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

Jimena Rey, Félix Clemente García, José Miguel García *

Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Plaza de Misael Bañuelos s/n, 09001 Burgos, Spain

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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-

* Corresponding author. Tel.: +34 947 25 80 85; fax: +34 947 25 88 31.
E-mail address: jmiguel@ubu.es (J.M. García).
URL: http://www2.ubu.es/quim/quimorg/polimeros/polimeros.htm (J.M. García).

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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).

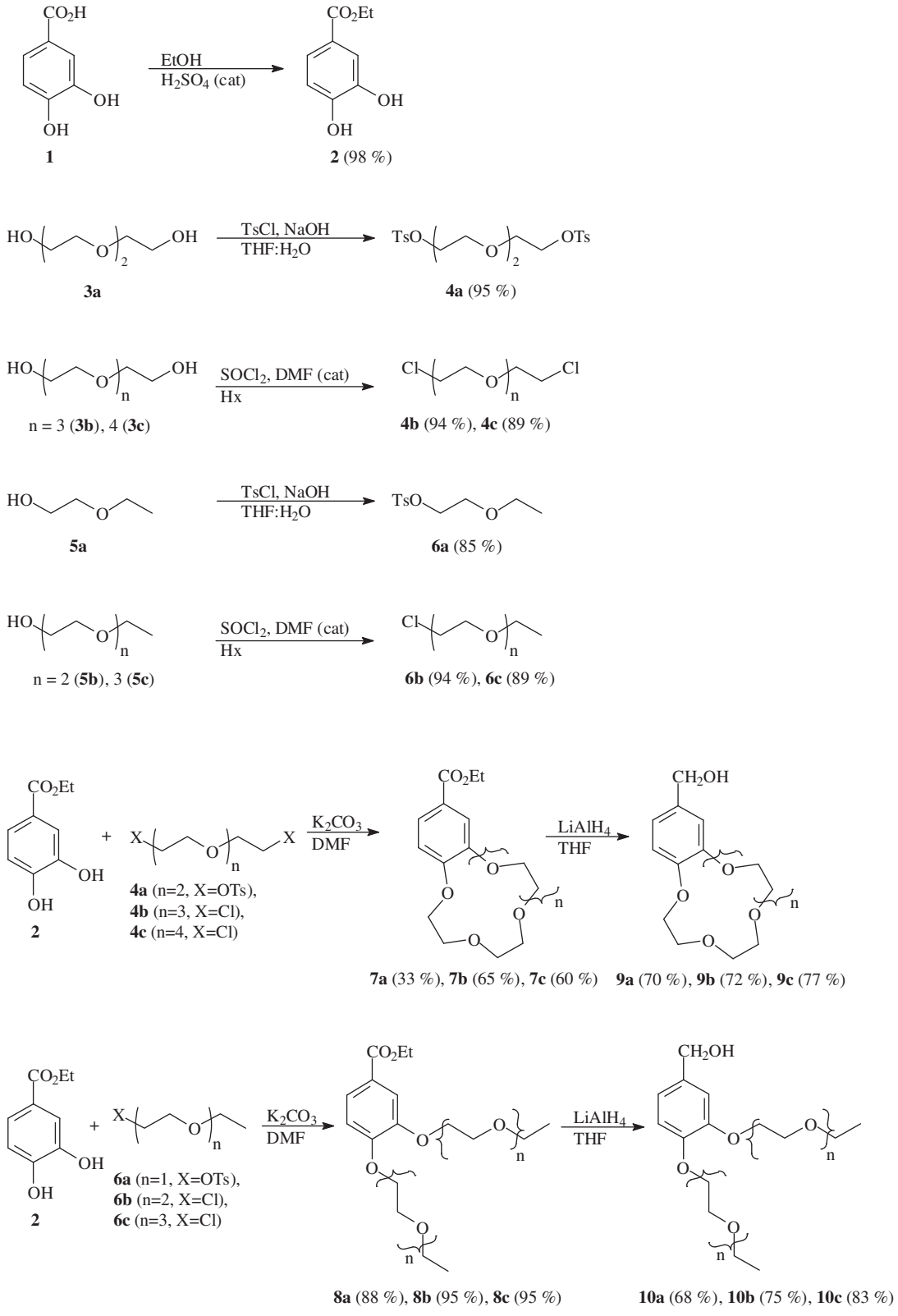
2.2.2. Monomers

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;



Scheme 1. Sequence for the synthesis of monomer intermediates.

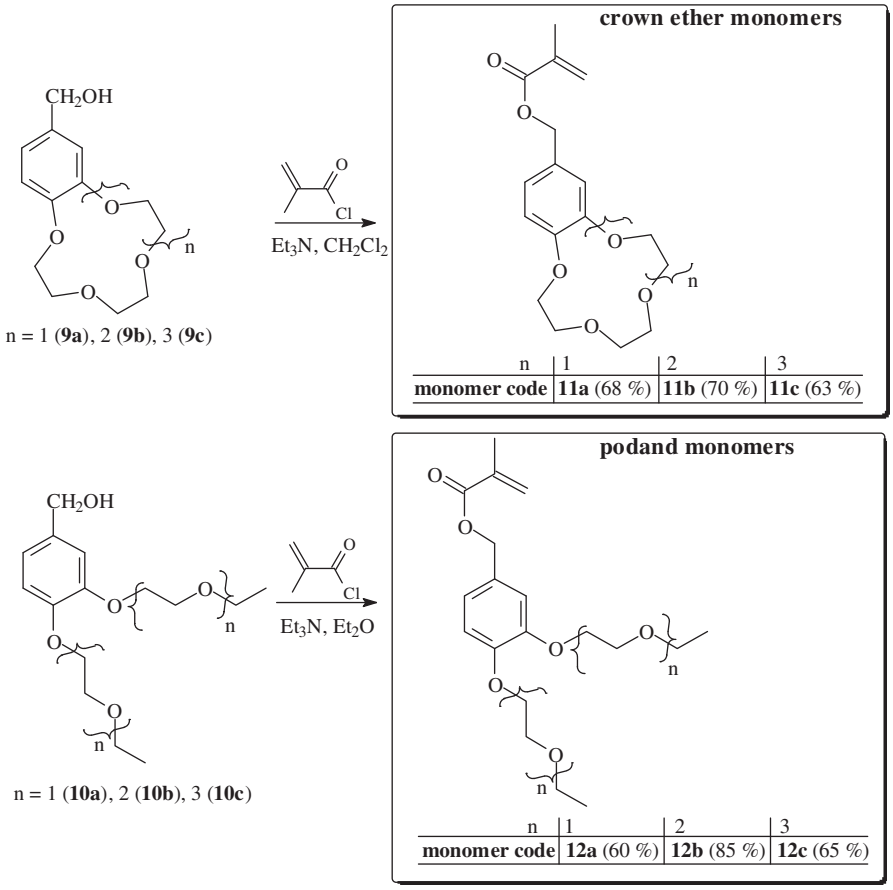
OCH_2Ar); 4.20–4,10 (m; 4H; $2\times OCH_2$); 3.85–3.80 (m; 4H; $2\times OCH_2$); 3.75 (s; 4H; OCH_2CH_2O); 1.93 (dd; $J = 0.9$ and 1.5 Hz; 3H; CH_3).

^{13}C NMR (100,6 MHz, $CDCl_3$): 167.26; 150.57; 150.51; 136.22; 130.56; 125.57; 122.81; 118.24; 117.87; 71.80; 71.72; 71.12; 69.87; 66.15; 18.41.

EI-LRMS (m/z, rel. int.): 322 (65), 149 (100), 137 (40), 69 (52), 45 (30), 43 (23), 41 (38).

2.2.2.2. 4-(Methacryloxymethyl)-benzo-15-crown-5. M.p.: 72–74 °C.

^1H NMR (400 MHz, $CDCl_3$): 6.92–6.84 (m; 2H; ArH); 6.80 (d; $J = 8$ Hz; 1H; ArH); 6.11–6.07 (m; 1H; =C*H*H); 5.56–5.50 (m; 1H;



Scheme 2. Sequence for the synthesis of the monomers.

=CH*H*); 5.06 (s; 2H; OCH_2Ar); 4.18–4.01 (m; 4H; 2×OCH_2); 3.96–3.81 (m; 4H; 2×OCH_2); 3.72 (s; 8H; 2×OCH_2CH_2O); 1.91 (dd; J = 0.9 and 1.5 Hz; 3H; CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): 167.27; 149.11; 149.04; 1336.24; 129.07; 125.77; 121.57; 114.30; 113.66; 71.09; 70.45; 69.55; 69.40; 69.02; 66.39; 18.39.

EI-LRMS (m/z, rel. int.): 366 (95), 367 (18), 189 (23), 165 (20), 164 (23), 149 (100), 148 (21), 137 (37), 69 (22).

2.2.2.3. 4-(Methacryloxymethyl)-benzo-18-crown-6. R_f: 0.09. (AcOEt). Brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): 6.92–6.85 (m; 2H; ArH); 6.80 (d; J = 8.5 Hz; 1H; ArH); 6.13–6.04 (m; 1H; =C*H*H); 5.58–5.47 (m; 1H; =CH*H*); 5.05 (s; 2H; OCH_2Ar); 4.16–4.06 (m; 4H; 2×OCH_2); 3.92–3.83 (m; 4H; 2×OCH_2); 3.75–3.70 (m; 4H; 2×OCH_2); 3.69–3.65 (m; 4H; 2×OCH_2); 3.62 (s; 4H; OCH_2); 1.90 (dd; J = 0.9 and 1.5 Hz; 3H; CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): 167.44; 149.12; 149.05; 136.42; 129.25; 125.95; 121.73; 114.53; 113.92; 71.03; 70.89; 69.77; 69.27; 66.55; 18.58.

EI-LRMS (m/z, rel. int.): 410 (16), 189 (18), 164 (21), 165 (22), 148 (20), 137 (19), 69 (45), 45 (46), 43 (34), 41 (24), 28 (31).

2.2.2.4. 3,4-Bis(2-ethoxyethoxy)benzyl methacrylate. R_f: 0.50 (AcOEt). Colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 6.95 (d; J = 1.8 Hz; 1H; ArH); 6.92 (dd; J = 1.8 and 8.2 Hz; 1H; ArH); 6.88 (d; J = 8.2 Hz; 1H; ArH); 6.15–6.08 (m; 1H; =C*H*H); 5.58–5.52 (m; 1H; =CH*H*); 5.08 (s; 2H; OCH_2Ar); 4.18–4.11 (m; 4H; 2×OCH_2); 3.82–3.75 (m; 4H; 2×OCH_2); 3.59 (2c; J = 7.0 Hz; 4H; OCH_2CH3); 1.94 (dd; J = 0.9 and 1.7 Hz; 3H; CH_3); 1.21 (2t; J = 7.0 Hz; 6H; 2×OCH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): 167.34; 149.10; 149.02; 136.33; 129.40; 125.80; 121.93; 121.79; 115.17; 11.58; 114.47; 69.01; 68.88; 66.89; 66.40; 18.44; 15.29.

EI-LRMS (m/z, rel. int.): 352 (59), 149 (18), 73 (91), 69 (24), 45 (100), 41 (10).

2.2.2.5. 3,4-Bis-[2-(2-ethoxyehtoxy)ethoxy] benzylmethacrylate. R_f: 0.47 (AcOEt). Colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 6.94–6.87 (m; 1H; ArH); 6.85 (d; J = 8.2 Hz; 1H; ArH); 6.12–6.06 (m; 1H; =C*H*H); 5.57–5.49 (m; 1H; =CH*H*); 5.06 (s; 2H; OCH_2Ar); 4.18–4.11 (m; 4H; 2×OCH_2); 3.88–3.79 (m; 4H; 2×OCH_2); 3.73–3.66 (m; 4H; 2×OCH_2); 3.61–3.54 (m; 4H; 2×OCH_2); 3.49 (2c; J = 7.0 Hz; 4H; OCH_2CH3); 1.92 (dd; J = 1.0 and 1.5 Hz; 3H; CH_3); 1.18 (t; J = 7.0 Hz; 6H; 2×OCH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): 167.24; 148.94; 148.86; 136.52; 129.31; 125.75; 121.70; 114.94; 114.40; 70.92; 69.91; 69.72; 68.92; 68.89; 66.67; 66.33; 18.38; 15.19.

EI-LRMS (m/z, rel. int.): 440 (11), 149 (19), 117 (98), 73 (89), 69 (27), 59 (10), 45 (100).

2.2.2.6. 3,4-Bis-(2-(2-(2-ethoxyethoxy)ethoxy)ethoxy)benzyl methacrylate. R_f: 0.28 (AcOEt). Colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 6.95–6.89 (m; 1H; ArH); 6.88 (d; J = 8.3 Hz; 1H; ArH); 6.14–6.09 (m; 1H; =C*H*H); 5.59–5.53 (m; 1H; =CH*H*); 5.08 (s; 2H; OCH_2Ar); 4.21–4.11 (m; 4H; 2×OCH_2); 3.89–3.81 (m; 4H; 2×OCH_2); 3.77–3.70 (m; 4H; 2×OCH_2); 3.69–3.61 (m; 8H; 4×OCH_2); 3.61–3.55 (m; 4H; 2×OCH_2); 3.51 (c;

J = 7.0 Hz; 4H; OCH_2CH3); 1.94 (dd; J = 1.0 and 1.5 Hz; 3H; CH_3); 1.19 (t; J = 7.0 Hz; 6H; $2\times OCH_2CH_3$).

^{13}C NMR (100.6 MHz, $CDCl_3$): 167.49; 149.10; 149.05; 136.46; 129.51; 125.98; 121.91; 115.11; 114.60; 71.04; 70.88; 70.72; 70.02; 69.90; 69.04; 66.85; 66.54; 18.59; 15.37.

EI-LRMS (m/z, rel. int.): 528 (1), 161 (17), 73 (96), 69 (19), 59 (10), 45 (100).

2.3. Synthesis of the polymers

The linear polymethacrylates were prepared by conventional radical polymerisation of the corresponding monomers in solution. A 0.3 M or 0.7 M benzene solution of the monomers with crown ether (**11a–c**) or podand (**12a–c**) moieties, respectively, were prepared in a jacketed reactor. The solutions were deoxygenated by nitrogen bubbling, AIBN was added to achieve a concentration of 0.003 M, and then the reaction was heated to 60 °C under a nitrogen blanket. The polymerisation was quenched when the conversion was approximately 50%, followed gravimetrically with aliquots taken periodically to avoid anomalous effects. The quenching and isolation of the polymers was accomplished by lowering the temperature and precipitating in a mixture of ethyl acetate/hexane (1:1) or pure hexane for polymers containing crown ether or podands, respectively, in the pendant structure. The polymer structures and codes are depicted in Scheme 3.

The crosslinked polymethacrylates, used in the solid–liquid extraction experiments were prepared by means of bulk polymerisation of the corresponding monomers using 1% AIBN (by weight, dissolved in acetonitrile) and 1 mol% crosslinker (ethylene glycol dimethacrylate). Thus, the nominal crosslinking ration (NCR), i.e., the ratio between number of moles of the monomer to the crosslinking agent, was 100. Acetonitrile was used as a solvent promoter in a few cases. The solutions were thoroughly deoxygenated by nitrogen bubbling, with the concomitant elimination of most of the acetonitrile. Then, the solution was heated to 60 °C under a nitrogen atmosphere for 5 h. Finally, the system was washed in acetone, giving rise to an insoluble white powder.

2.4. Measurements

The NMR spectra of polymers were recorded on a Varian INOVA 400 spectrometer operating at 399.92 MHz (^1H) and 100.57 MHz (^{13}C) using deuterated chloroform as solvent and tetramethylsilane (TMS) as the internal standard. A Varian GEMINI 200 NMR spectrometer with the temperature controlled at ±0.05 °C was used to control the changes in monomer concentration during the polymerisation reactions. These experiments used deuterated benzene as solvent and TMS as the internal standard.

The polymerisation kinetics experiments in solution were carried out as follows: the monomers were dissolved in 5 mL of deuterated benzene to a concentration of 1 M and adding AIBN to a concentration of 0.1 M. Then, 0.75 mL of this solution was introduced into a 5 mm NMR tube after elimination of oxygen by bubbling nitrogen into the solution. The reaction was then carried out between 50 and 70 °C. The kinetics of polymerisation was followed by measuring changes in the monomer concentrations by NMR spectroscopy. The area changes in the resonance signals corresponding to the methylene protons of the double bond of the methacrylic residue that appeared at 5.6 and 6.1 ppm were used to determine the variation of monomer concentration. As an illustrative example, Fig. 1 shows the ^1H NMR spectra corresponding to the polymerisation of monomer **11c**.

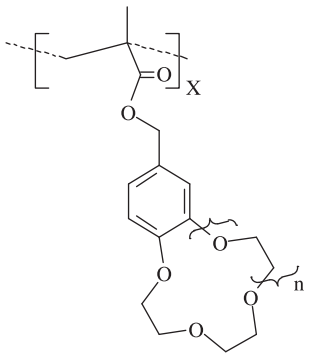
The solid–liquid extraction of each target cation (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, and Tb^{3+} as their perchlorate salts was carried out as follows: 10 mg of the proper crosslinked polymer was shaken with 1 mL of a water or acetonitrile solution of the proper cation series for a week at 25 °C (liquid phase). The molar ratio of the overall cations in each cation series to crown subunits (polymeric structural units) was 1:1, and all of the cations of a series were at the same concentration. After filtration, the concentration of the cations in the aqueous phase was determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500i), and direct information on the selectivity of polyamides toward metal ions was obtained.

Low-resolution electron impact (LR-EI) mass spectra were obtained at 70 eV on an Agilent 6890*N* mass spectrometer.

Gel Permeation Chromatography (GPC) analyses were carried out by using PSS-GRAM columns of nominal pore size 30, 100 and 3000 Å. *N,N*-Dimethylformamide (DMF)/0.01 M LiBr was used as solvent and the measurements were done at 70 °C with flow rate of 1.0 mL/min, and using a RI detector. The columns were calibrated with narrow distribution standards of poly(methyl methacrylate).

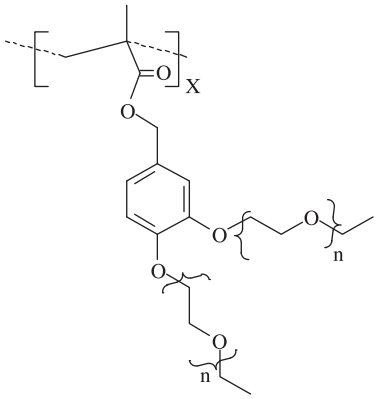
The thermal properties of the polymers were determined calorimetrically (DSC) with a Perkin-Elmer Pyris I calorimeter at a heating rate of 10 °C min^{-1} by measuring the glass transition

polymers with pendant crown ether moieties



n	1	2	3
polymer code	**13a**	**13b**	**13c**

polymers with podand moieties



n	1	2	3
polymer code	**14a**	**14b**	**14c**

Scheme 3. Polymer structures and codes.

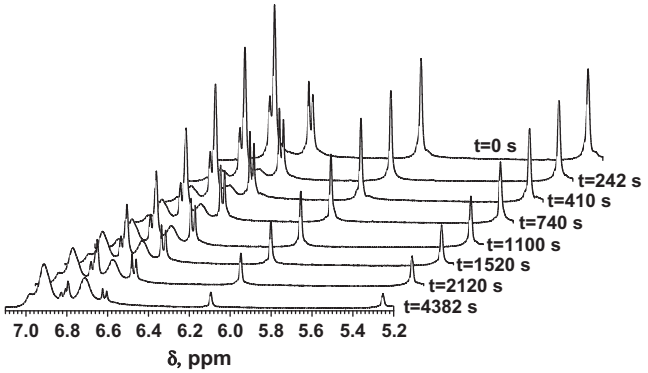


Fig. 1. ^{1}H NMR spectra corresponding to the polymerisation kinetics experiment on monomer **11c** to give the polymethacrylate **13c** (solvent: deuterated benzene; temperature: 60 °C).

temperature (T_g) at the onset of the separation of endotherms from the baseline.

3. Results and discussion

3.1. Polymer synthesis and characterisation

The preparation of the monomers was carried out following conventional organic chemistry methodology, as depicted in Schemes 1 and 2. The preparation of the benzo-crown ethers and their dipodal counterparts was achieved by cyclisation reactions using the conventional Williamson ether synthesis from the 1,2-benzenediol derivative and the corresponding organohalide giving rise to products with high yield and purity (**7b–c** and **8b–c**), except for the lower crown or dipodal compounds of the two series. Regarding this point, the substitution of the organohalide by the tosylate increased the yield of **7a** from 20% to 33%. This yield corresponded to the isolated product and was ~30% higher than the reported previously for other benzo-12-crown-4 derivatives [38,39]. This improved yield could be achieved using high dilution, but not templates. The preparation of **7a** gave rise to a by-product diester, bis(4-ethoxycarbonyl-1,2-diphenylene)-24-crown-8, which was eliminated by means of column chromatography. Interestingly, the diester by-product was not detected in benzo-crown ethers with higher oxyethylene sequences (**7b–c**). The subsequent reduction of the esters (**7a–c** and **8a–c**) to the alcohols (**9b–c** and **10b–c**), and from there to the methacrylates (**11a–c** and **12b–c**), was easily accomplished with good yield. The methacrylates were column purified to ensure high purity products.

Conventional radical solution polymerisation of the monomers gave rise to polymers. The conversion was maintained around 50%, followed gravimetrically during polymerisation, to avoid anomalous reactions usually observed at higher yields. The polymer structures were confirmed by NMR, as depicted in Figs. 2 and 3 for polymers **14c** and **13b,** as illustrative examples. The average number molecular weight and molecular weight distribution were $M_n = 2.8 \times 10^4$, 2.1×10^4, 2.4×10^4, 3.2×10^4, 2.0×10^4, 3.3×10^4 g/mol, and $M_w/M_n = 1.72, 1.81, 1.86, 1.91, 1.78, 1.89$ for polymers **13a**, **13b**, **13c**, **14a**, **14b**, **14c**, respectively. These results are in accordance with those obtained by other researchers for vinyl polymers with bulky side groups [40].

The polymer microstructure was determined by ^{13}C and ^{1}H NMR. The molar fractions of the diads and triads were determined by measuring the relative peak areas corresponding to the signals of CO, C, α-CH_3, and CH_2, as shown for polymer **13b** in Fig. 4. Three resonance signals appeared for each carbon, except the C=O that had greater sensitivity to the stereochemical configuration. Following classical, and previously described, assignment in other methacrylic polymers [41–43], the resonance signals were attributed to different tactic triads and pentads (in the case of the carbonylic carbon, Fig. 4) from which the molar fractions of different configurations were calculated. An average molar fraction of syndiotactic dyads of 0.81 ± 0.03 was obtained. Comparison with the values for triad and pentad units indicated Bernoullian stereochemical control [44]. This result was similar to that found for a wide set of polymethacrylates obtained by radical polymerisation, indicating the predominance of syndiotactic over isotactic sequences [45,46].

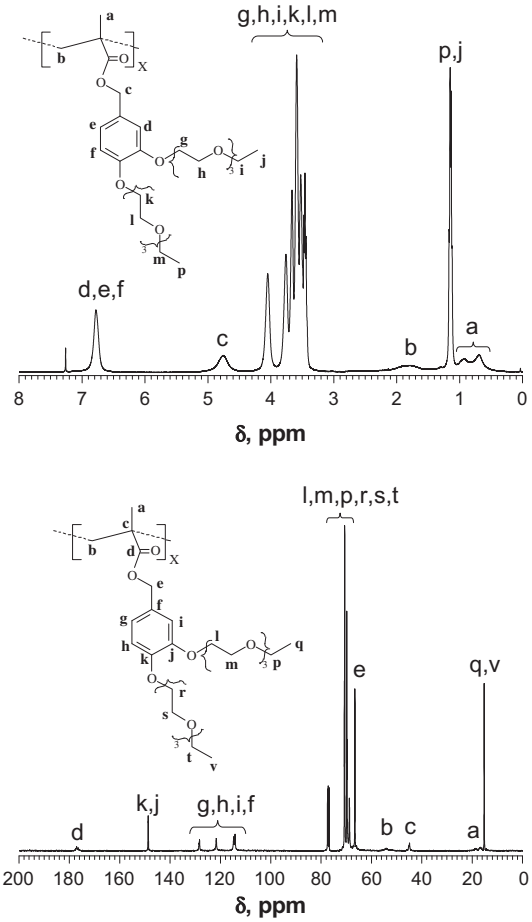


Fig. 2. ^{1}H and ^{13}C NMR spectra (400 and 100.6 MHz, $CDCl_3$) of polymer **14c**.

The values of T_gs of the linear polymers ranged between −90 and 55 °C, as depicted in Fig. 5 for all of the polymers. Interestingly, the transition showed a huge dependence on the flexibility of the pendant structure. Thus, the differences between series **14a–c** and **13a–c** ranged from 57 to 79 °C because of the conformational restrictions imposed by the alicycle in the former. In each series, the increasing mobility of the oxyethylene sequences gave rise to a decreased transition temperature. These data related well with previously reported polymethacrylates containing a lateral methyl-12-crown-4 and its open chain counterpart, [poly(tetraethyleneglycol monoethyl ether) methacrylate], with T_gs values of 35 and −48 °C, respectively [33–47]. Regarding the T_gs of the crosslinked materials, they could not be detected by DSC. Nevertheless, the crosslinking of polymer chains impairs the generalized chain movement increasing this transition. For example, a polymer network with a related structure, comprised of poly[2-(2-aminoethoxyethanol) methacrylamide], and, NCR, had a glass transition 20 °C higher than the corresponding linear polymer.

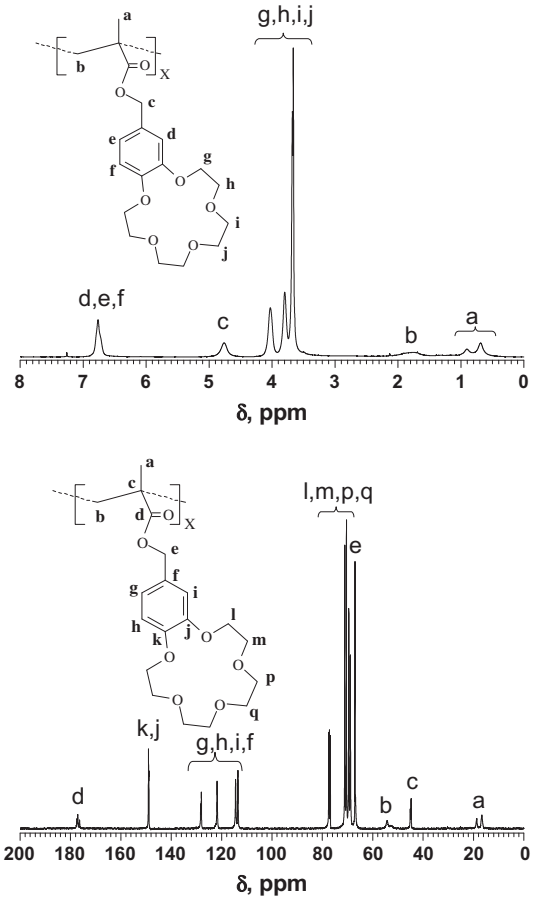


Fig. 3. ^{1}H and ^{13}C NMR spectra (400 and 100.6 MHz, $CDCl_3$) of polymer **13b**.

3.2. Kinetics of polymerisation

The data for radical polymerisation kinetics followed by ^{1}H NMR were analysed using Eq. (1), which is straightforwardly derived from the classical radical polymerisation scheme by assuming equal initiation and termination rates (i.e., the so-called stationary state, where k_d, is the rate constant for initiator decomposition and k_p and $\langle k_t \rangle$ are the overall averages of propagation and termination rate constants, respectively). In the equation, $[M_0]$ and $[M]$ are the initial and instantaneous concentrations of monomer, respectively, $[I_0]$ is the initial concentration of initiator, and f is the efficiency of the initiator. Eq. (1) is therefore a suitable equation to describe the polymerisation whenever $(2f)^{½}k_p/\langle k_t \rangle^{½}$ remains throughout the reaction.

$$\ln\frac{[M_0]}{[M]} = 2k_p\left(\frac{2f[I_0]}{k_t k_d}^{1/2}\right)\left[1-\exp\left(\frac{-k_d t}{2}\right)\right] \quad (1)$$

The variation of the monomer concentration throughout the polymerisation reaction is depicted in Fig. 6 for monomer **11c** at temperatures ranging from 50 to 70 °C. The lines correspond to the fitting of the data using Eq. (1).

From these data, the relationship to low conversions can be extracted when the concentration of the radical initiator was considered constant. Eq. (1) could then be transformed into the following equation:

$$\ln\frac{[M_0]}{[M]} = k_p\left(\frac{2f[I_0]k_d}{k_t}^{1/2}\right)t \quad (2)$$

Thus, the least square adjustment of the time *vs.* $\ln([M_0]/[M])$ data gave rise to a straight line with a slope corresponding to $(2f)^{½}[I_0]^{½}k_p/\langle k_t \rangle^{½}$, as depicted in Fig. 7 for the polymerisation of monomer **12a**. From the slopes at time zero and the averaged values of k_d for AIBN reported in the literature, [48–51] the values of the rate parameter $(2f)^{½}k_p/\langle k_t \rangle^{½}$ at different temperatures were determined (Table 1). At high conversions, the so-called gel or Norrish-Tromsdorff effect was not observed, a phenomenon previously described in the polymerisation of methacrylates having short aliphatic oxyethylene sequences [45,46].

The values of $(2f)^{½}k_p/\langle k_t \rangle^{½}$ for all of the monomers were very high, exceeding those corresponding to the methacrylate with the aliphatic crown ether residue by almost twofold [52] and their open chain methacrylates homologues by almost threefold [45,53]. Furthermore, the polymerisation rates for the monomers with less bulky side groups (**12a** and **11a**) resembled those observed in the polymerisation of functional hydrophilic monomers such as 2-hydroxyethylmethacrylate (HEMA) [33] and 2,3-dihydroxypropylmethacrylate [54]. Meanwhile, this parameter was much higher in the monomers with bulkier groups (**12b–c**, **11b–c**). Fig. 8 shows the relationship of the monomer conversion at a given polymerisation time *vs.* side group bulkiness (i.e., the dependence of the rate

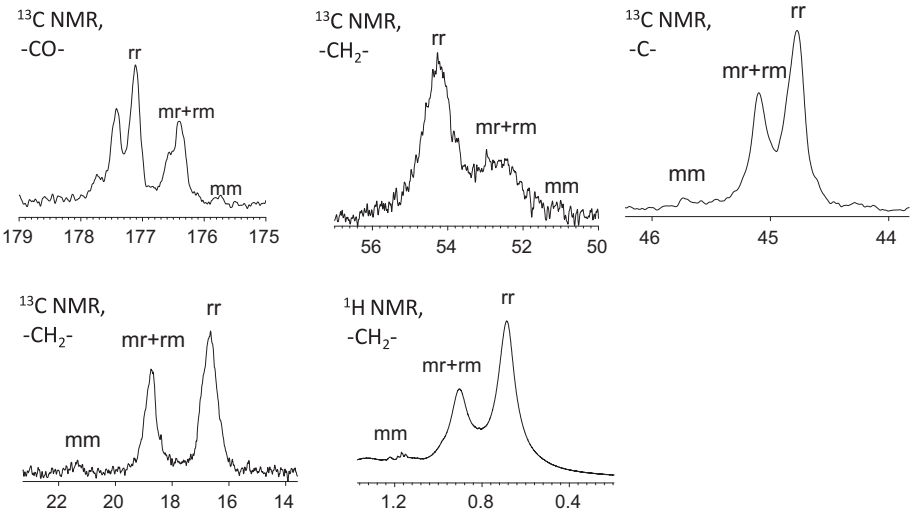


Fig. 4. Molar fractions of tactic triads and diads in polymethacrylate **13b** determined by NMR.

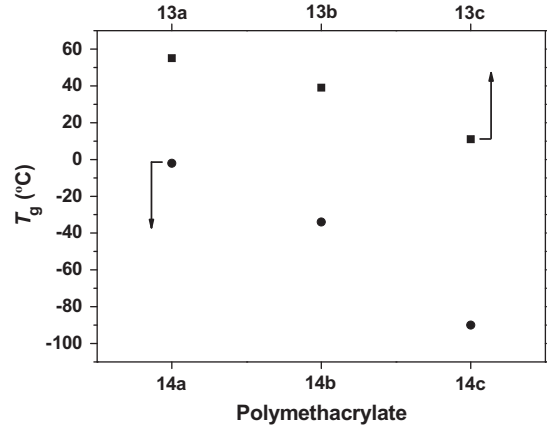


Fig. 5. T_gs of the polymethacrylates with crown ether moieties (■) and with podand subgroups (●).

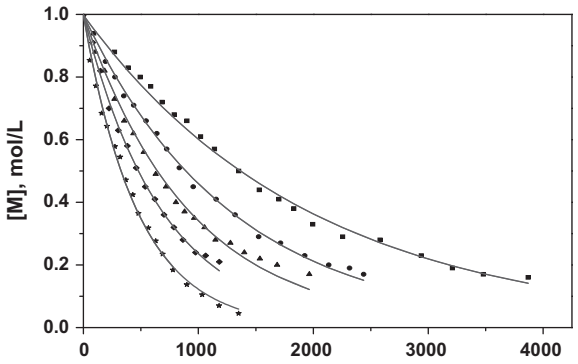


Fig. 6. Changes in the monomer concentration in the radical polymerisation of **11c** at 70 °C (★), 65 °C (♦), 60 °C (▲), 55 °C (●), 50 °C (■), $[M_0] = 1$ mol L^{-1}, and $[I_0] = 0.1$ mol L^{-1}). The lines correspond to the fitting of the data using Eq. (1).

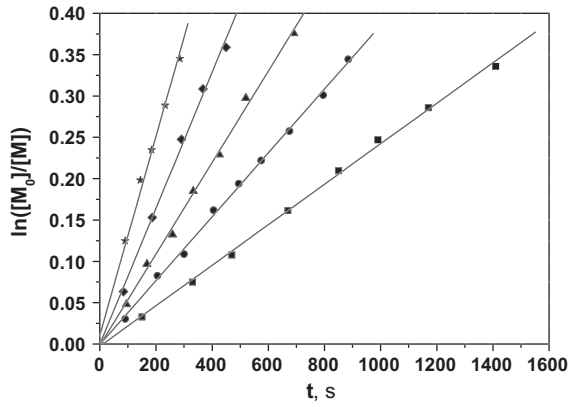


Fig. 7. Monomer concentration vs. time in the polymerisation of **12a** at different temperatures [70 °C (★), 65 °C (♦), 60 °C (▲), 55 °C (●), 50 °C (■)]. Polymerisation conditions: $[M_0] = 1$ mol L^{-1}, $[I_0] = 0.1$ mol L^{-1}). The straight lines correspond to the fitting of the data using a least square adjustment.

parameter on the number of oxyethylene sequences in crown and dipodal containing monomers). This incremental change in the polymerisation rate with increasing molecular weight of the methacrylic monomers is usually found in radical polymerisation [55], with steric effects playing a major role in this change, probably because of the decrease in $\langle k_t \rangle$ [56]. In our system, this behaviour can be graphically observed in Fig. 9.

Table 1
Kinetic rate parameter for the polymerisation of the methacrylates in 1 M benzene solution using an initiator concentration (AIBN) of 0.1 M. The last column lists the values of k_d used for the calculations.

$(2f)^{½}k_p/\langle k_t \rangle^{½}$ (L^{½} mol$^{-½}$ s$^{-½}$)[a]								
T (°C)	**12a**	**12b**	**12c**	**11a**	**11b**	**11c**	Reference[b]	$k_d \times 10^6$ (s^{-1})
50	0.53_7	0.73_4	1.09_3	–	0.62_7	0.96_6	0.42_7	2.2
55	0.56_4	0.77_7	1.11_8	0.45_1	0.64_6	1.02_9	0.44_4	4.5
60	0.58_1	0.81_1	1.15_4	0.47_1	0.67_5	1.09_8	0.45_6	9.1
65	0.60_5	0.87_1	1.17_8	0.48_8	0.69_5	1.15_5	0.46_4	18.6
70	0.63_1	0.92_3	1.22_6	0.50_7	0.71_3	1.22_6	0.48_0	36.5

[a] f is usually considered to be 0.6 for most systems.
[b] Poly(hydroxymethyl-12-crown-4) methacrylate.

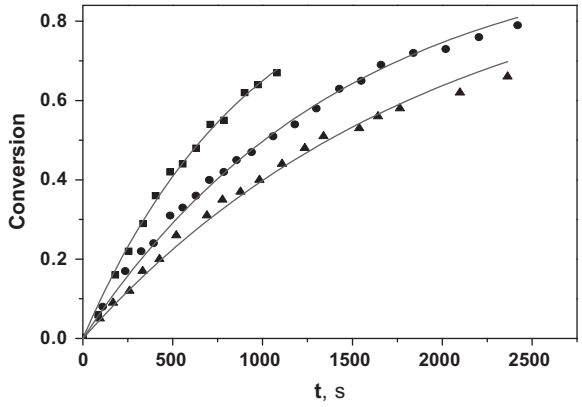


Fig. 8. Variation in monomer concentration with polymerisation time (**12a** (▲), **12b** (●), **12c** (■); 60 °C, $[M_0] = 1$ mol L^{-1}, $[I_0] = 0.1$ mol L^{-1}).

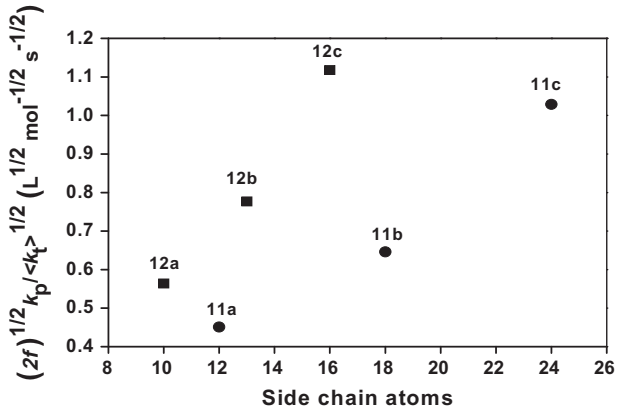


Fig. 9. Rate parameter $(2f)^{½}k_p/\langle k_t \rangle^{½}$ *vs.* number of side chain atoms at a polymerisation temperature of 55 °C for monomers with alicyclic (●) and acyclic (■) structures.

3.3. Solid–liquid extraction of cations from organic and aqueous media

The solid–liquid extraction technique is based on the extraction of a chemical from solution with a solid phase. The extraction effectiveness is based on physical interactions of the target chemical in solution with the solid phase through the solid–liquid interphase. Polymer networks take advantage of their solvent swelling ability, sometimes giving rise to gels, easily allowing the solvated target chemicals to reach the chemical subgroups within the polymer structure. Interactions then take place by means of diffusion,

Table 2
Solid–liquid extraction percentage (%E) of lanthanide cations in acetonitrile and aqueous solution (between brackets) using crosslinked methacrylates.[a]

Polymer	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}
13a	8 (–)	6 (–)	7 (–)	5 (–)	7 (–)	9 (–)	9 (–)	12(–)
13b	21 (–)	19 (–)	18 (–)	20 (–)	21 (–)	23 (–)	23 (–)	24 (–)
13c	62 (11)	49 (12)	39 (12±)	31 (11)	21 (12)	19 (11)	17 (9)	15 (8)
14a	13 (7)	12 (7)	13 (6±)	12 (7)	12 (6)	13 (6)	12 (5)	12 (5)
14b	18 (14)	18 (18)	17 (19±)	18 (19)	18 (20)	18 (19)	19 (15)	18 (13)
14c	44 (23)	40 (28)	41 (30±)	39 (30)	35 (33)	35 (30)	37 (24)	35 (20)

[a] Negligible extraction percentages are denoted with two consecutive hyphens (–). The error that represent the 95% confidence interval of the mean corresponding to measurements of lanthanide concentration in solid–liquid extraction experiments was previously estimated to be lower than 19% – Ref. [31].

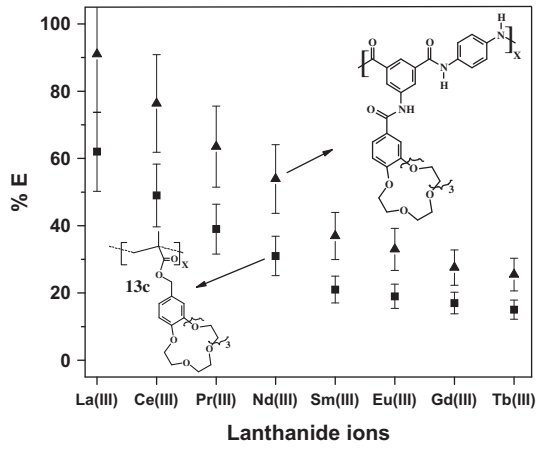


Fig. 10. Solid–liquid extraction of lanthanide ions in acetonitrile solution using solid-phase polymers (**13c** and a polyamide with a benzo-18-crown-6 pendant structure-data and error bars representing the 95% confidence interval of the mean were taken from Ref. [31]).

with the difference in concentration being part of the driving force of the process.

As previously mentioned, crown ethers are key structures in supramolecular chemistry as species that have a cavity specially suited for the complexation of cations whose cation radii fit well into the diameter of this cavity. Nevertheless, in aqueous media the strong solvation of charged species hinders the interaction of an organic supramolecular entity in this environment. This fact is more important in neutral host molecules, such as crown ethers. Thus, as noted previously, the very low stability constants (K_s) of crown ether polymers exist in aqueous solution for charged species, such as lanthanide cations. For instance, the interaction of Tb^{3+} and Eu^{3+} with a methacrylate with pendant aliphatic 12-crown-4 moieties gave rise to a $K_s = 22$ and 1.9 M^{-1}, respectively. These interactions caused a loss of one to two water coordination molecules, out of the possible 9. The interaction in the solid state is much higher, as it also is in the gel state, as demonstrated using water-swelled membranes that lost 5 water coordination molecules for Tb^{3+} (a water-swelled, crosslinked membrane prepared with a methacrylate with a pendant aliphatic residue of 15-crown-5, indicating the replacement of a coordination molecule of water for each oxygen of the crown moiety) [35,36]. In a similar fashion, these interactions in organic solvents are much stronger than in water.

Considering the above, the solid–liquid extraction experiments for lanthanide cations, both in organic (acetonitrile) and aqueous solution, using crosslinked polymers were carried out (Table 2). The results showed the effect of the solvent, as mentioned above, with the extraction strongly favoured in organic media. The extraction selectivity of these polymers was similar to those found for polyamides having the same host motifs, as can be seen in Fig. 10 for polymers having pendant benzo-18-crown-6 receptors. The extraction data also illustrate difficulty in interpretation of the results, as polymers with crown motifs have good extraction percentages and selectivities in organic media, but polymers with podand host motifs have better results in water. In this regard, podands are likely not restricted to a fixed cavity size, as are crowns, and conformational changes can adapt the shape and size of the podand arms to the cation guest.

The rationalisation of the interaction of crown ether species with cations, both in aqueous and organic media, is cumbersome and cannot be easily carried out, as pointed out by Calderon et al. [31]. In principle, the better the fit of the cation radii to the crown ether cavity, the higher stability constant of the complex, and the higher expected extraction percentage. On the other hand, the polymethacrylates having pendant crown ethers have a comb-like structure that could give rise, upon interaction with cations, to sandwich structures with the participation of two or three vicinal crown moieties (e.g., zip structures and pseudo-cryptands), modifying the expected extraction selectivity due to the generation of cavities of different sizes and shapes.

4. Conclusion

The synthesis and characterisation of methacrylic polymers having pendant crown ethers or their dipodal, open chain counterparts is reported, along with the study of their polymerisation kinetics and thermal properties in terms of structure–property relationships. The potential applications of these materials have been exemplified in the extraction of cations from aqueous and organic media using crosslinked polymers as solid phases in solid–liquid extraction experiments.

Acknowledgments

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