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Synthesis and polymerization of a bulky styrenic monomer as an in-chain 'knot' for polyrotaxanes

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p-[Tris(*p*-t-butylphenyl)methyl]phenoxymethylstyrene (**10**) was prepared as a mixture of *meta* and *para* isomers via Williamson ether synthesis from vinylbenzyl chloride. Monomer **10** polymerizes smoothly under free-radical conditions. Under anionic polymerization conditions, nucleophilic attack at the benzylic position displaces the substituted phenoxide ion; by using an excess of n-butyllithium, however, a polymer of complex structure, high molecular weight and polydispersity of 2.2 was formed. On the basis of its steric bulk and polymerizability, new monomer **10** is therefore a useful in-chain 'knot' or 'stopper' for polyrotaxane synthesis using free-radical techniques, but not via anionic methods.

(Keywords: bulky styrenic monomer; synthesis; in-chain 'knot')

INTRODUCTION

Low-molecular-weight rotaxanes consist of cyclic molecules threaded onto linear molecules. (Refs 1–5 represent leading articles on low-molecular-weight rotaxanes.) As shown in **1** the macrocycles are constrained by bulky groups attached to the ends of the linear species after assembly; the bulky substituents are called 'stoppers', 'knots' or 'end blocking groups'[1–6]. Similarly, in main-chain polyrotaxanes **2** it is desirable, but often not necessary, to attach end blocking groups[6–17]. We have reported the synthesis of a number of triarylmethyl derivatives suitable for end blocking low-molecular-weight rotaxanes **1** and polyrotaxanes of type **2** made by step-growth (condensation) and anionic polymerizations[18]. Azo initiators containing triarylmethyl moieties have been made and used to ensure end blocking in free-radical polymerizations that terminate by combination[6,7].

However, the design of polyrotaxanes for some sophisticated applications may demand a new type of blocking group or knot. One such system is represented by structure **3**; knots or stoppers are incorporated into the linear backbone, confining the cyclic species to certain domains or cells. This structure resembles a molecular abacus and the knots act as spacers. Given sufficient control, adjacent cells might contain different cyclic and backbone species, as indicated in structure **4**, a main-chain block polyrotaxane.

Once a system such as **4** has been constructed, it may be useful to be able to remove the knot and enable the macrocycles in adjacent cells to interact, e.g. in the case where the cyclic species are electroactive, as in generic structure **5**. This requires that the knot contains bonds that are cleavable under certain specific conditions.

Moreover, the construction of side-chain polyrotaxanes of type **6** can in principle be achieved by the chain-growth polymerization or copolymerization of a vinyl monomer of type **7** in the presence of the cyclic species[6].

This paper describes the synthesis and polymerization of a prototypical monomer to address these needs for new knots or stoppers, specifically for chain-growth polymerizations.

RESULTS AND DISCUSSION

Blocking-group monomer

Reaction of a mixture of *m*- and *p*-vinylbenzyl chlorides (**8**) and *p*-[tris(*p*-t-butylphenyl)methyl]phenol (**9**)[18] under conditions similar to those reported by Gibson and Bailey[19] afforded monomer **10** as a mixture of isomers in 93% yield.

Polymerizations

Free-radical. Free-radical polymerization of **10** was done using azobisisobutyronitrile (AIBN) in benzene to obtain polymer **11**. The number-average molecular weight of the polymer by g.p.c. in tetrahydrofuran (THF) was found to be 37×10^3 (according to polystyrene (PS) standards) with a polydispersity index of 1.7. The polymer had a T_g of 210°C and was not crystalline (no T_m).

The T_g of the polymer is higher than typically observed for styrenic polymers. This is attributable to the reduced free volume due to the bulky pendent group. The proton n.m.r. spectrum of **11** showed broad

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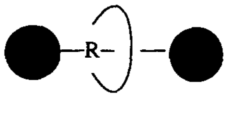

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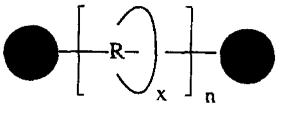

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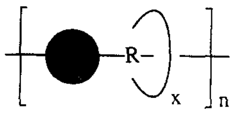

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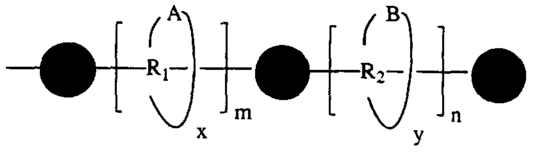

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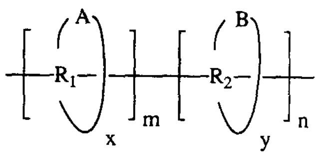

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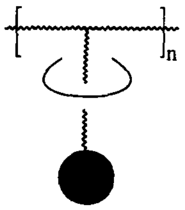

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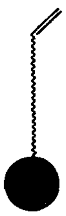

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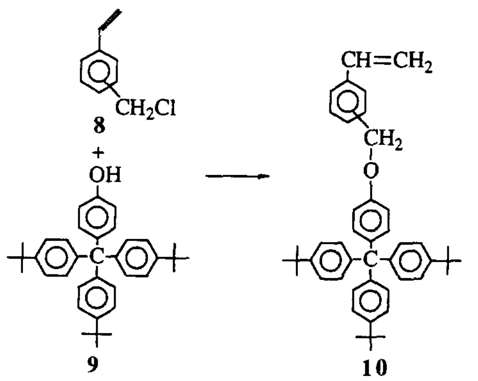
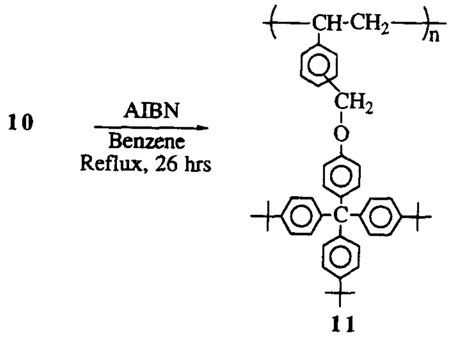




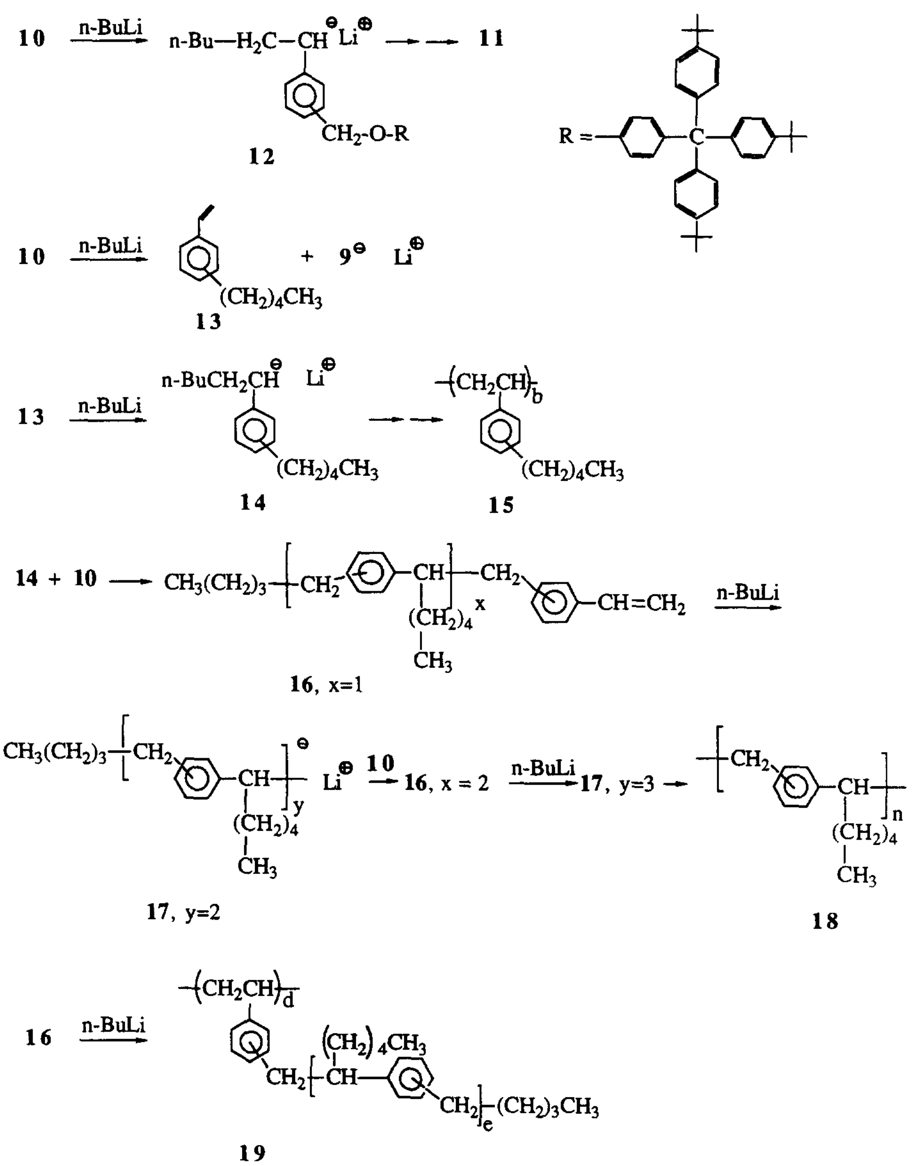
peaks for aromatic protons at 7.2–6.3 ppm, benzylic protons at 4.8–4.3 ppm and aliphatic methylene protons at 1.5–1.7 ppm. Multiple peaks were seen at 1.29–1.0 ppm for methyl protons of the t-butyl groups of the polymer, presumably because of the conformational restrictions of this very crowded structure; in monomer **10** the t-butyl signal was a sharp singlet.

The benzyl ether linkage of **11** is cleavable by either acidic hydrolysis or hydrogenolysis. This process represents one means of removing the knot or stopper, thereby enabling the generic **4** → **5** conversion in polyrotaxanes.

Anionic. Anionic polymerization of **10** was of interest for several reasons. The first was to study the feasibility of using this monomer to end-block living polystyryl anions during the synthesis of rotaxanes[6,20], since no study on the anionic polymerization of benzyl ether derivatives of vinylbenzyl chloride had been reported. Further, the monomer has a bulky *p*-tris-(*p*-t-butylphenyl)methyl group, which owing to its steric bulk might preferentially orient the living polymeric anion and the incoming monomer to give syndiotactic polymer.

In various attempts to polymerize **10** by n-butyllithium or sodium naphthalide in THF at 5–10°C, anions were found to terminate instantly after being formed, as evidenced by the occurrence and disappearance of red colour. Initially it was thought that monomer or solvent was impure; however, after careful purification of both the solvent and monomer, the same phenomenon was observed. Thus, n-butyllithium was added to the monomer solution in small quantities until the red colour of the anion persisted; this required an almost equimolar amount of base. During the work-up, one of the components of the product was found to be soluble in methanol and its proton n.m.r. spectrum was identical to that of the phenol **9**. A 73% yield of **9** was isolated. G.p.c. analysis of the methanol-insoluble component showed it to be a polymer with number-average molecular weight of 80×10^3 with a polydispersity index of 2.2; the polymer showed a T_g at 177°C by d.s.c.

Direct anionic vinyl polymerization of **10** via anion **12** will produce repeat units **11** (*Scheme 1*). There are several possible side reactions that can occur by displacement of the anion of **9**. One leads to formation of n-pentylstyrene (**13**) and its subsequent polymerization via **14** to **15**. Attack of anion **14** on **10** could produce substituted styrene **16**, $x = 1$; a sequence of anion **17** formation by reaction with n-butyllithium and subsequent reaction with another **10** would yield homologous macromonomers



Scheme 1 Possible reactions in the anionic polymerization of **10**

16, $x = 2$, then **17**, $y = 3$, and ultimately structures of type **18** via this step-growth polymerization process. Anionic vinyl polymerization of **16** would produce comb structures of type **19**. By similar routes, attack of anions **12** or **14** and their polymeric homologues on **10** could lead to structures analogous to **19**. Note that attacks of anions **12**, **14** and **17** on units of type **11** constitute branching and potentially crosslinking reactions.

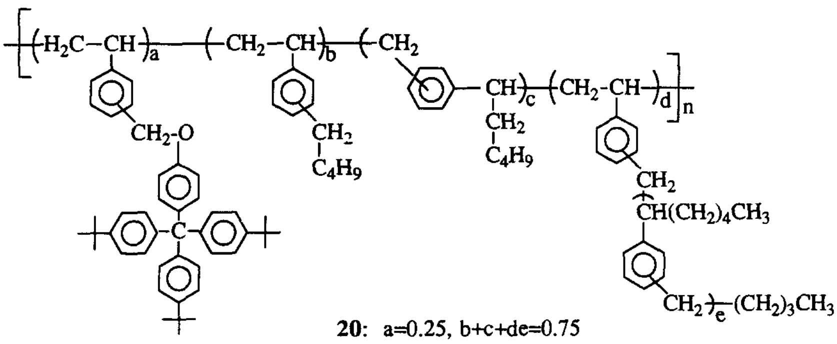
Formation of a red colour upon each addition of n-butyllithium as well as formation of the polymer indicated that styryl anion formation followed by its attack on the benzyl ether linkages was predominant. The polymer was soluble in THF, acetone and chloroform, indicating that it was not crosslinked. In the proton n.m.r. spectrum of the product, the aromatic protons appear as broad peaks from 7.3 to 6.0 ppm, whereas $-CH_2$ and $-CH_3$ protons of t-butyl and n-pentyl groups appear at 0.7–1.3 ppm; the methylene and methine groups attached to phenyl groups appear as broad peaks at 1.5–3.0 ppm and the $-OCH_2$ protons appear at 4.2–4.9 ppm. The ratio of the integral values of aromatic protons to aliphatic protons could not be determined with precision because of peak broadness. The ^{13}C n.m.r. spectrum (APT, attached proton test) contained a large number of aliphatic and aromatic signals.

Based on these results, the polymer is proposed to be a copolymer of **11**, **15**, **18** and **19**; note that **15**, **18** and **19** are isomeric, making more detailed structure determination very difficult. Structure **20** is a representation of the proposed structure. Of course, the structure is expected to be statistical and not a block copolymer.

EXPERIMENTAL

Measurements

Melting points were taken in capillary tubes with a Haake-Buchler melting-point apparatus and have been corrected. Proton and carbon n.m.r. spectra were obtained on a Bruker WP 270 MHz spectrometer or a Varian Unity 400 MHz spectrometer using chloroform solutions with tetramethylsilane as an internal standard. Elemental analyses were performed by Atlantic Microlab of Norcross, GA. D.s.c. data were obtained using a Perkin-Elmer DSC-2 instrument at a scan rate of 10°C min^{-1}. *FT* i.r. spectra were obtained on a Nicolet



20: a=0.25, b+c+de=0.75

MX-1 instrument. G.p.c. analyses of the polymers were done at 20°C in THF using a Waters system (r.i. and u.v. detectors) after calibration with PS standards.

Synthesis of m- *and* p-{p-[*tris*(p-*t-butylphenyl*)*methyl*]-*phenoxymethyl*}*styrene* (**10**)

The procedure of Gibson and Bailey[19] was slightly modified as follows. *p*-Hydroxyphenyl-tris(*p*-t-butylphenyl)methane (**9**) (7.0 g, 14 mmol), 1.35 g of 87% KOH (1.7 eq.), 50 ml dioxane and 25 ml ethanol were placed in a 500 ml round-bottomed flask. Upon heating, **9** dissolved. The resulting potassium phenolate precipitated and dissolved upon addition of an additional 50 ml dioxane and heating. After 10 min, 3.6 ml (1.5 eq) of vinylbenzyl chloride (70% *meta* and 30% *para* mixture) was added dropwise using a syringe. The reaction mixture was refluxed for a total of 64 h, cooled and 300 ml water was added. The resultant solid was filtered and then washed with water (4 x 400 ml). It was then placed in methanol and stirred for 30 min, filtered and washed with methanol. The filtrate was light yellow in colour; hence, the above step was repeated one more time. The monomer was precipitated from THF into 10-fold excess methanol and dried under vacuum. Yield, 8.01 g (93%) of white powder; m.p. 233.8–234.6°C. Efforts to isolate *meta* and *para* isomers using a variety of combinations of solvents were not successful. I.r. (KBr): 3088, 3033 (aromatic), 2960, 2902, 2866 (aliphatic), 1605, 1581, 1507, 1473, 1460 (aromatic), 1223, 1186, 1109, 1019, 987, 906, 841, 825, 712–707, 597–578 cm^{-1}. ^1H n.m.r.: 7.46–7.33 (m, 4H), 7.23, 7.08 (2d, $J = 8$, 12H), 7.05–7.1 (buried under other aromatic peaks, m, 2H), 6.84 (d, $J = 9$, 1H), 6.83 (d, $J = 12$, 1H), 6.73 (C of ABC, =CH, 1H), 5.76 (dd, $J = 18, 2.4$, $=CH_2$, 1H), 5.25 (dd, $J = 11, 2.4$, $=CH_2$, 1H), 5.01 ($-CH_2$, s, 2H), 1.30 ppm ($-CH_3$, s, 27H). Elemental analyses: calculated for $C_{46}H_{52}O$, C 88.98%, H 8.44%, O 2.58%; found, C 88.87%, H 8.46%.

Free-radical polymerization of **10**

Monomer **10** (2.17 g, 3.5 mmol) was dissolved in 25 ml dry benzene at 70°C (in an oil bath) followed by addition of 7.0 mg (4.0×10^{-5} mol) of azobisisobutyronitrile (AIBN) dissolved in 5 ml dry benzene. The solution was refluxed for 26 h. The reaction mixture was cooled and precipitated in 10-fold excess methanol, filtered and dried; yield, 2.10 g (97%). G.p.c. molecular weight (polystyrene standards), 37×10^3; polydispersity index, 1.7. D.s.c.: $T_g = 210°C$, no T_m. The *FT* i.r. spectrum of the polymer was identical to that of vinyl monomer **10** except that peaks at 987 and 906 cm^{-1} were absent in the polymer. ^1H n.m.r.: 7.5–6.7, 6.7–6.1 (very broad, 16H), 4.9–4.2 ($-OCH_2$, very broad, 2H), 1.5–1.9 (broad, $-CH-$, $-CH_2$, 3H), 1.29–1.0 ppm (CH_3, 27H).

Anionic polymerization of **10**

THF was distilled from sodium benzophenone and then styrene and n-butyllithium were added to it; the red solution was freeze-thawed on the vacuum line (ca. 10^{-5} Torr) six times, distilled on the vacuum line and the THF was then stored in a glove-box ($[H_2O] = 0.6$ ppm, $[O_2] = 0.32$ ppm). Monomer **10** (5.4 g, 8.69 mmol) was dissolved in 100 ml THF by warming the mixture using a heat gun in the glove-box. Upon addition of 0.50 ml of 0.22 M n-butyllithium (0.11 mmol) the red colour of the anion formed and disappeared immediately. Thus, more n-butyllithium was added in small quantities until the red colour persisted. It took almost 8.7 mmol of n-butyllithium to get the red colour of the anion to persist. The reaction was terminated using methanol and the polymer was precipitated in 1 litre of methanol followed by purification of the polymer by suspending it in hot ethanol and then filtering (repeated thrice). The solid was filtered and dried; yield, 2.5 g. G.p.c.: $M_n = 80 \times 10^3$ (polystyrene standards); polydispersity index, 2.2. ^1H n.m.r.: 7.5–5.8 (broad, aromatic), 5.1–4.1 ($-OCH_2$, broad), 1.5–3.0 (broad, $-CH_2$ and $-CH$), 1.3–0.7 ppm (CH_3); integration values were inaccurate owing to peak broadness. ^{13}C n.m.r. (APT): 14.06 (CH_3), 22.47 (CH_2), 27.13 (CH_2 or quat., weak), 31.40 (CH), 34.25 (CH_2), 63.05 (OCH_2, weak), 63.50 (OCH_2, weak), 113.26 (arom. CH, weak), 113.93 (arom. CH, weak), 124.04 (arom. CH), 125.57 (arom. CH, med.), 128.18 (arom. CH, weak), 128.87 (arom. CH, weak), 130.75 (arom. CH), 131.26 (arom. CH), 132.25 (arom. CH, weak), 132.37 (arom. CH, weak), 139.76 (arom. quat., weak), 141.07 (arom. quat., weak), 143.47 (arom. quat., weak), 143.83 (arom. quat.), 144.13 (arom. quat.), 146.56 (arom. quat., weak), 148.25 (arom. quat.), 153.41 (arom. quat. CO?, very weak), 156.69 ppm (arom. quat. C–O?, very weak). D.s.c.: $T_g = 177°C$, no T_m. The methanol–ethanol-soluble part yielded 3.2 g (73%) of **9**, whose proton n.m.r. spectrum was identical to that of an authentic sample.

CONCLUSION

A new bulky substituted styrene monomer (**10**) has been synthesized. It polymerizes smoothly under free-radical conditions and is therefore suitable as a new type of in-chain knot or stopper for free-radical polyrotaxane syntheses. Cleavage of the benzyl ether linkages of the resultant polymer **11** by acid hydrolysis or hydrogenolysis will enable removal of the knot as shown in

4 → **5**. Under anionic polymerization conditions, nucleophilic displacement of the substituted phenolate anion takes place, yielding a soluble polymer, but demonstrating that this monomer is not suitable for use as a knot monomer in anionic polyrotaxane syntheses. Recently we have described other bulky difunctional compounds suitable for use in step- and chain-growth polyrotaxane syntheses[21,22].

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