April 2018

Available online 1 May 2018

Keywords:

Copolymer

Ethyl 2-[4-(dihydroxyphosphoryl)-2-oxabutyl]-acrylate copolymer

Thermal decomposition mechanism

Evolved gas analysis

TGA/FTIR

Microscale combustion calorimetry

ABSTRACT

The synthesis of novel phosphonate-containing copolymers with methyl methacrylate (MMA) is reported. As phosphonate comonomers ethyl-2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate (EDHPOBA), with free phosphonic acid group, and the respective methyl ester ethyl-2-[4-(dimethoxyphosphoryl)-2-oxabutyl]acrylate (EDMPOBA) are employed. The impact of the phosphonate-containing comonomers on the thermal decomposition of P(MMA) copolymers is discussed using data obtained from thermogravimetric analysis (TGA). P(MMA) decomposes completely under nitrogen leading to a negligible residue, while the decomposition of copolymers containing the phosphonate comonomer EDHPOBA yields a significant residue (up to 32 wt.%) indicating a significant alteration of the decomposition mechanism. TGA/FTIR experiments are performed to determine the volatile decomposition products of the copolymers. It is demonstrated that incorporation of the phosphonic acid-containing monomer in P(MMA) suppresses the depolymerization of P(MMA). Alternative pyrolysis reactions take place and MMA is not detected in the gas phase. The decomposition proceeds essentially in four steps: transesterification between acrylate ester groups and phosphonic acid, anhydride formation, decarboxylation, McLafferty rearrangement and cyclization (char forming). It is found that this reaction sequence cannot occur in copolymers with the ester EDMPOBA comonomer, thus resulting in a less favored influence on the decomposition mechanism. Microscale combustion calorimetric measurements prove that incorporation of the phosphonate monomers drastically reduces the total heat release and heat release capacity.

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1. Introduction

Poly(methyl methacrylate) (P(MMA)) is an important thermoplastic processable material and engineering resin owing to its mechanical properties and weather resistance. The high transparency makes it ideal for diverse applications. However, P(MMA) belongs to the class of easily combustible polymer materials [1]. It decomposes quickly under thermal stress into volatile, combustible gases. Thus, addition of flame retardants (FRs) is indispensable. Halogen-containing FRs should be avoided in future due to their special risks [2–4] and current EU regulations [5]. Acrylate resins for ceilings, side walls, panels and structural parts are often flame retarded by addition of aluminum trihydroxide, aluminum polyphosphate and different intumescent systems [6]. Aluminum polyphosphate alters the decomposition mechanism of P(MMA).

Cyclization and formation of anhydrides prevents depolymerization of MMA units [7]. The use of compounds mentioned above follows the concept of non-reactive flame retardant additives. The major problem of additive flame retardants is that they have to be applied in high concentrations (20–40 wt.%), leading to a drastic deterioration of mechanical properties and, in case of P(MMA), loss of transparency [8]. For this reason, the second concept – use of reactive flame retardants – seems to be more promising in particular for P(MMA). In this case, flame retardants are integrated in the polymer matrix to be flame retarded by reactions taking place upon melt mixing, or by blending in phosphorus-containing polymers. Because of the chemical incorporation, migration to the material surface (so called blooming) is prevented. Moreover, these flame retardants can be used in lower concentrations [9,10]. The concept of using phosphorus-containing polymers has been followed in our group for several years and resulted in selection of suitable structures for flame retardancy of epoxy resins [11], polyesters [12–14], and bio-based polyesters [15].

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Solutions for P(MMA) have been proposed by Ebdon et al. [16] who studied MMA copolymers with phosphorus-containing acrylate and methacrylate comonomers with widely varied chemical structure and derived possible decomposition mechanisms. Surveys are given by Lu et al. [17] and Joseph et al. [18] mentioning further phosphorus-containing acrylic comonomers like (6-oxidobenz[c,e][1,2]oxaphosphorin-6-yl) methacrylate that was reported by Jiang et al. [19]. One of the key points to achieve positive effects on flame retardancy appeared the interruption of depolymerization of P(MMA). It was found that among others the monomer diethyl (methacryloyloxymethyl) phosphonate (DEMMP) is a promising candidate to incorporate flame retardancy in copolymers due to its effect in the condensed phase (char promotion). In further work, DEMMP, its derivatives and copolymers were investigated as flame retardants [20–22]. Cochez et al. studied the decomposition mechanisms of MMA copolymers with DEMMP derivatives [23,24]. In DEMMP, the phosphonic unit is bound via the ester unit to the acrylic backbone. Moszner et al. [25–27] developed monomers such as ethyl-2-[4-(dihydroxyphosphoryl)-2-oxa-butyl]acrylate (EDHPOBA) and ethyl-2-[4-(dimethoxyphosphoryl)-2-oxa-butyl]acrylate (EDMPOBA), which are structurally comparable to DEMMP. In these monomers, the phosphonate group is not bound to the MMA ester group, but linked via an ether bridge [25,26] to the vinyl carbon (see Fig. 1), resulting in an interesting variation of the chemical structure. The successful polymerization of both monomers (EDHPOBA and EDMPOBA) as homopolymers [27] or with comonomers like HEMA [28] by radical polymerization has already been reported. The scope of the study presented here was to compare the decomposition and combustion mechanisms of MMA copolymers of EDHPOBA and EDMPOBA, respectively, with the DEMMP copolymers reported in literature [23,24].

In the study presented here, the thermal decomposition and combustion behavior of MMA copolymers with the comonomer EDHPOBA was explored and compared to unmodified P(MMA) and the corresponding EDHPOBA homopolymer. Selected copolymers were prepared with the ester monomer EDMPOBA. Also, for a potential use as flame retardant coating, the monomer benzoylphenyl methacrylate (BPMA) was incorporated into the copolymer structure. This monomeric unit is an UV-active crosslinker which gives the opportunity to stabilize the polymeric material by crosslinking. The copolymers and terpolymers were synthesized by free radical polymerization and analyzed by thermogravimetric analysis (TGA), TGA coupled with FTIR (TGA/FTIR), and microscale combustion calorimetry (MCC). Decomposition mechanisms are proposed based on the data obtained and discussed together with literature reports.

2. Experimental

2.1. Materials

Chloroform (Acros Organics, 99%), diethyl ether (VWR

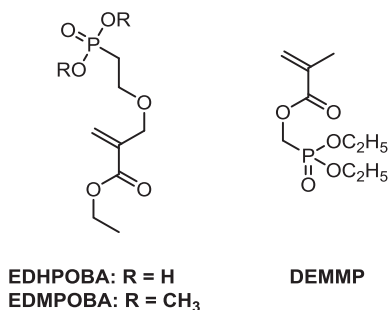


Fig. 1. Chemical structures of EDHPOBA, EDMPOBA and DEMMP monomers.

Chemicals, 99%) and methanol (Acros Organics 99.9%) were used without further purification. Methyl methacrylate (MMA) (Alfa Aesar, 99%) was purified by column chromatography using basic aluminum oxide as stationary phase. 2,2'-azobisisobutyronitrile (AIBN) (Fluka, 98%) was purified by recrystallization in diethyl ether. The phosphorus-containing monomers EDHPOBA and EDMPOBA were kindly supplied by Ivoclar Vivadent AG, Schaan, FL, and used as received.

2.2. Synthesis

2.2.1. Synthesis of P(MMA)

The radical solution polymerization of MMA was carried out in chloroform at 60 °C under argon atmosphere. AIBN (2 mol% respective to the monomer) was used as initiator. The mixture was degassed by three freeze-pump-thaw cycles and stirred for 4 h. After 4 h, the mixture was precipitated into an excess of methanol. The product was purified by re-dissolving in chloroform and re-precipitation in methanol. After filtration, the white polymeric product was dried under reduced pressure at 50 °C for 20 h to yield pure P(MMA).

¹H NMR (500 MHz, CDCl₃, ppm) δ 0.67–1.30 (m, 3H, -CH₃), 1.36–1.53 (m, 2H, -CH₂-), 3.60 (s, 3H, -O-CH₃).

2.2.2. Synthesis of P(EDHPOBA) homopolymer

The polymerization of EDHPOBA was carried out according to Moszner et al. [27]. Methanol was used as solvent and AIBN (2 mol% respective to the monomer) was used as initiator. After the reaction time of 4 h at 60 °C the polymeric product was precipitated in an excess of cold diethyl ether. For purification, the product was re-dissolved in methanol and again precipitated in cold diethyl ether. After filtration, the residual solvent of the white polymeric product was removed under reduced pressure at room temperature for 20 h to yield pure P(EDHPOBA). The product was water soluble and highly hygroscopic. Therefore, it was stored under argon atmosphere.

¹H NMR (500 MHz, DMSO-d₆, ppm) δ 1.06–1.46 (s, 3H, -CH₃), 1.47–2.32 (br, 4H, P-CH₂-, C-CH₂-), 3.23–3.75 (br, 4H, CH₂-CH₂-O, C-CH₂-O), 3.74–4.21 (br, 2H, CH₃-CH₂-O), 8.15–10.98 (br, 2H, OH); ³¹P NMR (202 MHz, DMSO-d₆, ppm) δ 19.80–24.14 (br, 1 P).

2.2.3. Synthesis of P(EDMPOBA) homopolymer

Polymerization of EDMPOBA was done as described for P(EDHPOBA) except the purification of the colorless product which was performed differently. P(EDMPOBA) was dialyzed for three days in ethanol and water and dried under reduced pressure.

¹H NMR (500 MHz, DMSO-d₆, ppm) δ 1.09–1.37 (s, 3H, -CH₃), 1.41–2.21 (br, 4H, P-CH₂-, C-CH₂-), 3.11–3.57 (br, 4H, CH₂-CH₂-O, C-CH₂-O), 3.57–3.80 (br, 2H, P-OCH₃), 3.80–4.20 (br, 2H, CH₃-CH₂-O).

2.2.4. Synthesis of copolymers P(MMA-EDHPOBA) and P(MMA-EDMPOBA)

Copolymers were prepared by free-radical polymerization in methanol. Thus, MMA and the phosphonate-containing monomer were used in systematically varied molar ratios with AIBN (2 mol% respective to monomers) as initiator. The mixture was degassed by three freeze-pump-thaw cycles and stirred at 60 °C. After the reaction time of 4 h the polymeric products were precipitated in an excess of cold diethyl ether for P(MMA-EDHPOBA), or water for P(MMA-EDMPOBA), respectively. For purification the products were re-dissolved in methanol and again precipitated. The residual solvent of the white polymeric products was removed under reduced pressure at room temperature for 20 h to yield pure copolymers. Products with high contents of phosphonate-containing comonomer were hygroscopic. Therefore, they were stored under argon atmosphere.

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