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Star polymers synthesised with flexible resorcinarene-derived ATRP initiators

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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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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-tetramethyl-resorcinarene (*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, $>\mathrm{CH}-$, 4H), 4.23 (m, CH_2, 32H), 1.46 (d, $>\mathrm{CHC}H_3$, 12H), 1.28 (t, $-\mathrm{CH_2C}H_3$, 24H).

^{13}C NMR (50.3 MHz, $CDCl_3$) δ ppm: 169.35 ($>\mathrm{C{=}O}$, 8C), 154.25 (ArOR, 8C), 129.69 (Ar, 4C), 125.82 (ArH, 8C), 100.60 (ArH, 4C), 67.21 ($\mathrm{ArO}C\mathrm{H_2}-$, 8C), 60.97 ($-C\mathrm{H_2CH_3}$, 8C), 30.89 ($>\mathrm{CH}-$, 4C), 19.69 ($>\mathrm{CH}C\mathrm{H_3}$, 4C), 14.12 ($-\mathrm{CH_3}$, 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 $[M+Na]^+$.