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ScienceDirect
Polymer 48 (2007) 3938–3951
polymer
www.elsevier.com/locate/polymer

Star polymers synthesised with flexible resorcinarene-derived ATRP initiators

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Received 1 November 2006; received in revised form 20 February 2007; accepted 10 May 2007
Available online 18 May 2007

Abstract

Two octafunctional resorcinarene-based ATRP initiators were synthesised where the initiating sites were separated from the macrocyclic ring with a short spacer. The spacer was introduced to reduce the steric hindrance at the initiating sites and to increase the number of arms in the resulting star polymers. Higher functionalities of starlike poly(*tert*-butyl acrylates), P*t*BA, and poly(methyl methacrylates), PMMA, were obtained, compared to the results by the initiators without a spacer. The kinetics of the polymerisations of *t*BA and MMA were investigated using various catalysts and solvents. The spacer increased the rate of the polymerisation of bulkier *t*BA monomer, but had little effect on the polymerisation of MMA.

Keywords: Star polymers; Atom transfer radical polymerisation (ATRP); Initiators

1. Introduction

The synthesis of materials with controlled compositions and architectures continues to be a focus of current polymer research. The control can be achieved by the 'living' radical polymerisation methods, such as atom transfer radical polymerisation (ATRP) that allows the synthesis of well-defined macromolecular architectures like block copolymers, graft copolymers and various branched structures [1]. Among these tailor-made macromolecules, multiarm polymers, such as starlike and dendritic ones are those, which show interesting rheological properties arising from their spatial shape and which can have a high number of functional groups allowing specific applications [2–5]. The starlike polymers can basically be synthesized using two different approaches: 'arms first' and 'core first'. The 'arms first' technique involves the synthesis of preformed arms that are bound together with a multifunctional linking agent [6,7]. Further variations of this method involve the block copolymerisation of divinyl reagents to the arms, followed by the formation of a microgel core and core–core coupling [8,9]. The 'core first' method utilises multifunctional initiators.

In ATRP, the initiators usually contain a halogen, most frequently chlorine or bromine. A straightforward way to prepare ATRP initiators is to derivatise any substrate bearing a hydroxyl group by 2-bromopropionyl bromide or by 2-bromoisobutyryl bromide. Macrocyclic compounds often provide a number of functional groups that can be further derivatised to obtain starlike polymers. For instance, β-cyclodextrin has been used as a starting compound for 21-functional ATRP initiators [10,11] and calixarene-based 4-, 6- and 8-functional initiators have been used successfully in the synthesis of starlike polymers [12–14]. We have recently reported the synthesis of poly(*tert*-butyl acrylate) and poly(methyl methacrylate) star polymers by octafunctional resorcinarene-based ATRP initiators [15]. Resorcinarenes, like calixarenes, carry a circular array of hydrogen bonds between the phenolic hydroxyl groups, which breaks upon the derivatisation, altering the conformational and the complexing properties of the macrocycle [16–18]. This was also verified for the resorcinarene-based

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0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.05.024

initiators by various NMR techniques and molecular modelling. According to our polymerisation studies, the resorcinarene-based octafunctional initiators produced four-arm stars. The result did not depend of the size and activity of the catalyst, in which the ligands were varied from bulky 2,2′-bipyridine to smaller and more active multidentate ligands like *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) [19].

Some examples of the initiation systems where the steric properties play an important role are dendrimer-based initiators and brush-like macroinitiators [20–26]. The possible side reactions when using multifunctional initiators are intermolecular and intramolecular radical coupling. The coupling between the stars mostly depends on the reactivity of the monomer, and hence also on the reaction conditions [13,14]. The probability of the star–star coupling increases when the growing stars reach their critical overlap concentration c^* [14]. The intramolecular coupling may occur already at low conversions, for example, due to steric hindrance of the initiator or due to the backfolding of the growing polymer chains, that is, due to intramolecular cyclisation [20,23,27]. The backfolding of the initiator end groups themselves may be prevented by increasing the rigidity of the initiator, for instance by introducing aromatic groups to the structure [28]. The initiation conditions, such as the composition of the catalyst, may also influence the initiation efficiency [26].

We proposed earlier that the number of arms in the star polymer is determined by the conformation of the eight-functional resorcinarene-based initiators [15,19]. We have successfully used these initiators in the syntheses of four-armed amphiphilic diblock copolymers, in which the inner block connected to the macrocycle is poly(methyl methacrylate) and the outer one is poly(acrylic acid). The polymers dissolve in water but show a strong tendency to aggregate. In dilute aqueous solutions the polymers build up spherical micelles which upon the addition of salt further assemble into cylindrical micelles [29]. Because the number of arms affect the shape of the polymer [30], and thus probably also the association behavior, we have further elaborated the synthesis of eight-armed stars starting from a slightly more flexible resorcinarene than earlier. To increase the reactivity of the initiator, its flexibility has been increased by adding a short spacer between the macrocycle and the initiating unit. The new initiators have been used in the polymerisation of *tert*-butyl acrylate and methyl methacrylate. The functionalities of the resulting star polymers as well as the kinetics of the polymerisations have been investigated in detail using various catalysts and solvents, and the results have been compared to those of the initiators without spacers.

2. Experimental

2.1. Materials

2,8,14,20-Tetramethylresorcinarene was purchased from Aldrich and used without further purification. Ethyl bromoacetate, 2-bromopropionyl bromide, 2-bromoisobutyryl bromide, ethylene carbonate, diphenyl ether, 2,2′-bipyridine (2,2′-bipy), 4,4′-dinonyl-2,2′-bipyridine (dNbpy), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), CuBr (99.999%) and $LiAlH_4$ (all from Aldrich), 1,4-dioxane and triethylamine (both from Merck), dichloromethane (Rathburn), trifluoroacetic acid and toluene (both from Riedel-de-Haën), sodium methoxide solution in methanol (30%, from Fluka), and 2-propanol (Mallinckrodt) were used without further purification. CuCl (Merck) was purified as described by Nikitine et al. [31]. Acetone (Mallinckrodt, HPLC grade) was dried with CaH_2 and distilled. Tetrahydrofuran (THF, Rathburn) was distilled over sodium in the presence of benzophenone under nitrogen atmosphere. *Tert*-butyl acrylate (Aldrich) and methyl methacrylate (Fluka) were dried with $CaCl_2$ or CaH_2 and distilled in vacuum, the last one after the addition of a small amount of hydroquinone. The syntheses of the ATRP initiators octa-2-bromopropionyl-tetraethylresorcinarene (Scheme 3: **5**) and octa-2-bromoisobutyryl-tetraethylresorcinarene (Scheme 3: **6**) have been reported earlier [15].

2.2. Synthesis of 4,6,10,12,16,18,22,24-Octakis (ethoxycarbonylmethoxy)-2,8,14,20-tetramethylresorcinarene (*1*)

The compound was synthesized using the procedure described by Yonetake et al. [32]. A mixture of 2,8,14,20-tetramethylresorcinarene (2.5 g, 4.60 mmol) and potassium carbonate (6.25 g, 0.45 mol) in acetone (125 mL) was refluxed for 30 min under nitrogen atmosphere. Ethyl bromoacetate (8.2 mL, 12.35 g, 0.72 mol) was added to the pink, milky reaction mixture. The mixture was refluxed for 20 h, during which it turned yellow. The mixture was cooled to room temperature and the solution was decanted. The solvent was evaporated and replaced by CH_2Cl_2 (100 mL), after which the solution was washed with dilute aqueous HCl (0.01 M, 2 × 100 mL), followed by distilled water (2 × 100 mL). The washed solution was evaporated to dryness, giving yellow viscous liquid. The product was crystallized from 2-propanol to give light yellow solid, yield 4.92 g (87%).

^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 6.57 (br, ArH, 4H), 6.25 (s, ArH, 4H), 4.71 (q, >CH−, 4H), 4.23 (m, CH_2, 32H), 1.46 (d, >CHCH_3, 12H), 1.28 (t, −CH_2CH_3, 24H).

^{13}C NMR (50.3 MHz, $CDCl_3$) δ ppm: 169.35 (>C=O, 8C), 154.25 (ArOR, 8C), 129.69 (Ar, 4C), 125.82 (ArH, 8C), 100.60 (ArH, 4C), 67.21 (ArOCH_2−, 8C), 60.97 (−$CH_2$$CH_3$, 8C), 30.89 (>CH−, 4C), 19.69 (>CHCH_3, 4C), 14.12 (−CH_3, 8C).

IR (solid, ATR) cm^{-1}: 2966 (w), 2934 (w), 2873 (w), 1749 (s), 1717 (m), 1614 (w), 1588 (w), 1450 (m), 1443 (w), 1408 (w), 1377 (w), 1305 (m), 1283 (m), 1269 (m), 1243 (w), 1200 (s), 1186 (s), 1164 (s), 1131 (s), 1079 (s), 1024 (m), 970 (w), 937 (w), 906 (w), 893 (w), 860 (w), 840 (m), 820 (m), 721 (w).

MALDI-TOF MS molar mass calculated for $C_{64}H_{80}O_{24}$: *m*/*z* 1256.33 $[M + Na]^+$.

Found: *m*/*z* 1255.65 $[M + Na]^+$.

Elemental analysis: calculated for $C_{64}H_{80}O_{24}$: C, 62.33%; H, 6.54%; O, 31.13%.

Found: C, 62.25%; H, 6.55%; O, 31.36%.

2.3. Synthesis of 4,6,10,12,16,18,22,24-Octakis-(2-hydroxyethoxy)-2,8,14,20-tetramethylresorcinarene (**2**)

The compound was synthesized using the procedure described by Yonetake et al. [32]. To a mixture of $LiAlH_4$ (2.46 g, 0.062 mol) in dry THF (100 mL) a solution of **1** (4.90 g, 3.98 mmol) in THF (40 mL) was added drop wise. The mixture was refluxed for 45 h. Water (14 mL) was added drop wise to the cooled mixture. The precipitate was filtered off and the solution was evaporated to dryness. The crude product was recrystallised from 2-propanol to give a white solid, yield 1.01 g (30%).

^{1}H NMR (300 MHz, DMSO-d_6, 70 °C) δ ppm: 6.45 (br, Ar, 8H), 4.57 (CH, 4H), 4.38 (OH, 8H), 3.88, 3.71, 3.57 and 3.14 (CH_2, 32H), 1.34 (CH_3, 12H).

^{13}C NMR (50.3 MHz, DMSO-d_6) δ ppm: 154.89 (ArOR, 8C), 127.73 (Ar, 4C), 124.73 (ArH, 8C), 99.75 (ArH, 4C), 70.84 (ArO*C*H_2−, 8C), 60.29 (−*C*H_2OH, 8C), 30.16 (>CH−, 4C), 20.71 (>CH*C*H_3, 4C).

IR (solid, ATR) cm^{-1}: 3311 (br), 2957 (w), 2930 (w), 2871 (w), 1606 (w), 1580 (w), 1497 (m), 1452 (w), 1408 (w), 1365 (w), 1297 (m), 1240 (w), 1185 (m), 1128 (m), 1113 (m), 1076 (s), 1048 (s), 984 (w), 900 (m), 823 (w).

MALDI-TOF MS molar mass calculated for $C_{48}H_{64}O_{16}$: *m/z* 936.14 $[M + K]^+$.

Found: *m/z* 935.52 $[M + K]^+$.

Elemental analysis: calculated for $C_{48}H_{64}O_{16}$: C, 64.27%; H, 7.19%; O, 28.54%.

Found: C, 63.25%; H, 7.19%; O, 29.60%.

2.4. Synthesis of 4,6,10,12,16,18,22,24-Octakis(2-bromopropionyl)-2,8,14,20-tetramethylresorcinarene (**3**)

In a 250-mL double-necked flask equipped with a magnetic stirrer, **2** (1.0 g, 1.11 mmol) was added to 30 mL of dry THF, followed by triethylamine (3.75 mL, 2.71 g, 26.8 mmol). The white suspension was cooled to 0 °C and a solution of 2-bromopropionyl bromide (3.0 mL, 6.18 g, 28.6 mmol) in 30 mL of THF was added drop wise to the vigorously stirred suspension over 0.5 h. The solution was stirred at room temperature for 48 h. The reaction mixture was filtered, and the solution was concentrated with a rotary evaporator. The concentrate was dissolved in diethyl ether (100 mL) and washed with a 0.1 M aqueous K_2CO_3 solution (4 × 70 mL), followed by water (3 × 100 mL). The ether layer was dried over $MgSO_4$ overnight, after which the solution was evaporated to give dark orange viscous liquid. This was dissolved in ethyl acetate and passed through a column filled with SiO_2. The yellow solution was collected. The concentrated solution was purified by column chromatography using 5:1 petroleum ether−ethyl acetate as an eluent. Yellow viscous oil was obtained after evaporation and evacuation, yield: 1.51 g (68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.24, 6.50, 6.16 and 5.84 (ArH), 4.58 (>CH−, 4H), 4.39 (>C*H*(CH_3), 8H), 4.32, 4.09, 3.91 and 3.44 (CH_2, 16H), 1.76 (CH_3, 48H), 1.43 (>CHC*H*$_3$ resorcinarene,12H).

^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 170.36 (>C═O, 8C), 155.19 and 153.71 (ArOR, 8C), 130.42 (ArR, 8C), 127.70 and 125.75 (ArH lower, 4C), 101.88 and 97.69 (ArH, upper, 4C), 67.08 and 66.68 (−*C*H_2OAr, 8C), 64.57 (−*C*H_2OR, 8C), 39.95 (>*C*H(CH_3), 8C), 30.86 (>CH, 4C), 21.74 (−CH_3, 8C), 19.91 (>CH*C*H_3 resorcinarene, 4C).

IR (film, ATR) cm^{-1}: 2963 (w), 2930 (w), 2874 (w), 1735 (s), 1610 (w), 1584 (w), 1499 (m), 1448 (m), 1407 (w), 1377 (w), 1335 (m), 1300 (m), 1282 (m), 1263 (m), 1220 (s), 1190 (s), 1156 (s) 1127 (s), 1108 (s), 1062 (s), 985 (m), 921 (w), 900 (m), 853 (w), 827 (w), 763 (w), 674 (w).

MALDI-TOF MS molar mass calculated for $C_{72}H_{88}Br_8O_{24}$: *m/z* 1999.71 $[M + Na]^+$.

Found: *m/z* 1999.14 $[M + Na]^+$.

Elemental analysis: calculated for $C_{72}H_{88}Br_8O_{24}$: C, 43.75%; H, 4.49%; Br, 32.34%; O, 19.43%.

Found: C, 44.56%; H, 4.60%; Br, 29.81%; O, 20.99%.

2.5. Synthesis of 4,6,10,12,16,18,22,24-Octakis(2-bromoisobutyryl)-2,8,14,20-tetramethylresorcinarene (**4**)

In a 250-mL double-necked flask equipped with a magnetic stirrer, **2** (1.0 g, 1.11 mmol) was added to 30 mL of dry THF, followed by triethylamine (3.75 mL, 2.71 g, 26.8 mmol). The white suspension was cooled to 0 °C and a solution of 2-bromoisobutyryl bromide (3.3 mL, 6.15 g, 26.8 mmol) in 30 mL of THF was added drop wise to the vigorously stirred suspension over 0.5 h. The solution was stirred at room temperature for 48 h. The reaction mixture was filtered, and the solution was concentrated with a rotary evaporator. The concentrate was dissolved in diethyl ether (100 mL) and washed with a 0.1 M aqueous K_2CO_3 solution (3 × 100 mL), followed by water (3 × 100 mL). The ether layer was dried over $MgSO_4$ overnight, after which the solution was concentrated. The product was crystallized in methanol and purified twice by recrystallisation in the same solvent. Light brown solid was obtained, yield 1.41 g (61%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.24, 6.51, 6.20 and 5.85 (ArH); 4.60 (>CH−, 4H); 4.35, 4.09, 3.94 and 3.53 (CH_2, 32H), 1.92 (CH_3, 48H), 1.41 (>CHC*H*$_3$, 12H).

^{13}C NMR (75.4 MHz, $CDCl_3$) δ ppm: 171.82 (>C═O, 8C), 155.29 and 153.88 (ArOR, 8C), 130.17 (ArR, 8C), 127.51 and 125.64 (ArH lower, 4C), 101.88 and 97.34 (ArH, upper, 4C), 67.25 and 66.61 (−*C*H_2OAr, 8C), 64.71 (−*C*H_2OR, 8C), 55.80 (>*C*(CH_3)$_2$, 8C), 30.95 (>C(*C*H_3)$_2$, 16C and >CH, 4C), 20.02 (−CH_3, 4C).

IR (solid, ATR) cm^{-1}: 2961 (w), 2927 (w), 2874 (w), 1728 (s), 1610 (w), 1583 (w), 1497 (m), 1460 (m), 1408 (w), 1389 (w), 1371 (w), 1338 (w), 1273 (s), 1233 (m), 1161 (s), 1130 (m), 1105 (s), 1031(m), 998 (m), 949 (w), 909 (w), 880 (w), 838 (w), 816 (w), 762 (w).

MALDI-TOF MS molar mass calculated for $C_{80}H_{10}Br_8O_{24}$: *m/z* 2111.93 $[M + Na]^+$.

Found: *m/z* 2111.08 $[M + Na]^+$.

Elemental analysis: calculated for $C_{80}H_{10}Br_8O_{24}$: C, 46.00%; H, 5.02%; Br, 30.60%; O, 18.38%.

Found: C, 46.26%; H, 5.11%; Br, 30.49%; O, 18.39%.

2.6. Polymerisations

2.6.1. Polymerisation of tert-butyl acrylate with octafunctional initiator **3**

A typical procedure is given below. The polymerisation was carried out in a flask equipped with a high vacuum valve. The flask was charged with the octafunctional initiator **3** (72.3 mg, 3.7×10^{-5} mol), 2,2′-bipyridine (91.4 mg, 5.9×10^{-4} mol), ethylene carbonate (0.857 g, 9.7 mmol, 11.4% from the mass of the monomer) and *tert*-butyl acrylate (7.5 g, 8.6 mL, 58.5 mmol). The solution was degassed by two freeze-thaw cycles under high vacuum, after which CuBr (42.0 mg, 2.9×10^{-4} mol) was added, followed by three freeze-thaw cycles. The flask was placed in an oil bath thermostated at 100 °C. After the reaction, the solution was cooled by dipping the flask into liquid nitrogen. The solution was brought to room temperature, after which the content was dissolved in THF and passed through a column packed with silica (4/5) and neutral alumina (1/5) in two layers to remove the copper salts. The polymer was precipitated in a mixture of methanol and water (8:2) and dried *in vacuo* at room temperature. The polymer was purified by reprecipitation.

The kinetics of the polymerisation of *tert*-butyl acrylate using PMDETA as a ligand was studied by carrying out the reaction in a Schlenk tube under nitrogen atmosphere. The procedure of adding the reactants and removing the gases was the same as described above, but the vacuum was replaced by N_2 atmosphere before immersing the flask into the oil bath. Small (0.5 mL) aliquots of the reaction mixture were withdrawn at regular intervals. The samples were purified and precipitated as described above.

The conversion of poly(*tert*-butyl acrylate), P*t*BA, has been determined from the samples of the reaction mixture in $CDCl_3$ by comparing the signals of the monomer at 5.4–6.7 ppm (3H, vinyl group) with the signal of P*t*BA at 2.17 ppm (1H, –CH–) [19].

2.6.2. Polymerisation of methyl methacrylate with octafunctional initiator **4**

A typical procedure used was the following; the polymerisation was carried out in a flask equipped with a high vacuum valve. The flask was charged with octafunctional initiator **4** (97.8 mg, 4.7×10^{-5} mol), 2,2′-bipyridine (117 mg, 7.5×10^{-4} mol), diphenyl ether (8.0 mL, 50% from the total volume of the reaction mixture) and methyl methacrylate (7.5 g, 8.0 mL, 75.9 mmol). The solution was degassed by two freeze-thaw cycles under high vacuum, after which CuCl (37 mg, 3.7×10^{-4} mol) was added, followed by three freeze-thaw cycles. The flask was placed in an oil bath thermostated at 90 °C. After the reaction, the solution was cooled by dipping the flask into liquid nitrogen. The solution was brought to room temperature, after which the content was dissolved in THF and passed through a column packed with silica (4/5) and neutral alumina (1/5) in two layers to remove the copper salts. The polymer was precipitated in methanol and dried *in vacuo* at room temperature. The polymer was purified by reprecipitation. The kinetics of the polymerisation of methyl methacrylate was studied by simultaneous polymerisations taken to different conversions.

The conversion of poly(methyl methacrylate), PMMA, has been determined from the samples of the reaction mixture in $CDCl_3$ by comparing the signals of the monomer at 5.5 and 6.0 ppm (2H, vinyl group) as well as at 3.51 ppm (3H, $-CH_3$) with the signal of PMMA at 3.64 ppm (3H, $-CH_3$) [19].

2.7. Hydrolyses

2.7.1. Hydrolysis of poly(tert-butyl acrylate) stars to poly(acrylic acid) stars and the detachment of arms by alkaline hydrolysis

A sample of poly(*tert*-butyl acrylate) star polymer (0.3 g, 2.34 mmol) was dissolved in 6 mL of CH_2Cl_2. The solution was degassed for 10 min, after which 0.9 mL of trifluoroacetic acid (TFA, 11.7 mmol) was injected into the flask. The solution was stirred at room temperature for 24 h, after which it was evaporated to dryness and redissolved in 1,4-dioxane. The polymer was precipitated in diethyl ether and dried *in vacuo* at room temperature. The absence of signals from poly(*tert*-butyl acrylate) indicating complete hydrolysis was verified by ^1H NMR and the intactness of the starlike structure was checked by aqueous SEC.

To detach the arms, a sample of poly(acrylic acid) star (0.120 g) was dissolved in 4 mL of 1 M aqueous NaOH solution and refluxed at 80 °C for 24 h. The solution was evaporated to dryness and the solid was dispersed in diethyl ether, filtered and dried *in vacuo* at room temperature.

2.7.2. Alkaline hydrolysis 1 of star polymers

A procedure described by Angot et al. [13] was utilised to detach the arms from the resorcinarene core. A sample of the star polymer (0.15 g) was dissolved in 13.3 mL of THF in a 100 mL double-neck flask equipped with a condenser and N_2 inlet. The solution was degassed for 20 min before injecting 1.3 mL of KOH (1 M solution in ethanol) into the flask. The solution was refluxed at 60 °C for 8 min. The solvent was evaporated without further heating. The polymer was precipitated in a mixture of methanol and water (8:2), washed with water and freeze-dried overnight.

2.7.3. Alkaline hydrolysis 2 of poly(methyl methacrylate) stars

A sample of star polymer (0.15 g) was dissolved in 10 mL THF in a 100 mL double-neck flask equipped with a condenser and N_2 inlet, followed by the addition of 3 mL methanol. The solution was degassed for 20 min before injecting 0.25 mL sodium methoxide solution (5.4 M solution in methanol) into the flask. The solution was refluxed at 80 °C for 22 h, after which the solvent was evaporated. The polymer was precipitated in

a mixture of methanol and water (8:2), washed with water and freeze-dried.

2.8. Instrumentation

The NMR spectra were measured with a 200 MHz Varian Gemini 2000 NMR spectrometer (operating at 200 MHz for ^{1}H and at 50.3 MHz for ^{13}C), with a Varian $^{\text{UNITY}}$INOVA NMR spectrometers (the one operating at 300 MHz for ^{1}H and at 75.4 MHz for ^{13}C, the other operating at 500 MHz for ^{1}H). The chemical shifts are presented in part per million downfield from the internal TMS standard or using the solvent signal as a reference. Additionally, DEPT (distortionless enhancement by polarization transfer), COSY (^{1}H, ^{1}H-correlated NMR spectroscopy) and HSQC (heteronuclear single quantum coherence spectroscopy) measurements were used to help in the interpretation of the spectra.

The IR spectra were measured from solid samples or a film with a Perkin Elmer spectrum one FT-IR spectrometer. MALDI-TOF mass spectrometry was performed on a Bruker microflex equipped with 337 nm N_2 laser in the reflector mode, using the following conditions: accelerating voltage 20 kV and pressure 5.0×10^{-6} mbar. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix. Samples were prepared from THF (except sample **2** from acetone) solution by mixing matrix (30 mg/mL) and sample (sample **1** and 4: 6 mg/mL, sample **2**: 4 mg/mL, sample **3**: 11 mg/mL) in a ratio of 10:1. Elemental analyses were performed by Analytische Laboratorien GmbH in Lindlar, Germany. The SEC analyses, giving molar masses and molar mass distributions, were performed with a Waters instrument equipped with Styragel guard column, 7.8×300 mm Styragel capillary column, and Viskotek 270 Dual Detector connected with the Waters 2487 UV and Waters 2410 RI detectors. THF was used as an eluent with a flow rate of 0.8 mL/min. The calibrations were performed with poly(*tert*-butyl acrylate) and poly(methyl methacrylate) standards from Polymer Standards Service GmbH. Aqueous SEC was conducted with a Waters instrument equipped with Ultrahydrogel guard column, 7.8×300 mm Ultrahydrogel capillary column, and a Waters 2410 RI detector, using aqueous 0.1 M $NaNO_3$ (with 3 vol% acetonitrile) as an eluent with a flow rate 0.8 mL/min. The calibration was performed with poly(acrylic acid) standards from Polymer Standards Service GmbH.

Light scattering (LS) measurements were also conducted, if necessary, with a Brookhaven Instruments BI-200SM goniometer and a BI-9000AT digital correlator. Ar laser (LEXEL 85; $\lambda = 514.5$ nm or 488.0 nm) was used as a light source. The LS data were analyzed by using Zimm's double extrapolation method or by Debye method. The specific refractive index increments of the polymers (dn/dc) were determined from refractive indices measured by Billingham & Stanley Abbe60 Refractometer using the He–Ne laser as a light source, being 0.0507 mL/g for star poly(*tert*-butyl acrylate) and 0.0805 mL/g for star poly(methyl methacrylate) in THF at 20 °C. The values determined for $\lambda = 514.5$ nm were 0.0532 mL/g for star poly(*tert*-butyl acrylate) and 0.0920 ml/g for star poly(methyl methacrylate) [15].

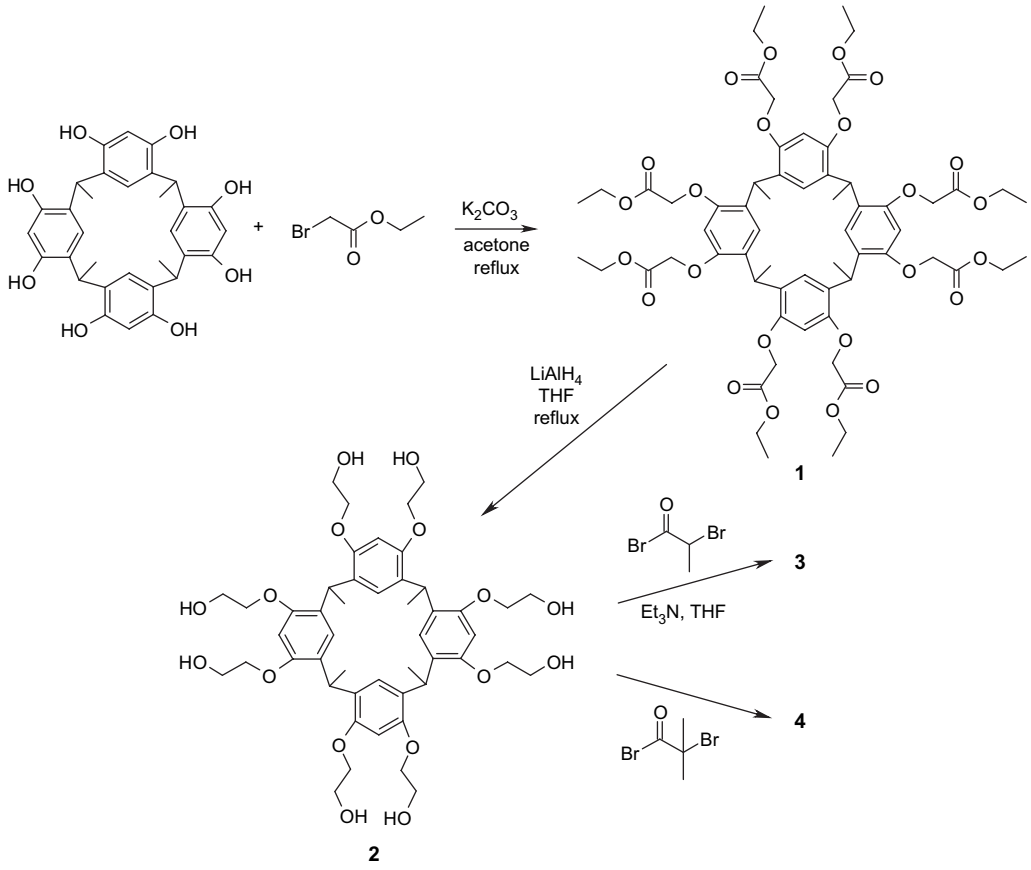
3. Results and discussion

3.1. Synthesis and characterization of octafunctional ATRP initiators

The resorcinarene-based initiators bearing a spacer between the initiating site and the macrocycle were synthesized in three steps from the parent compound, tetramethylresorcinarene. The parent compound was chosen because of the high flexibility of the resorcinarene ring due to the small size of the alkyl substituents, allowing the attachment of large substituents to the phenolic groups. The steps are shown in Scheme 1. The success of each step after the purification was verified by spectroscopic methods (NMR, FT-IR), mass spectrometry and elemental analysis. First, the resorcinarene was derivatised by a Williamson reaction between the phenolic hydroxyls and ethyl bromoacetate, producing compound **1** with a good yield. This was followed by the reduction of the ester groups by $LiAlH_4$ in THF, giving compound **2** which bears hydroxyl groups in the end of the alkyl spacers. The reaction was extremely sensitive to moisture and hence, the solvent as well as the glassware were carefully dried prior to the synthesis. Initiators **3** and **4** (Scheme 2) were synthesized by the reaction of compound **2** with either 2-bromopropionyl bromide (**3**) or 2-bromoisobutyryl bromide (**4**) in THF in the presence of triethylamine.

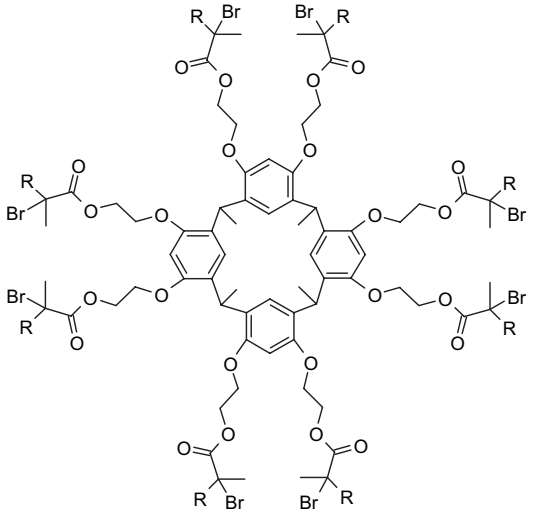
The parent compound used in the first step is an all-*cis* conformer of tetramethylresorcinarene, in which the four methyl groups hold an axial position in the macrocycle. The conformers can be designated according to the positions of the substituents in the methine bridges (*cis c*, *trans t*) relative to the reference group (*r*). For instance, the all-*cis* conformer is designated as *rccc* [33]. The principal arrangements which the resorcinarene ring itself may adopt are the *crown* (C_{4v}), *boat* (C_{2v}), *chair* (C_{2h}) [33], *diamond* (C_s) [34], and *saddle* (D_{2d}) [33] conformations. The ^{1}H NMR spectrum of the parent compound in Fig. 1 shows single peaks corresponding to the aromatic protons (assigned as *c* and *d*), indicating symmetric positions of these protons in a *crown* (C_{4v}) conformation.

The derivatisation of the phenolic hydroxyls in resorcinarene requires breaking the ring of four intramolecular hydrogen bonds [16,17], which makes the structure more flexible. The conformational change induced by the etherification of the phenolic groups (**1**) and the subsequent reduction of the substituents (**2**) is seen in the ^{1}H NMR spectra in Fig. 2. The signal from the 'lower rim' protons has broadened and moved to lower values of chemical shift upon derivatisation. Further acylation of the substituents to prepare initiators **3** and **4** resulted in splitting of the signals of aromatic protons in the ^{1}H NMR spectra (Fig. 3), indicating C_2-symmetric conformation, in which the aromatic groups lie spatially in pairs. The tetraethylresorcinarene-based initiators were investigated earlier, namely initiators **5** and **6** illustrated in Scheme 3, and they were observed to adopt C_2-symmetric *boat* conformation



Scheme 1. Syntheses of octafunctional initiators **3** and **4**.

at the same conditions. We have suggested that this particular conformation of the macrocycle increases the steric hindrance at the initiating sites. According to the ROESY NMR studies and molecular modelling this conformation brings the initiating sites close to each other [15]. Nevertheless, lower steric hindrance is expected for initiators **3** and **4** due to the higher flexibility of the macrocyclic ring as well as due to the spacer between the ring and the initiating sites.



Scheme 2. Structures of octafunctional initiators **3** and **4**.

3.2. Syntheses of starlike poly(tert-butyl acrylates) and poly(methyl methacrylates)

Because the initiating sites should mimic the growing chains [35], initiator **3** with 2-bromopropionyl groups was used to polymerise *tert*-butyl acrylate, *t*BA, and initiator **4** with 2-bromoisobutyryl groups was used in the polymerisation of methyl methacrylate, MMA, due to the higher rate of activation of its initiating sites [35,36]. The control over the polymerisation of *tert*-butyl acrylate was improved by the addition of a polar compound, ethylene carbonate [13], EC, whereas the polymerisation of methyl methacrylate was enhanced by the halogen exchange, that is, the polymerisation by R–Br initiator has been catalysed by CuCl [37]. Various ligands – 2,2′-bipyridine (2,2′-bipy), 4,4′-dinonyl-2,2′-bipyridine (dNbpy), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) – were used in order to estimate their effect on the polymerisations as well as to compare the results with those obtained by initiators **5** and **6**. The conversions were kept low to avoid bimolecular coupling of the stars. The polymerisations of methyl methacrylate were conducted in two common ATRP solvents, diphenyl ether (DPE) and toluene, to investigate

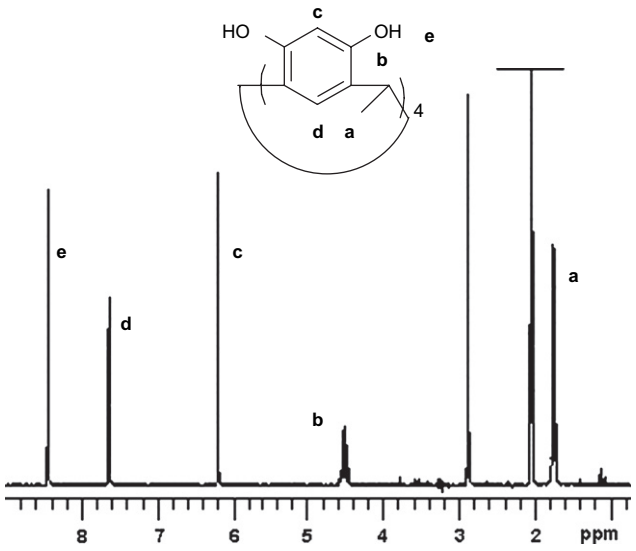


Fig. 1. Assigned ^{1}H NMR spectrum (200 MHz) of the parent compound, tetramethylresorcinarene, in d_6-acetone.

the effect of the viscosity of the solvent on the polymerisation at 90 °C (η (25 °C) = 2.6 cP and 0.5525 cP, respectively) [38]. Typical monomer-to-initiator ratios, [M]/[I], were 1600 or 3200 (Table 1), but the kinetic studies on the polymerisation of *tert*-butyl acrylate were performed using [M]/[I] = 800 to reduce the time needed for the experiments, because of the slow rate of polymerisation.

The results of the polymerisations are presented in Table 1. The conversions were determined from samples of the reaction mixture with ^{1}H NMR spectroscopy by comparing the signals from the monomer and the polymer, and the resulting values were used in calculating the theoretical molar masses M_n(theo). The molar masses were determined by ^{1}H NMR and by size exclusion chromatograph (SEC) equipped with both refractive index (RI) and light scattering (LS) detectors. In general, ^{1}H NMR spectroscopy is considered as a reliable method to determine the molar masses of starlike polymers [39,40]. The molar masses from NMR spectra, M_n(NMR), as well as the functionalities (number of arms) of the stars were calculated from the integrated signals of the initiator and the signals of the polymer as well as its endgroup. The functionalities (f) of poly(*tert*-butyl acrylate) stars were calculated from the aromatic signals of the initiator at 5.6–6.6 ppm (6H) and the signal of the endgroup at 1.22 ppm (9H, $-(CH_3)_3$) by f = 1H (endgroup)/1H (initiator), in which 1H stands for the integrated area of the signal corresponding one proton. The obtained value of f was used in calculating the molar mass from the same signal of the endgroup as above and the signal of P*t*BA at 1.44 ppm (9H, $-(CH_3)_3$): $M_n(\mathrm{NMR}) = M_m \times f \times (1\mathrm{H}\ \ (\mathrm{polymer})/1\mathrm{H}\ \ (\mathrm{endgroup})) + M_i$, in which M_m and M_i are the molar masses of the monomer and the initiator, respectively. The functionalities and the molar masses of poly(methyl methacrylate) stars were calculated as above from the aromatic signals of the initiator at 5.6–6.6 ppm (6H), the signal of the endgroup at 3.75 ppm (3H, $-CH_3$), and the signal of PMMA at 3.58 ppm (3H, $-CH_3$),

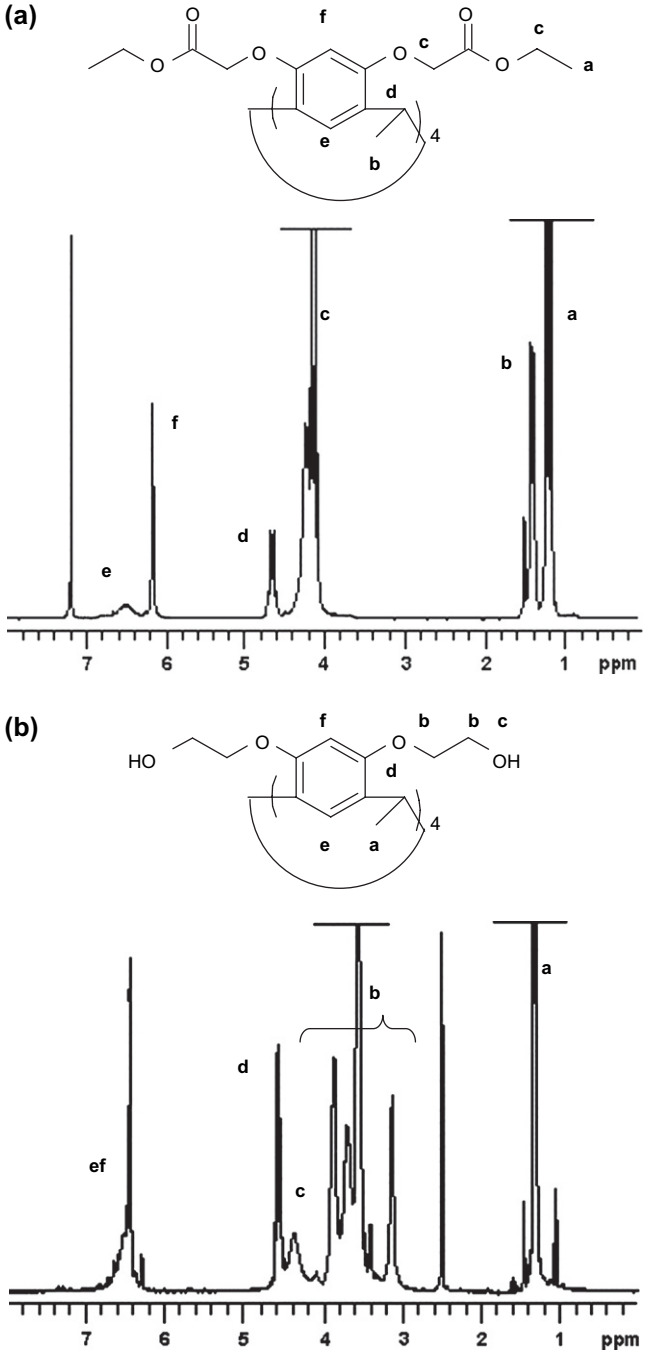


Fig. 2. Assigned ^{1}H NMR spectra (300 MHz) of (a) compound **1** in $CDCl_3$, and (b) compound **2** in deuterated DMSO at 70 °C.

however, subtracting the area of the signals from the initiator (36 H) that partially overlap the mutual area of PMMA and the endgroup. Typical ^{1}H NMR spectra of both poly(*tert*-butyl acrylate), P*t*BA, and poly(methyl methacrylate), PMMA, as well as their spectral assignments are shown in Fig. 4. Despite some overlap of the signals, ^{1}H NMR spectroscopy was our method of choice for determining the functionalities of the stars, because the signals from the initiators are well distinguishable in the spectra owing to the low molar masses of the arms.

Another approach to determine the functionalities of the stars is to detach the arms from the macrocyclic core by

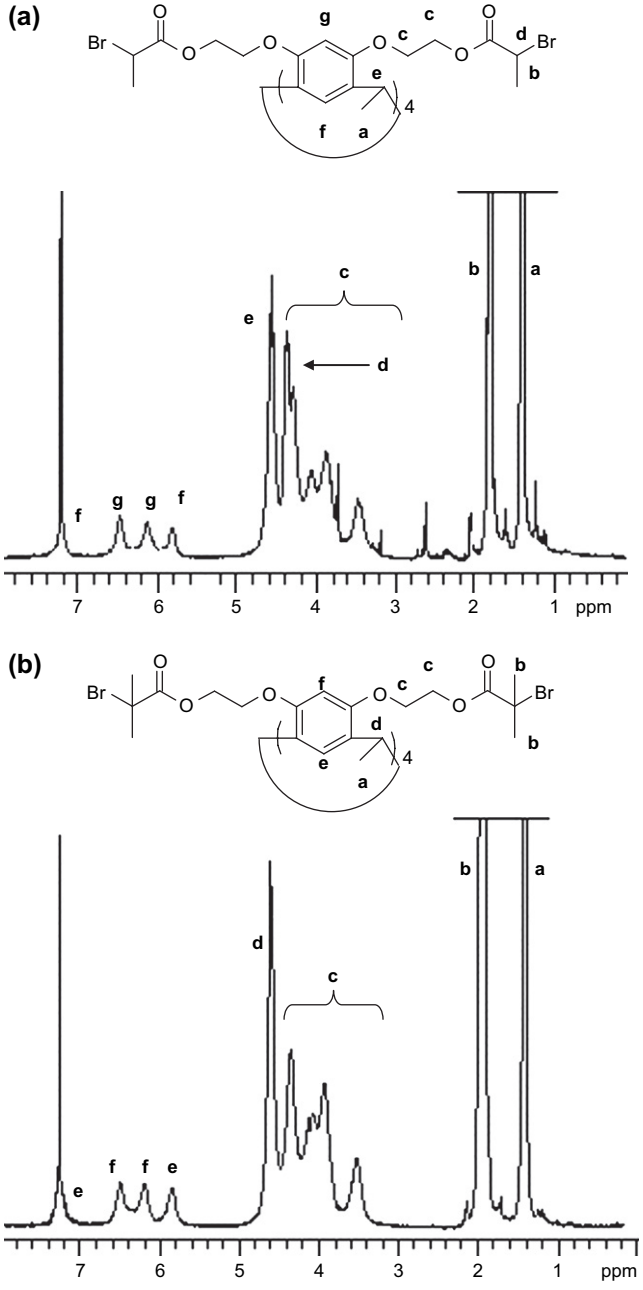
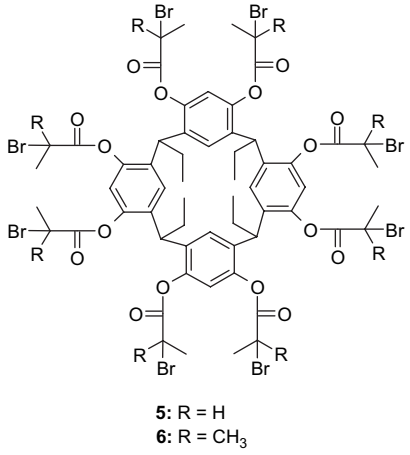


Fig. 3. Assigned ^{1}H NMR spectra (300 MHz) of (a) octafunctional initiator **3**, and (b) octafunctional initiator **4**, both in $CDCl_3$.



Scheme 3. Structures of octafunctional initiators **5** and **6**.

alkaline hydrolysis and to compare their molar masses with those of the intact stars. We attempted the alkaline hydrolysis (procedure 1) of both poly(*tert*-butyl acrylate) and poly(methyl methacrylate) stars in THF using potassium hydroxide in ethanol and short refluxing time (8 min), but according to the ^{1}H NMR spectra this procedure often hydrolysed also a part of the methyl and *tert*-butyl ester groups in the polymer chain, thus affecting the solubility of the polymer and the reliability of SEC results. Therefore, some of the poly(*tert*-butyl acrylate) stars were first hydrolysed to poly(acrylic acid) stars, after which the arms were detached by refluxing the polymer 24 h in aqueous NaOH solution. Although according to SEC, there was some uncleaved star present after the latter reaction indicating too mild reaction conditions, the number-average molar masses of the hydrophilic stars and the functionalities calculated from the molar masses of the arms (Table 1, footnotes f and g) were in agreement with those given by NMR and by SEC (RI). Another procedure of alkaline hydrolysis (procedure 2) was used for detaching the arms from a poly(methyl methacrylate) star utilising transesterification with sodium methoxide in a mixture of THF and methanol. After the detachment, the PMMA arms were readily soluble in THF and according to SEC (RI), the functionality of the star was 6.9 (Table 1, footnote h) while ^{1}H NMR gave the value as 8.0. The difference in the values of f by these two methods could originate from the residual resorcinarene impurities that are visible in the ^{1}H NMR spectrum of the cleaved arms and partially overlap the SEC trace (not shown here).

The number-average molar masses M_n determined by NMR and SEC (RI) were rather well in accordance with the theoretical ones and the apparent polydispersities were low (Table 1). The number-average molar masses determined from the signal of the light scattering detector of SEC were higher than those by the RI detector, as the latter results were obtained using calibration by linear P*t*BA and PMMA standards and the investigated polymers have smaller hydrodynamic volume owing to the starlike architecture than the linear polymers of corresponding molar masses. This discrepancy between the linear standards and the starlike samples is also the reason why the values of PDI were higher by light scattering. Due to the overlap of the NMR signals described above, there were deviations between the theoretical molar mass M_n(theo) and the one determined by NMR, suggesting that NMR method as such is not accurate enough for the determination of M_n. The polydispersities of the samples may also be estimated by the ratio of weight-average molar mass given by light scattering and number-average molar mass given by NMR, M_w (SEC LS)/M_n (NMR), or by the ratio M_w(SEC LS) and theoretical molar mass, M_w(SEC LS)/M_n(theo), which both yield even higher values than those by SEC (LS). These high polydispersities may stem from the distribution in the number of arms, which is reflected by the lower functionalities given by NMR.

Table 1
Atom transfer radical polymerisations using initiators **3** and **4**

Entry	M (I)[a]	Ligand[b]	Solvent	[M]/[I]	Time (min)	Conversion (%)	M_n(theo)[c] (g/mol)	M_n(NMR)[d] (g/mol)	f (NMR)[e]	M_n (SEC RI) (g/mol)	PDI (RI)	M_n (SEC LS) (g/mol)	PDI (LS)	M_w(SEC LS)/M_n(NMR)
1	*t*BA (**3**)	2,2′-bpy*	EC	1600	600	9.9	22 300	33 200	5.9	29 100	1.08	41 000	1.08	1.33
2	*t*BA (**3**)	2,2′-bipy*	EC	1596	840	19.7	42 200	42 300	6.1	39 000[f]	1.09	51 300	1.12	1.36
3	*t*BA (**3**)	2,2′-bipy	EC	1569	300	10.5	23 200	33 000	5.5	30 700	1.08	32 200	1.24	1.21
4	*t*BA (**3**)	2,2′-bipy	EC	1603	600	23.2	49 700	62 500	6.4	53 500	1.07	59 100	1.19	1.12
5	*t*BA (**3**)	2,2′-bipy	EC	3211	600	8	35 100	34 400	6.1	35 300	1.08	44 100	1.10	1.41
6	*t*BA (**3**)	dNbpy	EC	1597	300	15.1	33 100	34 600	6.3	33 600[g]	1.06	44 600	1.19	1.54
7	*t*BA (**3**)	PMDETA	EC	1560	22	6.6	15 100	21 000	5.6	20 600	1.07	*N/A*	*N/A*	*N/A*
8	MMA (**4**)	2,2′-bipy	DPE	1605	9	14.8	25 900	23 900	6.1	26 000	1.21	31 400	1.19	1.57
9	MMA (**4**)	2,2′-bipy	DPE	3199	18	17.1	57 000	45 700	6.0	47 600	1.17	*N/A*	*N/A*	*N/A*
10	MMA (**4**)	dNbpy	DPE	1603	9	19.7	33 600	32 400	7.1	31 800	1.16	39 600	1.23	1.50
11	MMA (**4**)	dNbpy	DPE	3272	18	14.2	48 700	43 600	7.1	36 300	1.11	46 500	1.11	1.24
12	MMA (**4**)	HMTETA	DPE	1603	3	14.5	25 400	32 300	6.9	22 000	1.13	33 800	1.37	1.44
13	MMA (**4**)	dNbpy	Toluene	1612	5	12.1	21 600	21 700	7.4	16 600	1.19	*N/A*[i]	*N/A*	1.41
14	MMA (**4**)	dNbpy	Toluene	3231	16	15.5	52 300	43 700	8.0	41 300[h]	1.18	49 800	1.25	1.42

[a] Conditions for *t*BA: $T = 100$ °C, 11.4 mass% ethylene carbonate is used as an additive, CuX = CuBr; for MMA: $T = 90$ °C, solvent 50 vol% diphenyl ether or toluene, CuX = CuCl.

[b] Assumed stoichiometry for 2,2′-bipyridine and 4,4′-dinonyl-2,2′-bipyridine: $[I_s]$:[CuX]:[ligand] = 1:1:2, where $[I_s]$ is the concentration of a single initiating group. For the entries marked by asterisks (*) $[I_s]$:[CuX]:[ligand] = 2:1:2 and for other ligands $[I_s]$:[CuX]:[ligand] = 1:1:1.

[c] $M_n(\text{theo}) = (\text{conversion} \times [M]/[I] \times M_m) + M_i$, where M_m and M_i are molar masses of the monomer and initiator, respectively.

[d] Calculated by ^{1}H NMR analysis: $M_n(\text{NMR}) = M_m \times f \times (1\text{H (polymer)}/1\text{H (endgroup)}) + M_i$, in which 1H corresponds to the integrated area of the signal for one proton, and f = functionality of the star, see footnote e.

[e] f = functionality, the number of arms in the star polymer, calculated by ^{1}H NMR analysis: $f = 1\text{H (endgroup)}/1\text{H (initiator)}$.

[f] Results from the hydrolyses: M_n(PAANa star, SEC RI) = 29 100 g/mol, M_n(PAANa arms, SEC RI) = 4450 g/mol, $f = 6.1$ from $f = (M_n(\text{PAANa star}) - M_i)/M_n(\text{PAANa arms})$. Calculated M_n for the P*t*BA star precursor M_n(P*t*BA star) = 39 000 g/mol from M_n(P*t*BA star) = (M(*t*BA)/M(AANa)) × M_n(PAANa star) + M_i.

[g] M_n(PAANa star, SEC RI) = 25 750 g/mol, M_n(PAANa arms, SEC RI) = 3600 g/mol, $f = 6.6$. Calculated M_n for the P*t*BA star precursor M_n(P*t*BA star) = 34 400 g/mol.

[h] Result from the hydrolysis: M_n (PMMA arms) = 5600 g/mol, f = 6.9 from f = (M_n(PMMA star SEC RI) − M_i)/M_n(PMMA arms).

[i] By static light scattering: M_w(SLS) = 30 500 g/mol, M_w(SEC) = 19 700 g/mol.

According to the NMR results, the average functionalities of the stars were 6.0 for P*t*BA and 6.9 for PMMA, which are higher than those observed earlier by initiators **5** and **6** ($f \sim 4$) [15,19]. Lower functionalities of P*t*BA stars could stem from the bulkiness of the monomer. According to Sumerlin and coworkers [23], lowering the concentration of the monomer by dilution would increase the initiation efficiency via decreasing the number of propagation events that occur before the deactivation of the radicals. Therefore, the higher functionalities of PMMA stars could also be attributed to the higher dilution (50 vol% solvent). From the chosen ligands 4,4′-dinonyl-2,2′-bipyridine provided the best results in the polymerisation of MMA, owing to its good solubility in the reaction mixture.

The polymerisation kinetics of *tert*-butyl acrylate by initiators **3** and **5** was investigated using CuBr/PMDETA catalyst and [M]/[I] = 800. Fig. 5(a) presents the semilogarithmic plots of $\ln([M]_0/[M]_t)$ as a function of time for initiators **3** and **5**. The polymerisations were first order with respect to the monomer and the concentrations of the radicals remained constant. The rate of polymerisation was higher by initiator **3**, that is, the initiator bearing the spacer. This refers to lower steric hindrance that increases the initiation site efficiency during the polymerisation of bulky *tert*-butyl acrylate monomer. The higher number of growing chains increases also the visible polymerisation rate [41]. The apparent polydispersities (Fig. 5(b)) were lower by initiator **3** indicating more controlled polymerisation. The lower polydispersities may also stem from the higher number of arms, as according to Flory, the polydispersities of the stars consisting of arms with 'the most probable distribution' of chain lengths depend on the number of arms (f): $M_w/M_n = 1 + (1/f)$ [42]. Gao and Matyjaszewski [41] have described the synthesis of miktoarm star polymers, where the polydispersity of the starlike polymer depends on the initiation efficiency of the multifunctional (macro) initiator, decreasing when higher number of initiating sites participate the polymerisation. The molar masses of the stars correspond well to the theoretical ones but grow larger at approximately 30% conversion, indicating star–star coupling reactions (Fig. 5(c)). The star–star coupling is also observed from the shoulder in the SEC traces at the higher molar masses, which is pointed out in Fig. 6.

Fig. 7(a) presents the semilogarithmic plots of $\ln([M]_0/[M]_t)$ as a function of time for the polymerisation of *tert*-butyl acrylate by initiator **3** using CuBr/PMDETA and CuBr/dNbpy as catalysts, and [M]/[I] = 800. The apparent polydispersities as well as the molar masses M_n are shown as a function of conversion in Fig. 7(b) and (c). Bipyridines form 1:2 complexes with copper (Cu:ligand), whereas multidentate amines like PMDETA or HMTETA form less bulky 1:1 complexes, in which the transition metal is well accessed by halogen, and hence the rate of activation is higher in the atom transfer process [43]. The polymerisation by CuBr/PMDETA catalyst was faster than by CuBr/dNbpy, as expected. The kinetic plot of the polymerisation by CuBr/dNbpy is linear until 42% conversion, after which the conversion does not increase due to the

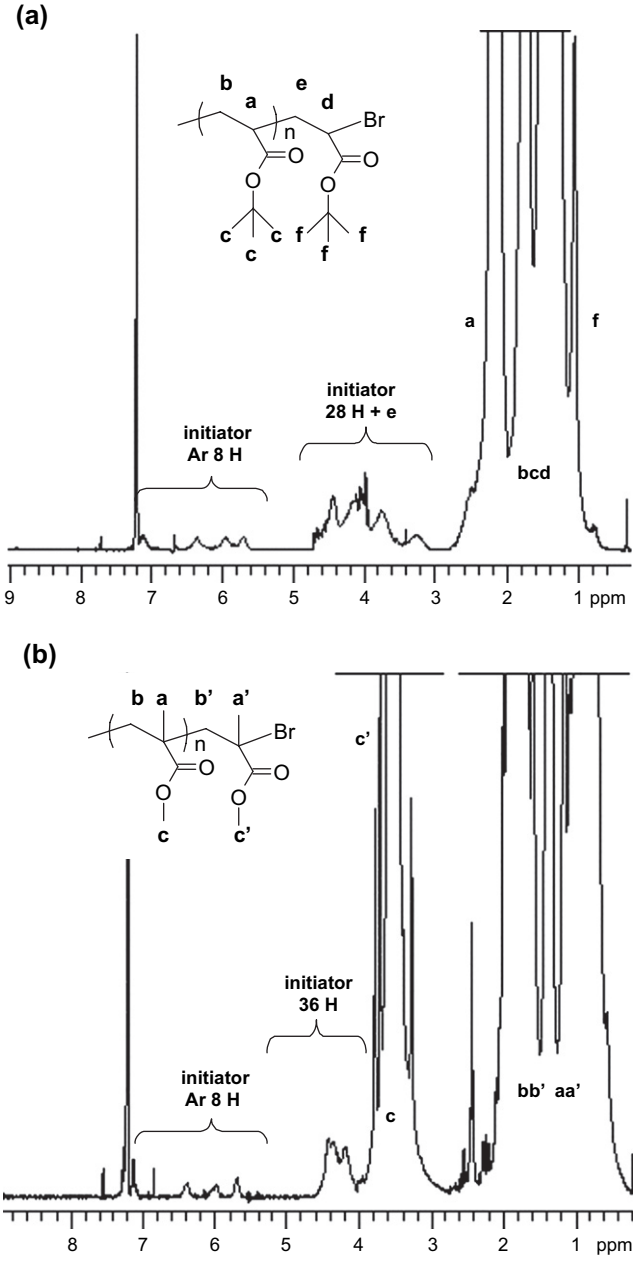


Fig. 4. Assigned ^{1}H NMR spectra used in the calculation of molar masses and functionalities of (a) starlike poly(*tert*-butyl acrylate) and (b) starlike poly(methyl methacrylate).

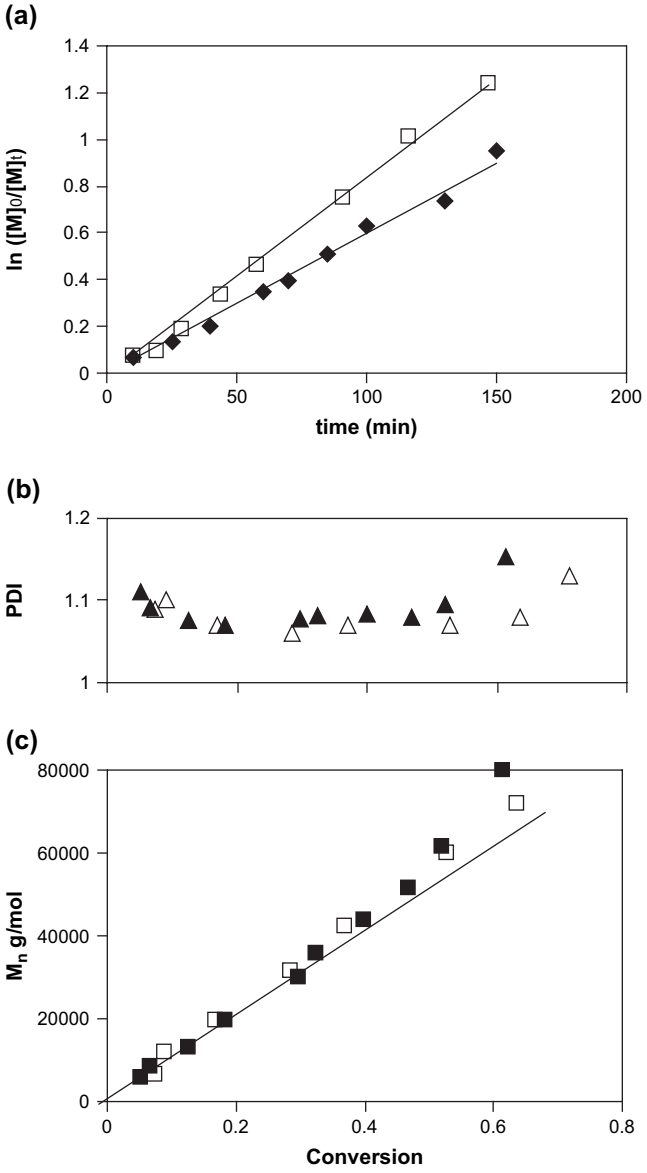


Fig. 5. Polymerisations of *tert*-butyl acrylate ([M]/[I] = 800) at 100 °C by initiator **3** (open symbols) and initiator **5** (solid symbols) using CuBr/PMDETA as catalyst in the presence of ethylene carbonate (11.4 mass%). (a) The kinetic plots of monomer conversion as a function of reaction time. Lines have been added for a guide to the eye, (b) apparent polydispersities and (c) number-average molar masses M_n, both determined by SEC (RI), as a function of conversion. The straight line represents the theoretical M_n.

loss of active propagating centers [44]. The polymerisation of *tert*-butyl acrylate by CuBr/dNbpy is very slow and therefore the termination reactions become very significant. It has been suggested that during the long reaction time some degradation of the monomer occurs via ester pyrolysis, resulting in catalyst poisoning, which would be observed as an increase in polydispersity during the course of polymerisation [45,46]. It also seems that the amount of initial termination reactions is high, as the molar masses M_n are higher than theoretical ones already at the early stages of polymerisation. The poor controllability of the polymerisation by CuBr/dNbpy catalyst may in our case stem from the decreased solubility of the catalyst in the reaction mixture containing a polar component, ethylene carbonate.

The polymerisation kinetics of methyl methacrylate by initiators **4** and **6** in diphenyl ether was investigated using CuCl/HMTETA catalyst and [M]/[I] = 1600. The semilogarithmic plots of $\ln([M]_0/[M]_t)$ are presented as a function of time for initiators **4** and **6** in Fig. 8(a), and the apparent polydispersities as well as the molar masses M_n are plotted against conversion in Fig. 8(b) and (c). The rates of polymerisations as well as the evolution of molar masses and polydispersities upon increasing conversion are nearly identical. The difference between the initiators is not as distinct as by those used in the

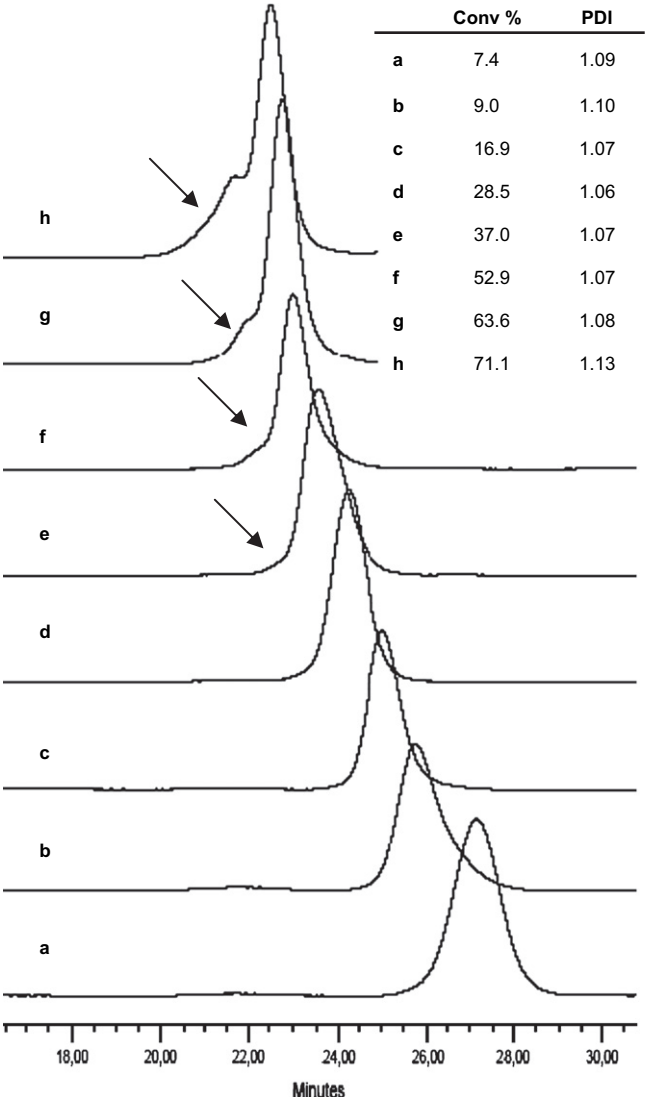


Fig. 6. Size exclusion chromatograms (RI signal) of starlike poly(*tert*-butyl acrylate) at different conversions. The polymerisation has been conducted by initiator **3** ([M]/[I] = 800) at 100 °C using CuBr/PMDETA as catalyst in the presence of ethylene carbonate (11.4 mass%). The arrows point the shoulder at high molar masses arising from the bimolecular coupling.

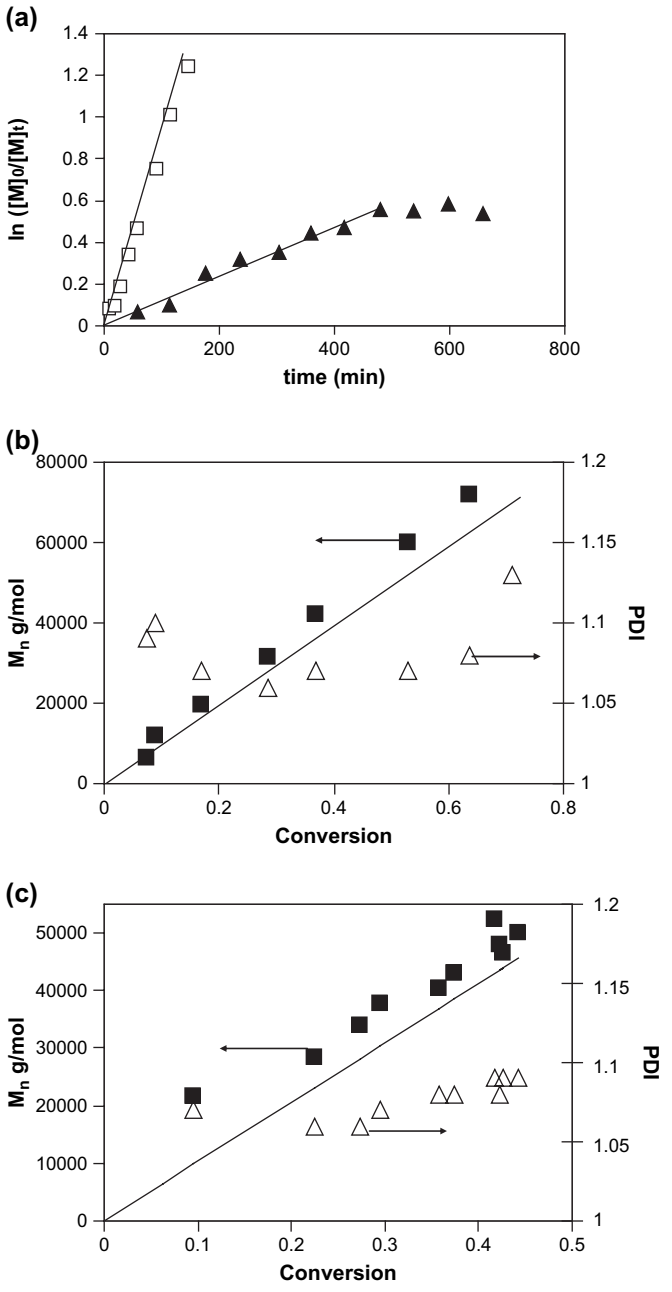


Fig. 7. Polymerisations of *tert*-butyl acrylate ([M]/[I] = 800) at 100 °C by initiator **3** in the presence of ethylene carbonate (11.4 mass%) using different catalysts. (a) The kinetic plots of monomer conversion as a function of reaction time using CuBr/PMDETA (open symbols) and CuBr/dNbpy (solid symbols) as catalysts. Lines have been added for a guide to the eye. Below, M_n (solid squares) and apparent polydispersity (open triangles), both determined by SEC (RI), and theoretical M_n (line) as a function of conversion for the polymerisation by (b) CuBr/PMDETA and (c) CuBr/dNbpy catalysts.

polymerisation of *t*BA, possibly due to the very fast and less controlled polymerisation of MMA. The kinetic plots for initiators **4** and **6** do not pass through the origin, this indicating initial termination reactions arising from either too high concentration of the catalyst or too fast initiation [47]. The polymerisation of MMA is more prone to bimolecular coupling than that of *tert*-butyl acrylate [14]. Fig. 9 shows that some star–star coupling has occurred already at the early stage of the polymerisation of MMA by CuCl/HMTETA, since a small shoulder is observed in the high molar mass side of the SEC trace at 14.5% conversion. Changing the ligand from HMTETA to dNbpy did not affect much the characteristics of the polymerisation of MMA by initiator **4** shown in Fig. 10. However, the polydispersities were lower by CuCl/dNbpy catalyst and the SEC traces of the polymers (not shown here) indicated that bimolecular coupling started to occur at higher conversions than by using HMTETA as a ligand, which is in accordance with our earlier observations from 2,2′-bipyridine and HMTETA [19].

In addition to diphenyl ether, the polymerisation of methyl methacrylate was conducted in toluene. The kinetics of the polymerisations in these two solvents by initiator **4** and CuCl/dNbpy catalyst is shown in Fig. 11. The initial polymerisations

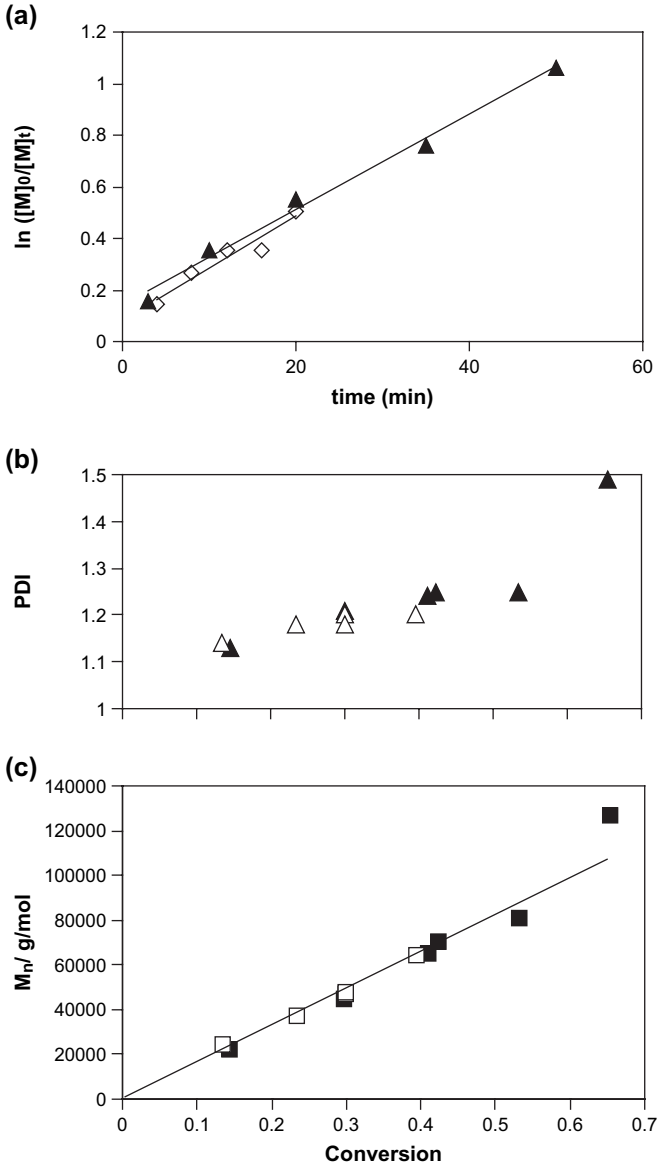


Fig. 8. Polymerisations of methyl methacrylate ([M]/[I] = 1600) at 90 °C by initiator **4** (solid symbols) and initiator **6** (open symbols) using CuCl/HMTETA as catalyst in diphenyl ether (50 vol%). (a) The kinetic plots of monomer conversion as a function of reaction time. Lines have been added for a guide to the eye. (b) Apparent polydispersities and (c) number-average molar masses M_n, both determined by SEC (RI), as a function of conversion. The straight line represents the theoretical M_n.

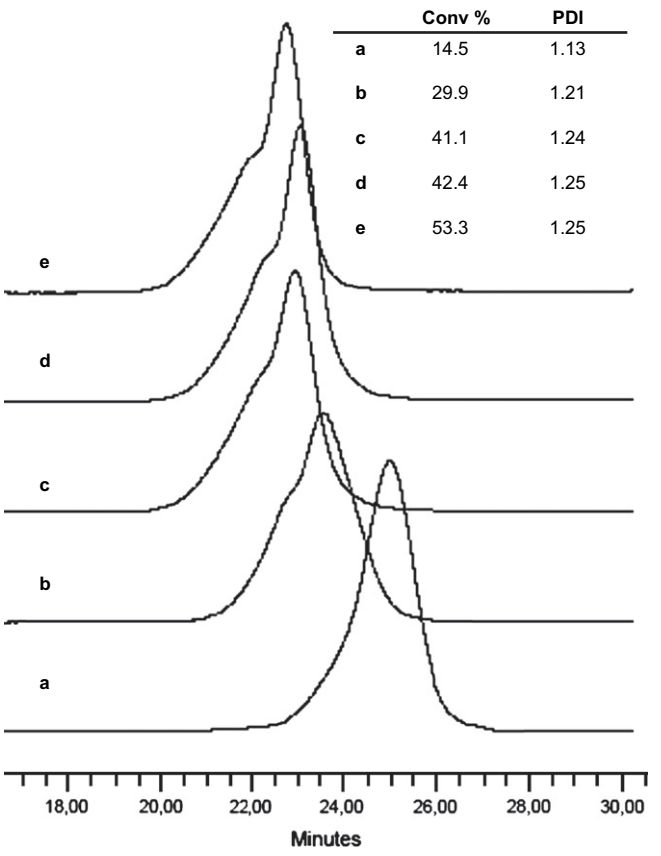


Fig. 9. Size exclusion chromatograms (RI signal) of starlike poly(methyl methacrylate) at different conversions. The polymerisation has been conducted by initiator **4** ([M]/[I] = 1600) in diphenyl ether (50 vol%) at 90 °C using CuCl/HMTETA as catalyst. The shoulder at high molar masses is seen already at low conversion as 14.5%.

gave good results as shown in Table 1. However, the kinetic investigations revealed that although the semilogarithmic plot of $\ln([M]_0/[M]_t)$ versus time was linear, the polymerisation was slower in toluene and the resulting polymers had higher apparent polydispersities than those synthesised in diphenyl ether. The plot did not pass through the origin, indicating initial termination reactions as above. Despite the lower viscosity of toluene, bimolecular coupling took place at lower conversion than in diphenyl ether, which is seen in increasing polydispersities (Fig. 11(b)), as well as in the SEC traces (not shown here). There have been reports of poor control over the polymerisation of MMA in toluene by CuBr/2,2′-bipy or by CuCl/amine catalysts due to unefficient initiation and poor deactivation, as well as due to chain transfer to solvent [48,49].

4. Conclusions

Resorcinarene-based ATRP initiators bearing a short spacer between the initiating sites and the macrocycle were synthesised and used in the preparation of star polymers of *tert*-butyl acrylate, *t*BA, and methyl methacrylate, MMA. The resulting polymers had molar masses close to the theoretical ones, and the apparent polydispersities were low. The ratio of monomer to initiator, [M]/[I], and the chosen catalyst influenced the controllability of the polymerisation. Owing to the lower steric hindrance by the initiating sites, the new initiators produced polymers with higher functionalities than those without spacers. The kinetic studies using various catalysts and solvents indicated controlled polymerisations of *t*BA and MMA. The spacer had little effect on the kinetics of the polymerisation of MMA, but it increased the rate of polymerisation of the bulkier *t*BA monomer. Since the incorporation of the spacer into the initiators increased the number of arms in the star polymers, the future studies will involve their use in the block copolymerisations of MMA and *t*BA, and the investigation of

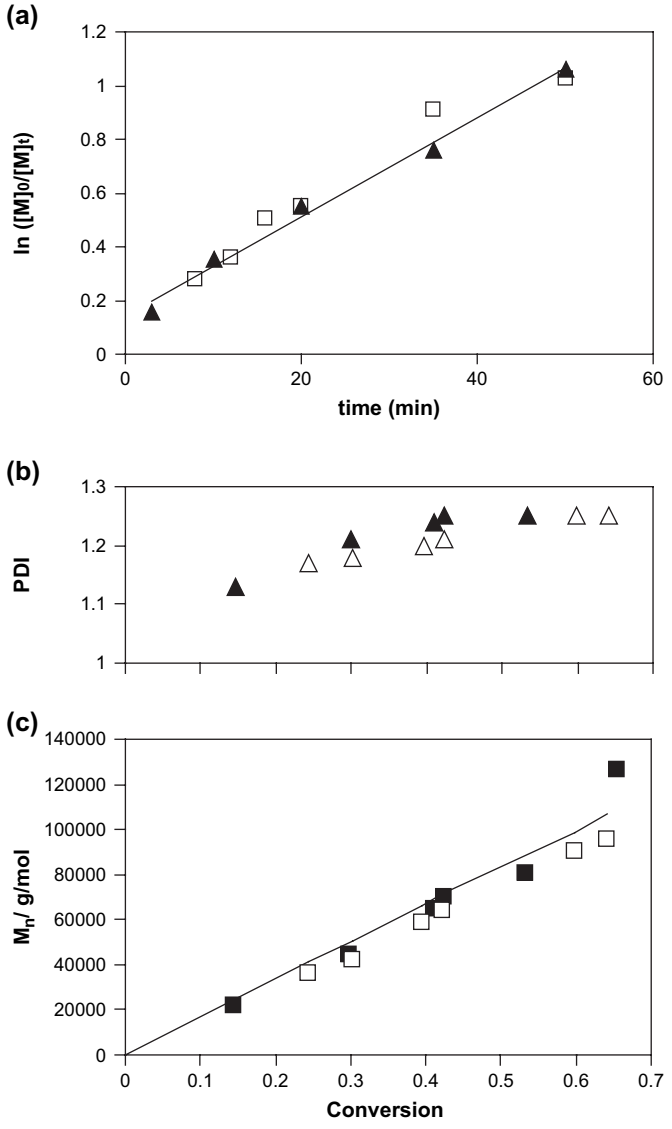


Fig. 10. Polymerisations of methyl methacrylate ([M]/[I] = 1600) at 90 °C in diphenyl ether (50 vol%) by initiator **4** using CuCl/HMTETA as catalyst (solid symbols) or CuCl/dNbpy as catalyst (open symbols). (a) The kinetic plots of monomer conversion as a function of reaction time. Line has been added for a guide to the eye. (b) Apparent polydispersities and (c) number-average molar masses M_n, both determined by SEC (RI), as a function of conversion. The straight line represents the theoretical M_n.

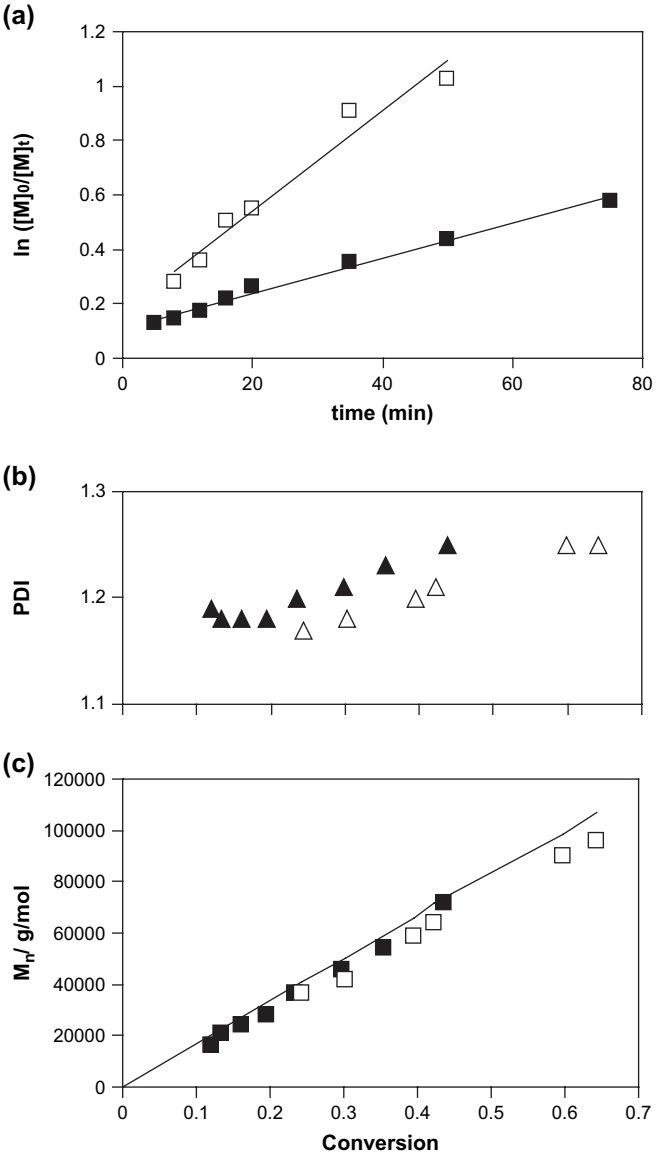


Fig. 11. Polymerisations of methyl methacrylate ([M]/[I] = 1600) at 90 °C by initiator **4** using CuCl/dNbpy catalyst in 50 vol% diethyl ether (open symbols) or in 50 vol% toluene (solid symbols). (a) The kinetic plots of monomer conversion as a function of reaction time. Lines have been added for a guide to the eye. (b) Apparent polydispersities and (c) number-average molar masses M_n, both determined by SEC (RI), as a function of conversion. The straight line represents the theoretical M_n.

the self-assembling properties of the amphiphilic stars prepared from the block copolymers.

Acknowledgments

The authors gratefully acknowledge the financial support by ESPOM Graduate School (Electrochemical Science and Technology of Polymers and Membranes including Biomembranes). The authors also wish to thank Markus Nuopponen (University of Helsinki) for MALDI-TOF measurements and Dr. Sami Hietala (University of Helsinki) for operating the 500 MHz NMR spectrometer.

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