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Synthesis and radical polymerisation of methacrylic monomers with crown ethers or their dipodal counterparts in the pendant structure

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ABSTRACT

The synthesis and radical polymerisation of methacrylic monomers with benzo-12-crown-4, benzo-15-crown-5, benzo-18-crown-6, and their dipodal counterparts in the ester residue is described. The radical polymerisation of the monomers in solution was carried out at different temperatures, and the polymerisation kinetics curves were obtained by direct measurement of the instantaneous monomer concentrations by nuclear magnetic resonance spectroscopy (NMR). Thus, the polymerisation rate parameter ($2fk_p/\langle k_t\rangle^{1/2}$), along with the polymer stereoregularity, were obtained in terms of the molar fractions of meso and racemo diads and of syndiotactic, isotactic and heterotactic triads. The interaction of the polymers with cations was studied using polymer networks as solid phases in the solid–liquid extraction of lanthanide cations from both organic and aqueous media.

1. Introduction

Acrylic polymers belong to one of the most important families of polymers, both from an industrial and from an academic point of view. Regarding the latter, intermediates with the desired chemical structure (having an alcohol or an amino group) are straightforward to prepare from an organic point of view, and they can be easily transformed into (meth)acrylates or (meth)acrylamides. These compounds can then be converted into polymers by conventional or living solution radical polymerisation to render homopolymers or copolymers with random or segmented structures [1–16].

Since the discovery of crown ethers [17,18], these compounds have received significant attention because of their ability to establish weak, but important, interactions with charged species through the formation of multi-highly directional ion–dipole interactions between a cation and the ether groups of the crown moiety [19,20]. These interactions were thought to resemble the important interactions in nature, such as the molecular recognition of enzymes, antigen/antibody recognition, the double helix structure, and membrane transport in cells, among others [21–26].

We previously studied different polymers containing crown ethers, along with potential applications related to their ability to interact with cations, such as water and organic insoluble aromatic polyamides [27–32], water soluble polymethacrylates [33–35], and crosslinked membranes with gel behaviour [36]. In this work, we expand our studies concerning polymers with crown ether and linear oxyethylene sequence, or podands, host motifs to polymethacrylates with benzo-crown subunits (benzo-12-crown-4, benzo-15-crown-5, and benzo-18-crown-6) in the ester residue. Their dipodal open chain counterparts were also studied. Thus, we describe below the synthesis of monomers, their polymerisation and polymerisation kinetics, and interaction of the polymers with cations through solid–liquid extraction of lanthanide cations from aqueous and organic media. We have chosen the lanthanide ions to test the ability of these polymers to interact with cations because we have previously determined the interaction of these cations with polymethacrylates containing a similar, but more flexible, pendant aliphatic crown receptor motif [34,35].

2. Experimental section

2.1. Materials

All materials and solvents used for the synthesis of the monomers were commercially available, and they were used as received unless otherwise indicated. Ethyl 3,4-dihydroxybenzoate was prepared by esterification of 3,4-dihydroxybenzoic acid with ethanol [27]. α-ω-Dichlorooligo(ethylene oxide)s, [1,2-bis(2-chloroethoxy)ethane, 1,11-dichloro-3,6,9-trioxaundecane, 1,14-dichloro-3,6,9,12-tetraoxatetradecane], ω-chlorooligo(ethylene oxide)s, 1-chloro-3,6-dioxaoctane, 1-chloro-3,6,9-trioxaundecane, and ethoxyethyl tosylate were synthesised and purified according to previously described procedures [37]. 4-Ethoxycarbonyl-benzo-12-

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crown-4, 4-Ethoxycarbonyl-benzo-15-crown-5,4-Ethoxycarbonyl-benzo-18-crown-6, ethyl 3,4-bis(2-ethoxyethoxy)benzoate, ethyl 3,4-bis-[2-(2-ethoxyehtoxy)ethoxy]benzoate, and ethyl 3,4-bis-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzoate were prepared and characterised by the procedure of Calderon et al. [27–29]. 2,2′-Azobis(isobutyronitrile) (AIBN, Fluka, 98%) was recrystallised from methanol and dried under high vacuum at room temperature prior to use.

2.2. Synthesis of the monomers

The synthetic route followed to prepare the monomers is depicted in Schemes 1 and 2. To obtain the monomer (Scheme 2), it was necessary to prepare different intermediates (Scheme 1), which were synthesised according to the following procedures.

2.2.1. Intermediates

The hydroxymethylbenzene derivatives **9a–c** and **10a–c** were synthesised by the same general method (Scheme 1). The synthesis of 4-hydroxymethyl-(benzo-12-crown-4) (**9a**) is described as an illustrative example.

*2.2.1.1. 4-Hydroxymethyl-(benzo-12-crown-4) (**9a**).* In a round bottom flask fitted with a mechanical stirrer and a condenser under nitrogen atmosphere, 150 mL of THF was cooled to 0 °C. Next, 3.8 g (0.1 mol) of $LiAlH_4$ was dissolved under stirring. Then, a solution of 4-ethoxycarbonyl-benzo-12-crown-4 in 50 mL of THF was added dropwise. Subsequently, the reaction mixture was heated to reflux, and the disappearance of the ester was followed by TLC. The solution was then cooled, poured cautiously into ice water, and treated with a few drops of HCl. The water/THF solution was then filtered through celite, and the THF was eliminated on a rotary evaporator. The water solution was extracted with CH_2Cl_2 (3 × 30 mL), dried with magnesium sulphate, and vacuum concentrated to give a yellowish oil.

R_f: 0.11 (AcOEt).

^1H *NMR (400 MHz, $CDCl_3$)*: 6.97 (d; J = 1.61 Hz; 1H; ArH); 6.92–6.90 (m; 2H; 2×ArH); 4.57 (s; 2H; $HOCH_2$); 4.16–4.11 (m; 4H; 2×OCH_2); 3.85–3.70 (m; 4H; 2×OCH_2); 3.77 (s; 4H; OCH_2CH_2O); 2.12 (s; 1H; OH).

^{13}C *NMR (100.6 MHz, $CDCl_3$)*: 150.54; 149.70; 135.95; 121.09; 118.11; 116.58; 71.92; 71.37; 71.13; 71.02; 69.86; 64.66.

EI-LRMS (m/z, rel. int.): 254 (100), 165 (41), 166 (40), 151 (52), 137 (84), 110 (25), 45 (27).

2.2.1.2. 4-Hydroxymethyl-(benzo-15-crown-5). M.p.: 43–45 °C.

^1H *NMR (400 MHz, $CDCl_3$)*: 6.82 (d; J = 1.6 Hz; 1H; ArH); 6.80 (dd; J = 1.6 and 8 Hz; 1H; ArH); 6.74 (d; J = 8 Hz; 1H; ArH); 4.50 (s; 2H; $HOCH_2$); 4.08–4.02 (m; 4H; 2×OCH_2); 3.90–3.81 (m; 4H; 2×OCH_2); 3.69 (s; 8H; 2×OCH_2CH_2O); 2.95 (s; 1H; $HOCH_2$).

^{13}C *NMR (100.6 MHz, $CDCl_3$)*: 148,97; 148.22; 134.52; 119.68; 113.57; 112.63; 70.84; 70.34; 69.49; 68.89; 68.59; 64.76.

EI-LRMS (m/z, rel. int.): 298 (29), 166 (82), 165 (58), 151 (56), 149 (52), 137 (100), 45 (40).

2.2.1.3. 4-Hydroxymethyl-(benzo-18-crown-6). R_f: 0.03. (AcOEt). White wax.

^1H *NMR (400 MHz, $CDCl_3$)*: 6.82 (d; J = 2.0 Hz; 1H; ArH); 6.80 (dd; J = 2.0 and 10.4 Hz; 1H; ArH); 6.77 (d; J = 10.4 Hz; 1H; ArH); 4.50 (s; 2H; $HOCH_2$); 4.08–4.03 (m; 4H; 2×OCH_2); 3.90–3.81 (m; 4H; 2×OCH_2); 3.72–3.68 (m; 4H; 2×OCH_2); 3.67–3.63 (m; 4H; 2×OCH_2); 3.62 (s; 4H; OCH_2CH_2O); 2.95 (s; 1H; $HOCH_2$).

^{13}C *NMR (100.6 MHz, $CDCl_3$)*: 148.76; 148.01; 134.50; 119.62; 113.57; 112.63; 70.67; 70.60; 70.57; 69.52; 68.92; 68.69; 64.70.

EI-LRMS (m/z, rel. int.): 342 (22), 166 (50), 165 (38), 164 (59), 163 (50), 150 (45), 149 (43), 137 (44), 45 (66), 43 (43), 28 (100).

2.2.1.4. 3,4-Bis(2-ethoxyethoxy)phenylmethanol. R_f: 0.40. (AcOEt). Brown oil.

^1H *NMR (400 MHz, $CDCl_3$)*: 6.88 (s; 1H; ArH); 6.82 (s; 2H; 2×ArH); 4.52 (s; 2H; $HOCH_2$); 4.11–4.05 (m; 4H; 2×OCH_2); 3.80–3.73 (m; 4H; 2×OCH_2); 3.56 (c; J = 7.0 Hz; 4H; 2×OCH_2CH_3); 2.67 (s; 1H; $HOCH_2$); 1.19 (2t; J = 7.0 Hz; 6H; 2×OCH_2CH_3).

^{13}C *NMR (100.6 MHz, $CDCl_3$)*: 149.01; 148.24; 134.72; 120.02; 114.72; 114.57; 113.60; 68.98; 68.74; 66.82; 64.91; 64.80; 15.20.

EI-LRMS (m/z, rel. int.): 284 (61), 212 (10), 166 (28), 140 (12), 73 (100), 45 (92).

2.2.1.5. 3,4-Bis-[2-(2-ethoxyehtoxy)ethoxy]phenylmethanol. R_f: 0.20. (AcOEt). Brown oil.

^1H *NMR (400 MHz, $CDCl_3$)*: 6.94 (s; 1H; ArH); 6.85 (s; 2H; 2×ArH); 4.55 (s; 2H; $HOCH_2$); 4.17–4.10 (m; 4H; 2×OCH_2); 3.87–3.80 (m; 4H; 2×OCH_2); 3.74–3.66 (m; 4H; 2×OCH_2); 3.61–3.55 (m; 4H; 2×OCH_2); 3.51 (c; J = 7.0 Hz; 4H; 2×OCH_2CH_3); 2.21 (s; 1H; $HOCH_2$); 1.19 (2t; J = 7.0 Hz; 6H; 2×OCH_2CH_3).

^{13}C *NMR (100.6 MHz, $CDCl_3$)*: 148.99; 148.37; 134.64; 120.14; 114.66; 113.80; 70.94; 70.89; 70.00; 69.95; 69.94; 69;80; 69;00; 68.82; 66.73; 65.03; 65.01; 15.24; 15.22.

EI-LRMS (m/z, rel. int.): 372 (2), 166 (13), 117 (100), 89 (9), 73 (86), 45 (82).

2.2.1.6. 3,4-Bis-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)phenylmethanol. R_f: 0.16. (AcOEt). Brown oil.

^1H *NMR (400 MHz, $CDCl_3$)*: 6.99 (s; 1H; ArH); 6.87 (s; 2H; 2×ArH); 4.58 (s; 2H; $HOCH_2$); 4.21–4.11 (m; 4H; 2×OCH_2); 3.87–3.81 (m; 4H; 2×OCH_2); 3.75–3.69 (m; 8H; 4×OCH_2); 3.68–3.61 (m; 4H; 2×OCH_2); 3.60–3.55 (m; 4H; 2×OCH_2); 3.51 (c; J = 7.0 Hz; 4H; 2×OCH_2CH_3); 1.84 (s; 1H; $HOCH_2$); 1.19 (2t; J = 7.0 Hz; 6H; 2×OCH_2CH_3).

^{13}C *NMR (100.6 MHz, $CDCl_3$)*: 149.13; 148.55; 134.64; 120.30; 114.79; 114.12; 70.92; 70.79; 69.94; 69.87; 69.03; 68.93; 66.78; 65.54; 15.27.

EI-LRMS (m/z, rel. int.): 460 (1), 208 (11), 207 (53), 161 (23), 117 (46), 73 (100), 45 (63).

2.2.2. Monomers

The methacrylate monomers **11a–c** and **12a–c** were synthesised by the same general method (Scheme 2). The synthesis of 4-(methacryloxymethyl)-benzo-12-crown-4 is described as an illustrative example. The reaction solvent was ethyl ether or dichloromethane for the preparation of methacrylates with pendant podand or crown ether substructures, respectively.

2.2.2.1. 4-(Methacryloxymethyl)-benzo-12-crown-4. 4-Hydroxymethyl-(benzo-12-crown-4) (7.4 g, 23 mmol) and 7.7 g (46 mmol) of Et_3N were dissolved in 50 mL of dichloromethane in a 100 mL round bottom flask fitted with a condenser under a nitrogen blanket and magnetic stirring. The solution was then cooled to 0 °C, and 4.9 g (46 mmol) of methacryloyl chloride was added dropwise. After the addition, the cooling was discontinued, and the system was stirred for a further 24 h. Then, the mixture was extracted repeatedly with water, the organic layer was dried with magnesium sulphate, and the solvent was removed under vacuum. To achieve high purity, the product was purified by flash column chromatography using ethyl acetate/hexane (1:1) as the mobile phase and silica gel (230–400 mesh) as the stationary phase, affording a colourless solid.

M.p.: 69–71 °C.

^1H *NMR (400 MHz, $CDCl_3$)*: 6.97 (d; J = 1.8 Hz; 1H; ArH); 6.94 (dd; J = 1.8 and 8 Hz; 1H; ArH); 6.91 (d; J = 8 Hz; 1H; ArH); 6.15–6.06 (m; 1H; =CHH); 5.56–5.51 (m; 1H; =CHH); 5.06 (s; 2H;