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Synthesis and radical polymerization of bifunctionalized aziridinic methacrylates

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ABSTRACT

The synthesis and controlled radical polymerization of 2-(1-aziridinyl)ethyl methacrylate (AZMA) and (1-phenylaziridin-2-yl)methyl methacrylate (PAZMA), which have two polymerizable groups in their structures, were performed. RAFT polymerization using CPDB as chain transfer agent (CTA) and AIBN as initiator was carried out in bulk and in solution at 60 °C with a good control of the molecular weight. A living behavior was observed for both monomers. ATRP polymerization (CuBr/PMDETA/EBiB) of AZMA led to a crosslinked material. For PAZMA a nonliving behavior in ATRP polymerization was reached, however no crosslink was observed due to higher stability of its aziridine ring.

1. Introduction

Aziridines are a compound class containing a three-membered saturated heterocyclic with one nitrogen atom. Due to the combination of Bæyer strain in the three-membered heterocycle and the nucleophilicity of the heteroatom aziridines ring cleavage reactions occur under relatively mild acidic conditions [1].

Several methods for the synthesis of aziridines are described in the literature, among them are aziridination of alkenes with chloramine – *T* using aqueous solution of H_2O_2/HBr [2] or Cu(II) [3] Rd(II) catalysts and other conditions [4–6]. Methods as cyclization of amino alcohols have already been described elsewhere [7–10]. The efficiency of these reactions depends on a series of factors, especially, on the substitutes of the reagents [1]. Aziridines can be important as synthetic intermediate in the preparation of pharmaceutical and agrochemical products [11]. The importance of aziridines is also recognized in asymmetric synthesis, where in many cases, the use of chiral ligands and auxiliaries is necessary to improve the efficiency of these synthesis [12]. Another subclass of these compounds are the vinylaziridines, which have been proved to be powerful intermediate for various types of natural products and synthetic compounds [13,14].

Aziridines that have a polymerizable double bond group as substitute make them a unique class of compounds which consists of two different polymerizable groups where it is possible to initiate a polymerization and/or to modify the polymer structure. Such type of bifunctionalized monomers are for example glicidyl methacrylate (GMA) [15] 2,3-epithiopropyl methacrylate (ETMA) [16] (4-maleimidophenyl)oxirane (MAPO) [17] 2-(1-aziridinyl)ethyl methacrylate (AZMA) [18]. Therefore, these compounds can undergo vinyl polymerization under free-radical or ionic conditions, as well as ring-opening polymerization. These functional polymers are of great interest as precursors of graft copolymers, hydrophilic polymers and crosslinked micelles or gels. Therefore can be used as dental adhesives [19] coatings [20] and thermosetting resins [21].

The ionic and radical polymerization of the AZMA has already been described in the literature [18]. Authors have achieved well-defined polymers bearing the aziridine ring by anionic polymerization with MWD $\leqslant$ 1.07 using a binary initiator system consisting of Ph_2CHK/Et_2Zn. In addition, crosslinked gels were obtained by the treatment of the poly(AZMA) with adipic acid in THF at room temperature due to aziridine ring opening at the polymeric chain. Conventional radical polymerization conditions performed using AIBN as initiator led to polymers with MWD around 3.8. However, no results about controlled radical polymerization of the AZMA have been described.

The controlled/living radical polymerization (CRP) techniques have been the most important development in polymer synthesis in the last 10 years [22]. Among these controlled radical polymerization, atom transfer radical polymerization (ATRP) [23–25] and reversible addition–fragmentation chain transfer (RAFT) [26,27] polymerization have become the most popular methods because of their adaptability to a wide range of functional monomers under

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less severe experimental conditions [28]. These techniques allow the synthesis of homopolymers and block copolymers with well-defined architectures and controlled molecular weight [29,30] finding applications in bioengineering and nanotechnology in order to manufacture biocompatible nanocontainers for drug delivery [31].

The present article reports the synthesis and radical polymerization behavior of two aziridinic monomers, 2-(1-aziridinyl)ethyl methacrylate (AZMA) and (1-phenylaziridin-2-yl)methyl methacrylate (PAZMA), under free-radical, ATRP and RAFT polymerization conditions. In addition, we discuss the stability of the new PAZMA monomer by introducing an aromatic group attached to the heterocycle.

2. Experimental

2.1. Materials

2,2′-Azobisisobutyronitrile (AIBN) (Aldrich, p.a.) was recrystallized in methanol before use. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%), and methacrylic acid (Merck, p.a.) were distilled before use. Acetone was dried on copper (II) sulfate and distilled. Dichloromethane was dried with calcium hydride and distilled under inert atmosphere. Toluene and tetrahydrofuran (Merck, p.a.) were dried with metallic sodium and distilled under inert atmosphere. CuBr (Aldrich, 98%) was purified as described in the literature [32]. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA), ethyl 2-bromoisobutyrate (EBiB), 2-bromopropionitrile (BPN), were purchased from Aldrich and used as received. All other reagents were used as received.

2.2. Characterization

^{1}H NMR and ^{13}C NMR measurements were performed in deuterated chloroform on a Varian VNMRS 300 MHz spectrometer.

Size exclusion chromatography was performed on Styragel columns connected to a Waters 410 differential refractometer using THF as solvent. The molecular weight was determined using a calibration curve with PS standards.

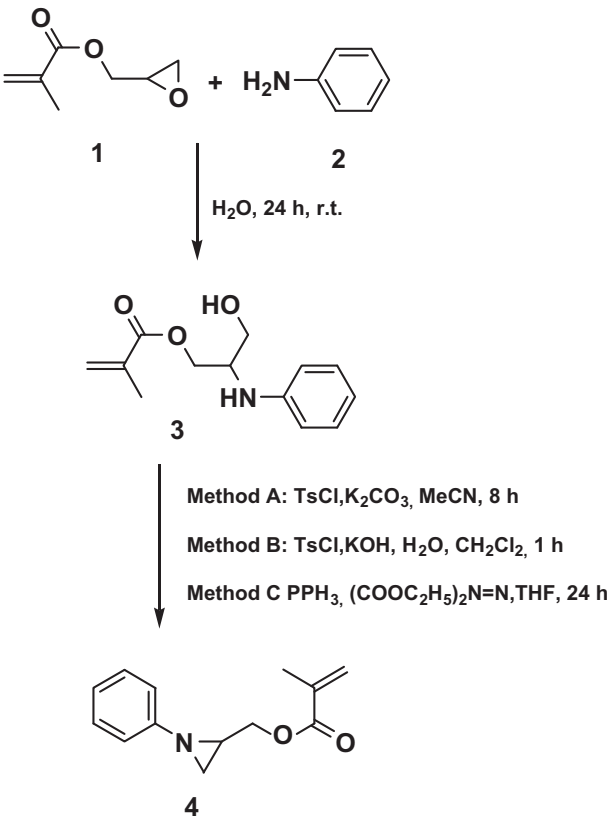
Differential Scanning Calorimetry: samples weighing ca.10 mg were heated from −50° to 150 °C in sealed capsules at heating rate of 20 °C/min in a Pyris 7 Perkin–Elmer DSC. The glass transition was measured on the second heating.

2.3. Synthesis

2.3.1. (1-Phenylaziridin-2-yl)methyl methacrylate (PAZMA)

An one-neck round-bottomed flask was charged with 3 g (0.021 mol) of GMA, 2 g (0.022 mol) of aniline and 0.4 g (0.022 mol) of distilled water. Then, the reaction was performed under magnetic stirring at room temperature. After 24 h, the aminoalcohol (Product 3, Scheme 1) was obtained quantitatively. Afterwards, to a solution of 0.5 g (0.002 mol) of product 3, THF and 0.83 g (0.003 mol) of triphenylphosphine were added 0.52 g (0.003 mol) of diethylazodicarboxylate (DEAD) dropwise under inert atmosphere, at 0 °C. After 24 h at room temperature, the reaction was quenched and the THF solvent was evaporated.

A colorless liquid (product 4, Scheme 1) was isolated by column chromatography (silica gel, diethyl ether and hexane – 5:95 vol.%) and it resulted in a 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.00 (s, 3H), 2.19 (d, 1H), 2.25 (d, 1H), 2.45 (m, 1H), 4.00 (dd, 1H), 4.50 (dd, 1H), 5.65 (s, 1H), 6.25 (s, 1H), 7.00 (d and t, 3H) e 7.25 (t, 2H). ^{13}C NMR: (75.4 MHz, $CDCl_3$): δ (ppm) 18.2 (CH_3), 31.2 (CH_2), 37.3 (CH), 66.5 (CH_2), 120.4 (2CH), 122.5 (CH), 125.8 (CH_2), 128.8 (2CH), 135.9 (C), 153.5 (C), 167.0 (C=O).



Scheme 1. Synthesis of (1-phenylaziridin-2-yl)methyl methacrylate (PAZMA).

2.3.2. 2-(1-Aziridinyl)ethyl methacrylate (AZMA)

Methacrylic acid (17.9 g, 0.208 mol) and DMAP (*N,N*-dimethylaminopyridine) (2.5 g, 0.020 mol) were dissolved in 500 mL of dichloromethane under inert atmosphere at 0 °C. Then, to this solution, 18.2 g (0.209 mol) of 2-(1-aziridinyl)ethanol and 43.0 g (0.208 mol) of DCC (dicyclohexylcarbodiimide) in 100 mL dichloromethane were added dropwise and stirred for 12 h at room temperature.

The reaction mixture was filtered to remove solid residues and the solvent evaporated under reduced pressure. Finally, the pure product was obtained by distillation under vacuum (19.4 g, yield 55%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.20 (t, 2H), 1.80 (t, 2H), 2.00 (s, 3H), 2.55 (t, 2H), 4.35 (t, 2H), 5.60 (s, 1H), 6.18 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ (ppm) 18.2 (CH_3) 27.0 ($2CH_2$), 59.6 (CH_2), 64.3 (CH_2), 125.5 (CH_2), 136.0 (C), 167.1 (C=O).

2.4. General polymerization description

2.4.1. Conventional radical polymerization

The polymerization was conducted in toluene (monomer concentration 10 wt.%) under inert atmosphere, at 60–70 °C using AIBN as initiator. After 8 h, the reaction was quenched by an ice bath and the polymer precipitated in hexane, filtrated, dried in vacuum at room temperature and stored at −18 °C.

2.4.2. RAFT

2-Cyanopropyl dithiobenzoate (CPDB) was synthesized as described elsewhere [24].

Solutions of the monomer (AZMA or PAZMA), solvent (anisole or toluene, 50 wt.%), RAFT agent, CPDB (in different concentrations)