Hexa-arm polyisobutene stars by the core-first method

Eric Cloutet,[a,b] Jean-Luc Fillaut,[a] Yves Gnanou*[b] and Didier Astruc[a]

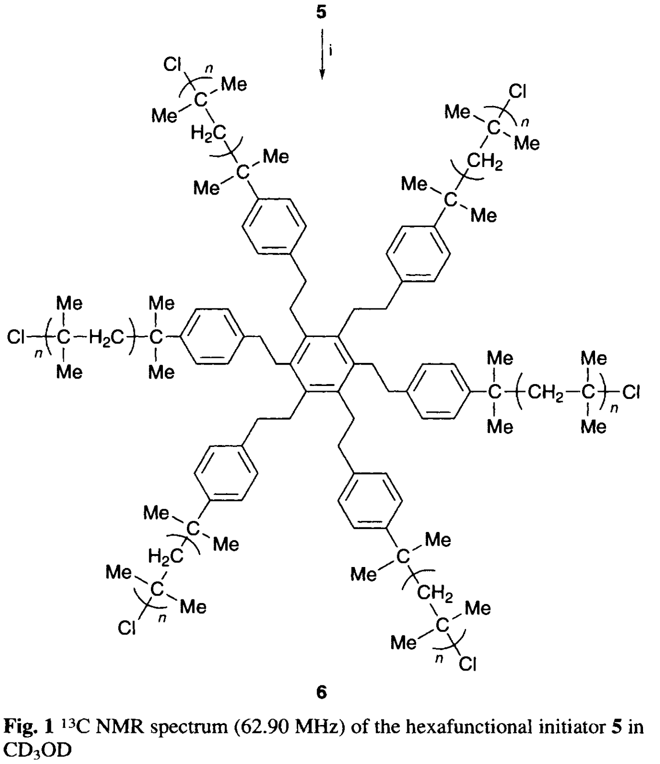
[a] *Laboratoire de Chimie Organique et Organométallique, URA CNRS No 35, Université Bordeaux I, 351, Cours de la Libération, 33405 Talence Cédex, France†*

[b] *Laboratoire de Chimie des Polymères Organiques, URA CNRS No 1192, ENSCPB, Université Bordeaux I, Avenue Pey Berland - B.P. 108, 33402 Talence Cédex, France*

The hexafunctional initiator 5 has been synthesized and used for the living cationic polymerization of isobutene by means of the core-first method, giving rise to the first hexa-arm polyisobutene stars 6.

Star polymers is an area of polymer chemistry which is now rapidly growing,[1–7] with a great underlying potential for specific mechanical properties due to segment density.[1d] It leads to star-block copolymers,[3d] dendritic polymers[5,6] and cross-linking agents.[1–3] No report has yet appeared on the core-first synthesis of star-shaped polyisobutene of precise functionality using a core with more than four branches.[8] We now report a new initiator **5** designed for the living star polymerization of isobutylene and the first synthesis of hexa-arm polyisobutene **6**.

The $[Fe(C_5H_5)]^+$ induced hexabenzylation of hexamethyl benzene in **1** is known to proceed smoothly with Bu^{t}OK and $PhCH_2Br$ in 1,2-dimethoxyethane (DME) and gives high yields of hexaphenylethylbenzene, **2**,[9,10] after removal of $[Fe(C_5H_5)]^+$ using photolysis with a Hg lamp.[10b] After regiospecific acetylation of **2** giving **3**, reaction of **3** with MeMgI gives the new hexol **4** (87% yield) which reacts with KH and MeI to provide the new hexacumyl methyl ether initiator **5** (60% yield, Scheme 1) characterized by elemental and spectroscopic analyses‡ (see Fig. 1 for the ^{13}C NMR spectrum). The synthesis of the hexa-arm polyisobutene **6** was carried out according to a method inspired by that developed by Kennedy[1a] using living cationic polymerization (Scheme 2). Prior to polymerization, 115 mg (0.1 mmol) of **5** was freeze-dried from dioxane solution (20 ml). Compound **5** was dissolved in a mixture of 122 ml of dichloromethane and 183 ml of methylcyclohexane (40 : 60) at −80 °C, 30 ml (337 mmol) of isobutene and 0.2 ml (0.9 mmol, *i.e.* 1 equiv. per branch) of 2,6-di-*tert*-butylpyridine were then added to the solution containing **5**. The polymerization was initiated by adding $TiCl_4$ (1 ml, 9 mmol, *i.e.* 15 equiv. per branch) and was quenched with prechilled methanol (10 ml) containing 1 ml aq. NH_3 (1 M) after 195 minutes. The quenched reaction mixture was diluted with CH_2Cl_2, filtered, concentrated and precipited twice with cold methanol. Filtration and drying yielded a polymer suitable for SEC coupled with a multi-angle laser light-scattering (MALLS) detector. The star samples obtained clearly exhibit a Poisson-type distribution with a polydispersity index $\bar{M}_w/\bar{M}_n$ = 1.27. The total molar mass $\bar{M}_w$ of 16500 g mol^{-1} corresponds to about 2750 g mol^{-1} for each of the six branches (*i.e.* 55 isobutylene units per branch, Fig. 2). Other polymers of this series with different $\bar{M}_w$ were similarly obtained by varying the amount of isobutene and the reaction time. The ^1H NMR spectrum ($CDCl_3$) of the hexa-arm polyisobutene **6** shows the classical sharps singlets of polyisobutene [δ_H 1.1 (6H, CH_3), 1.4 (2H, CH_2)].



6

Fig. 1 ^{13}C NMR spectrum (62.90 MHz) of the hexafunctional initiator **5** in CD_3OD

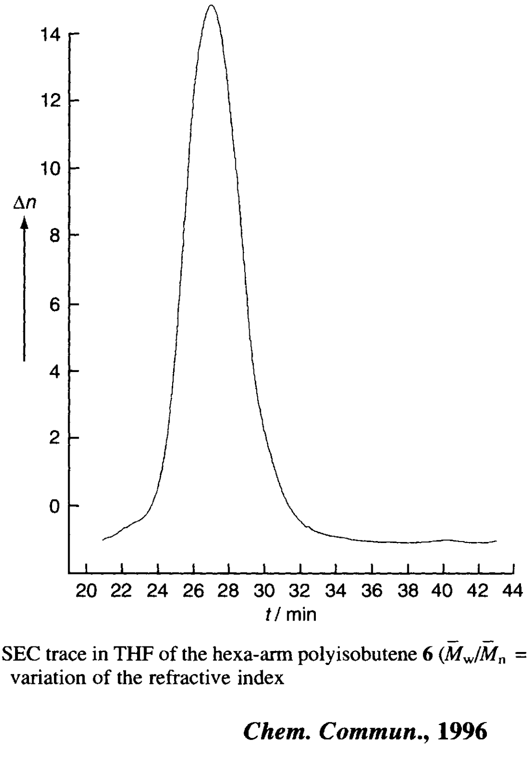
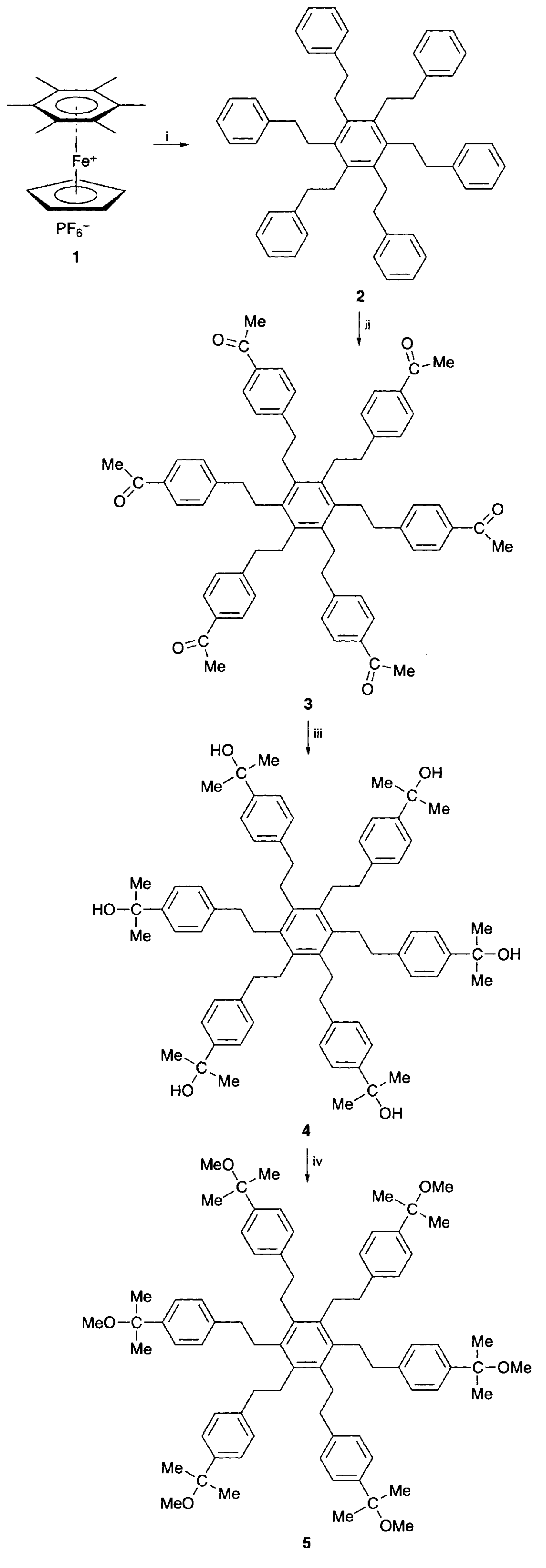
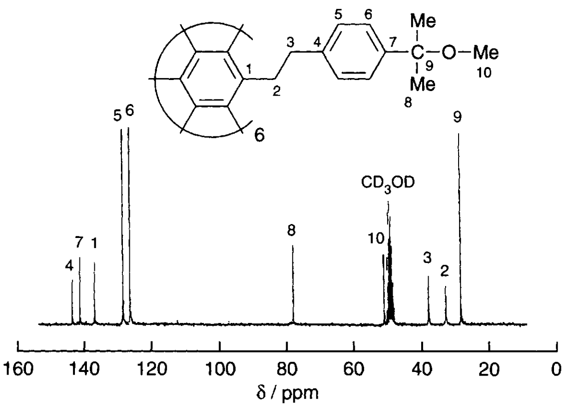


Fig. 2 SEC trace in THF of the hexa-arm polyisobutene **6** ($\bar{M}_w/\bar{M}_n$ = 1.27); Δn = variation of the refractive index



Scheme 1 *Reagents and conditions*: i, Bu^{t}OK, PhCH$_2$Br, DME, 40 °C, then photolysis (UV Hg lamp) in MeCN; ii, MeCOCl, AlCl$_3$, CH$_2$Cl$_2$, room temp.; iii, MeMgI, CH$_2$Cl$_2$, room temp.; iv, KH, MeI, THF, 50 °C



Scheme 2 *Reagents and conditions*: i, TiCl$_4$, 2,6-di-*tert*-butylpyridine, isobutene, in CH$_2$Cl$_2$–MeC$_6$H$_{11}$ (40:60), −80 °C

Footnotes

[†] E-mail: abstruc@cribx1.u-bordeaux.fr

[‡] *Spectroscopic data* for **5**: Calc. for C$_{78}$H$_{102}$O$_6$: C, 82.45; H, 8.99; O, 8.56. Found: C, 82.40; H, 9.01; O, 8.59%; 45% overall yield of white microcrystals from **2**; ^{1}H NMR (CD$_3$OD, 250 MHz): δ = 7.1 (m, AA 'BB', C$_6$*H*$_4$, 24 H), 3.0 (s, OC*H*$_3$, 18 H), 2.8 [m, (C*H*$_2$)$_2$, 24 H], 1.5 [s, (C*H*$_3$)$_3$, 36 H].

References

1 (*a*) J. P. Kennedy and B. Ivan, *Designed Polymers by Carbocationic Macromolecular Engineering*, Hanser, Munich, 1991; (*b*) T. P. Lutz, S. Graff, J. P. Lamps and P. Rempp, *Macromolecules*, 1991, **24**, 5897; (*c*) S. Kanaoka, M. Sawamoto and T. Higashimura, *Macromolecules*, 1991, **24**, 2309 and 5741; 1992, **25**, 6414; 1993, **26**, 744; (*d*) S. Bywater, *Adv. Polym. Sci.*, 1979, **30**, 89.

2 For seminal examples, see J. R. Schaefgen and P. J. Flory, *J. Am. Chem. Soc.*, 1948, **70**, 2709; J. G. Zilliox, P. Rempp and J. Parrod, *J. Polym. Sci., Part C*, 1968, **C22**, 145.

3 (*a*) H. Shobi, M. Sawamoto and T. Higashimura, *Makromol. Chem.*, 1992, **193**, 2027; (*b*) J. Y. Chang, H. J. Li, M. J. Han, S. B. Rhee, S. Cheong and M. Toon, *Macromolecules*, 1994, **27**, 1376; (*c*) M. Schappacher and A. Deffieux, *Macromolecules*, 1992, **25**, 6744; (*d*) R. F. Storey, B. J. Chisholm and Y. Lee, *Polymer*, 1993, **34**, 4330; (*e*) Y. Gnanou, P. Lutz and P. Rempp, *Makromol. Chem.*, 1988, **189**, 2885.

4 E. Cloutet, J.-L. Fillaut, Y. Gnanou and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1994, 2433; E. Cloutet, Y. Gnanou, J.-L. Fillaut and D. Astruc, *Chem. Commun.*, 1996, 1565.

5 For a recent, comprehensive review on dendrimers, see N. Ardoin and D. Astruc, *Bull. Soc. Chim. Fr.*, 1995, **132**, 875.

6 D. A. Tomalia and D. H. Dupont, *Top. Curr. Chem.*, 1993, **165**, 193; C. N. Moorefield and G. R. Newkome, in *Advances in Dendritic Macromolecules*, ed. G. R. Newkome, JAI, Greenwich, CT, 1994, **1**, 1; J. M. J. Fréchet, *Science*, 1994, **263**, 1710; J. Issberner, R. Moors and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2413; J.-L. Six and Y. Gnanou, *Macromol. Symp.*, 1995, **95**, 137.

7 Hexafunctional cores: ref. 3(*b*); J.-S. Wang, D. Crezta and K. Matyjaszewski, *Polym. Prep., Am. Chem. Soc., Div. Polym. Mat. Sci. Eng.*, 1995, **73**, 416; J.-i. Kadokawa and S. Kobayashi, *Makromol. Chem., Macromol. Symp.*, 1995, **95**, 121.

8 For polyisobutylenes with three and four arms, see ref. 1(*a*); M. Mishra, B. Wang and J. Kennedy, *Polym. Bull.*, 1987, **17**, 307; R. F. Storey and Y. Lee, *J. Macromol. Sci., Chem.*, 1992, **A29**, 1017.

9 D. Astruc, *Acc. Chem. Res.*, 1986, **19**, 377; *Pure Appl. Chem.*, 1990, **62**, 1165; *Top. Curr. Chem.*, 1991, **160**, 47.

10 (*a*) J.-R. Hamon, J.-Y. Saillard, A. Le Beuze, M. McGlinchey and D. Astruc, *J. Am. Chem. Soc.*, 1982, **104**, 7549; (*b*) D. Catheline and D. Astruc, *J. Organomet. Chem.*, 1984, **272**, 417; (*c*) C. Valerio, B. Gloaguen, J.-L. Fillaut and D. Astruc, *Bull. Soc. Chim. Fr.*, 1996, 133.

Received, 23rd April 1996; Com. 6/02812H