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Free-Radical Polymerization and Ring-Expansion of a Cubane Acrylate: a Unique Low-Shrink Polymer

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A pendant cubane substituent has been incorporated into an acrylate polymer side chain to give poly[methyl 4-(acryloyloxymethyl)cubane carboxylate]. Treating this polymer with a rhodium(I) salt triggers a catalytic, ring-opening rearrangement of the cubane substructure to cyclooctatetraene, with a concomitant expansion in molecular volume. This system offers a unique opportunity to reverse the shrinkage associated with polymerization.

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Introduction

Addition polymerization at constant temperature normally occurs with an increase in density and hence reduction in the volume of the reactants.^[1] A primary cause of contraction in volume during polymerization is due to the change from van der Waals distances to covalent bond lengths between monomer molecules. An additional factor is the relative packing efficiency of the monomer and polymer, which may vary greatly between monomers and polymers that are liquids, amorphous solids, or crystalline materials.

Shrinkage during polymerization frequently diminishes the performance, mechanical properties, and durability of bulk polymeric materials.^[2,3] Shrinkage in optical adhesives induces internal stress, leading to optical distortion. In adhesives, surface coatings, and encapsulating materials, voids are created and these serve as channels for contaminants to infiltrate the polymer. Matrix polymers in composite materials or coatings may retract from reinforcing fibres and fillers, thereby reducing the bond area between them. Excessive shrinkage in bulk polymers used for precision casting products may cause the product to improperly conform to the mould.

There have been several strategies employed for reducing or eliminating polymerization shrinkage, the most well known of which is ring-opening polymerization, pioneered (for this purpose) by Bailey.^[4] During the ring-opening polymerization of cyclic monomers, one or more rings are opened in each monomeric unit, and thus one or more bonds are broken for each new bond formed. Cyclic monomer structures occupy a smaller volume than their ring-opened counterparts, and hence the degree of shrinkage is lessened during ring-opening polymerization. Bicyclic and spiro monomers that ring-open on polymerization enhance this effect because two bonds are broken for every new bond formed. Significant effort in this area has led to the development of a wide variety of cyclic and bicyclic monomers, such as spiro orthoesters,^[5,6] bicyclo orthoesters,^[7] spiroketals,^[8] cyclic ethers,^[9] polycyclic ketal lactones,^[10,11] spiro orthocarbonates,^[12–14] and cyclic allylic sulfides^[15] that ring-open on polymerization to minimize polymer shrinkage.



Scheme 1.

One conclusion from this body of work is that to minimize polymer shrinkage, the monomer should occupy the smallest volume possible compared with the same unit in the final polymer. Multiple ring-opening strategies using spiro and bicyclic structures are effective in this approach and we reasoned that additional ring-opening would enhance the effect.

Among polycyclic hydrocarbons, the cubane (pentacyclo [4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane) structure is particularly fascinating by virtue of its symmetry and high strain, and because it has among the highest density of any stable hydrocarbon (1.29 g cm⁻³).^[16] Despite the enormous internal strain, cubane has a surprisingly high kinetic stability due to the lack of readily available thermal decomposition pathways.^[17] Nevertheless, the cubane skeleton is rapidly ring-opened by rhodium(1) catalysts^[18,19] to the corresponding tricyclooctadiene, which in turn thermally rearranges to cyclooctatetraene at 50–60°C (Scheme 1). Cyclooctatetaraene by comparison has the same molecular formula as cubane but a density of only 0.925 g cm⁻³. We anticipated that a cubane-containing monomer could be ringopened during or after polymerization to greatly decrease the final polymer density, and hence minimize polymer shrinkage.

There are few reported examples of cubane-containing polymers since Eaton envisioned the concept in a 1992 review.^[20] The first example of the formation of a cubane-containing polymer was reported by Chauvin,^[21] in which a metathesis polymerization of 1,4-bis(homoallyl)cubane afforded an oligomer with six to seven repeat units. The authors attributed the lack of further chain elongation to poor solubility. Other examples where the cubane structure forms part of the polymer backbone by polycondensation followed,^[22–24] but poor solubility again limited the extent of polymerization to oligomers of at best 68 repeat units.



Fig. 1. ¹H NMR spectrum of poly-4.

Harpp^[25] took an alternative approach by tethering cubane via an ester linkage to norbornene and polymerizing the monomer using Grubbs catalyst in a ring opening metathesis polymerization reaction.^[26] Polymers up to a molecular weight of 3.6×10^4 were obtained (approximately 143 repeat units), and these were soluble in low-polarity organic solvents.

Pendant attachment appears to have the most promise for incorporating cubane into a polymer structure. We now report the synthesis, polymerization, and cubane ring-opening of methyl 4-(acryloyloxymethyl)cubanecarboxylate.

Results and Discussion

Synthesis and Polymerization of Methyl 4-(Acryloyloxymethyl)cubanecarboxylate

The synthesis of acrylate ester **4** is outlined in Scheme 2. Cubane dicarboxylate **1** can be conveniently prepared by the method of Bliese and Tsanaktsidis.^[27] Careful half-hydrolysis of the diester **1** using methanolic sodium hydroxide afforded carboxylic acid **2** in good yield.^[28] The most efficient reduction of the carboxylic acid moiety was found to be using BH₃·SMe₂ with careful monitoring of the reaction time to avoid over-reduction. Alcohol **3** was acylated with acrylolyl chloride under basic conditions to afford the target monomer **4**.

The colourless crystalline methyl 4-(acryloyloxymethyl) cubanecarboxylate 4 was a stable, easily handled compound, which could be purified by column chromatography. In the 1 H

NMR spectrum of **4**, the three vinyl protons each appeared as doublet of doublets, with the characteristic pattern of *geminal–cis*, *geminal–trans*, and *cis–trans* coupling. The C3 axial symmetry of the 1,4-substituted cubane means that there are only two non-equivalent sets of three cubane protons, and these appeared as triplets centred at 3.90 ppm and 4.14 ppm, respectively.

Polymerization of methyl 4-(acryloyloxymethyl)cubanecarboxylate **4** was carried out under thermal conditions. A solution of **4** and azobisisibutyronitrile (AIBN) (0.5 wt-%) in benzene was degassed by three freeze–pump–thaw cycles to 0.1 Pa and the reaction tube was flame-sealed. The reaction was suspended in an oil bath at 70°C for 6 h. The isolated polymer was a malleable glassy solid and NMR analysis showed only a trace of starting material, and broad signals for the polymer (Fig. 1). Gel permeation chromatography (GPC) analysis of the polymer gave a number average molecular weight (M_n) of 64700 g mol⁻¹, indicating ~260 units of monomer. The weight average molecular weight (M_w) was 227400 g mol⁻¹, for a polydispersity of 3.5.

Rhodium(1) Catalyzed Cyclooctatetraene Formation

Various rhodium(I) and silver(I) salts are known to catalyze ring expansion of cubanes but $[Rh(norbornadiene)Cl]_2$ is one of the more efficient.^[19] A solution of $[Rh(norbornadiene)Cl]_2$ and the cubane polymer **poly-4** was heated at 60°C in toluene (Scheme 3). The reaction was followed by TLC. After 2 h, the



Scheme 3.

Table 1. Comparison of monomer and polymer densities and calculated shrinkages

Monomer	Density [g cm ⁻³]		Shrinkage [%]
	Monomer	Polymer	
Acrylonitrile ^[3]	0.797	1.17	31.9
Methacrylonitrile ^[3]	0.800	1.10	27.3
Methyl methacrylate ^[3]	0.940	1.19	21.0
Ethyl methacrylate ^[3]	0.911	1.11	17.9
n-Butyl methacrylate ^[3]	0.889	1.05	15.3
<i>n</i> -Propyl methacrylate ^[3]	0.902	1.06	14.9
4	1.084	1.252 (1.058) ^A	13.4 (-2.5) ^A

^AAfter ring-opening to give polymer 5.

starting material was completely consumed and a precipitate had formed. After cooling, the orange-brown amorphous solid polymer was collected, which proved to be insoluble in organic solvents. Typical NMR solvents such as chloroform, DMSO, tetrachloroethane, toluene, chlorobenzene, and trifluoroacetic acid failed to dissolve the polymer. NMR analysis of the filtrate revealed only a trace of the original cubane-containing polymer, indicating that the reaction had proceeded to give an insoluble material, most probably the cyclooctatetraene polyacrylate 5. The insolubility of the material is unlikely to be due to cross-linking because a variety of cubanes have been ring-expanded under these conditions without significant side reactions. The orange-brown colour may be due to some formation of cvclooctatetraene-rhodium complexes.^[29] Fouriertransform (FT)-IR spectroscopy of this solid in a KBr disk revealed a medium band at $1634 \,\mathrm{cm}^{-1}$, which is indicative of the carbon-carbon double bond stretching frequency of the cyclooctatetraene ring.^[30]

Volume Shrinkage

Density gradient columns of aqueous sodium bromide solutions at 20°C were set up according to British standards BS 2782-620D, and calibrated using a set of alkyl bromides. For the present report, polymerization volume shrinkage was calculated relative to the initial volume of monomer using the formula $[(\rho_{polymer} - \rho_{monomer})/\rho_{polymer}] \times 100\%$. The densities of the monomer 4, its polymer, and the ring-opened polymer 5, along with some representative methacrylates and acrylonitriles, are presented in Table 1. The shrinkage associated with polymerization of 4 was consistent with polymerization of other similar vinyl monomers (13.4%), as expected. Treatment of this polymer with rhodium catalyst triggered a rearrangement of the cubane skeleton to the much larger cyclooctatetraene structure, with a concomitant decrease in density from 1.252 to $1.058 \,\mathrm{g \, cm^{-3}}$, which represents an expansion of 18.3% from the cubane polymer (poly-4) to the cyclooctatetraene polymer 5. The overall



Fig. 2. Relationship of observed polymerization volume shrinkage and reciprocal molecular weight of the monomer: (a) acrylonitrile; (b) methacrylati; (c) methyl methacrylate; (d) ethyl methacrylate; (f) *n*-propyl methacrylate; (g) methyl 4-(acryloyloxymethyl)cubanecarboxylate 4; (h) cyclooctatetraene polymer 5.

change in density from monomer 4 to ring-opened polymer 5 is a slight decrease (1.084 to 1.058 g cm^{-3}), which represents a marginal expansion in volume of 2.5%.

The shrinkage that accompanies polymerization decreases roughly linearly with increasing molecular weight of the monomer, for a given series of similar functional monomers.^[31] Relationships between the reciprocal of the monomer's molecular weight and the shrinkage of some vinyl monomers are presented in Fig. 2. The shrinkage values, including for the cubane monomer, are roughly linear. However, on rearrangement from the cube skeleton to the cyclooctatetraene skeleton, there is a dramatic reversal of polymer shrinkage.

Conclusions

Incorporation of a pendant cubane substituent into the side chain of a polymer offers a unique opportunity to minimize polymer shrinkage by a catalytic, ring-opening rearrangement of the cubane to cyclooctatetraene. We have demonstrated such a ringopening expansion after polymerization. The cubane 1,4-diester offers convenient functionality to construct other monomers for free radical polymerization, and even alternative polymer systems including substrates for condensation and addition polymerization. These alternatives may alleviate the insolubility issues with polymer **5** and future work will focus on these areas.

Experimental

General

General experimental details and instrumentation have been described previously^[32] except that proton and carbon nuclear magnetic resonance (¹H and ¹³C NMR) spectra were recorded at room temperature on a Bruker AV400 operating at 400 and 100.6 MHz, respectively, using CDCl₃ as solvent and internal reference. Commercially available reagents and analytical grade solvents were obtained from Aldrich Chemical Co. and used as received. FT-IR spectra were recorded on a Bruker Equinox 55/S FT-IR spectrometer with samples in KBr disks. Densities were determined in gradient density columns using sodium bromide solutions at 20°C calibrated with a set of alkyl bromides of

known density (British standard BS 2782–620D). GPC was carried out on a Waters Associates liquid chromatograph equipped with differential refractometer and a set of six Ultra-Styragel columns (10^6 , 10^5 , 10^4 , 10^3 , 500, and 100 Å). Tetrahydrofuran was used as eluent at 20° C and a flow of 1.0 mL min^{-1} . The system was calibrated using narrow-distribution polystyrene standards (Waters).

4-Methoxycarbonylcubane Carboxylic Acid 2

A solution of 1.4-bis(methoxycarbonyl)cubane 1 (10.0 g. 45.4 mmol) in anhydrous THF (240 mL) was treated with a freshly prepared solution of NaOH (2.0 g, 50.0 mmol) in MeOH (60 mL) dropwise. The pale orange precipitate was stirred at room temperature for 16 h and then was concentrated under vacuum. The residue was taken up in H₂O (150 mL) and this was extracted with CHCl₃ (3×80 mL). The aqueous layer was carefully acidified to pH 3 with conc. HCl and this was extracted with chloroform $(3 \times 80 \text{ mL})$ and these organic extracts were dried (MgSO₄), filtered and concentrated to afford the title compound as a colourless solid (8.3 g, 89%). mp 178-180°C (lit.^[33] 182-183°C). δ_H (400 MHz, CDCl₃) 3.71 (3H, s, Me), 4.26-4.28 (6H, m, H2 and H3), CO_2H not observed. δ_C (101 MHz, CDCl₃) 47.05 (C2 or C3), 47.15 (C2 or C3), 51.7 (Me), 55.5 (C1 or C4), 55.8 (C1 or C4), 171.9 (C=O ester), 177.2 (C=O acid). m/z (Electron ionization (EI)) (intensity (int)) 206.1 (20), 160.1 (18), 146.0 (40), 102.0 (100). $\nu_{\rm max}({\rm KBr})/{\rm cm}^{-1}$ 3003, 2562, 1717, 1690, 1623, 1442, 1100, 849.

4-Methoxycarbonyl-1-(hydroxymethyl)cubane 3

A solution of 2 (5.0 g, 24.2 mmol) in anhydrous THF (250 mL) was cooled to 0°C and treated dropwise with BH₃·SMe₂ (3.7 mL, 39.4 mmol). The reaction mixture was stirred at 0°C for 30 min and then at room temperature for a further 30 min before quenching with H₂O (10 mL). The mixture was extracted with Et₂O (60 mL) and the organic layer was washed successively with brine (30 mL), saturated aqueous NaHCO3 solution (30 mL), and H₂O (30 mL). The ethereal solution was dried (MgSO₄), filtered, and concentrated to afford the *title compound* as a colourless crystalline solid (4.2 g, 90%). mp 84–86°C (lit.^[34] 86–90°C). $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.59 (1H, br s, OH), 3.70 (3H, s, Me), 3.77 (2H, s, CH₂OH), 3.85–3.91 (3H, m, H3), 4.12–4.17 (3H, m, H2). $\delta_{\rm C}$ (101 MHz, CDCl₃) 44.5 (C3), 46.3 (C2), 51.5 (Me), 56.4 (C1), 58.8 (C4), 63.2 (CH₂OH), 172.7 (C=O ester). m/z (electrospray ionization (ES)+) (int) 230.9 (40), 215.1 (30), 170.9 (20), 131.1 (20), 115.0 (100). ν_{max} (KBr)/cm⁻¹ 3298br, 2985, 1717, 1442, 1332, 1219, 1029, 842.

Methyl 4-(Acryloyloxymethyl)cubane Carboxylate 4

A solution of 4-methoxycarbonyl-1-(hydroxymethyl)cubane **3** (0.34 g, 1.8 mmol) in anhydrous CH₂Cl₂ (18 mL) was cooled to 0°C and treated with diisopropylethylamine (1.6 mL, 8.9 mmol), then slowly, dropwise with acryloyl chloride (0.6 mL, 7.1 mmol). The pale yellow solution was stirred and allowed to warm to room temperature. TLC (EtOAc/CHCl₃, 1:1) after 30 min indicated no remaining starting material and the reaction mixture was diluted with CH₂Cl₂ (30 mL) and H₂O (30 mL). The organic extract was washed successively with 1 M HCl (30 mL), saturated aqueous NaHCO₃ solution (30 mL), and brine (30 mL), and then dried (MgSO₄), filtered, and concentrated to afford the crude product as a brown solid. Column chromatography (eluting with hexane/EtOAc, 4:1) afforded the title compound as a colourless crystalline solid (0.29 g, 67%). mp 74–75°C. $\delta_{\rm H}$

(400 MHz, CDCl₃) 3.69 (3H, s, Me), 3.85–3.91 (3H, m, H3), 4.13–4.17 (3H, m, H2), 4.32 (2H, s, CH_2OR), 5.83 (1H, dd, *J* 10.4, 1.5 Hz, H6 *cis*), 6.14 (1H, dd, *J* 17.3, 10.4 Hz, H5), 6.40 (1H, dd, *J* 17.3, 1.5 Hz, H6 *trans*). δ_C (101 MHz, CDCl₃) 45.0 (C3), 46.5 (C2), 51.5 (Me), 56.2 (C1 or C4), 56.3 (C1 or C4), 64.4 (CH₂OR), 128.3 (C5), 130.8 (C6), 166.4 (C=O acryloyl ester), 172.5 (C=O methyl ester). *m/z* (ES+) (int) 269.0 (15), 223.0 (10), 199.2 (10), 142.8 (10), 114.9 (100). (Calc. for C₁₄H₁₄O₄: C 68.28, H 5.73. Found: C 68.35, H 5.78.) *m/z* (EI) Calc. for C₁₄H₁₄O₄: 246.0887. Found: 246.0898. v_{max} (KBr)/cm⁻¹ 2997, 2964, 1741, 1718, 1290, 1202, 973.

Poly-4

A solution of methyl 4-(acryloyloxymethyl)cubane carboxylate 4 (0.20 g, 0.8 mmol) was treated with a 2 mg mL^{-1} solution of AIBN in benzene (0.5 mL, 0.006 mmol). The resultant solution was degassed using the freeze-thaw method (\times 3) and then sealed in a tube using a blowtorch. The reaction mixture was heated at 70°C for 6 h and then allowed to cool to room temperature. The tube was cracked open and a small sample was removed, concentrated, and analyzed by NMR. GPC analysis of the polymer gave a number average molecular weight (M_n) of 64700 g mol⁻¹, indicating \sim 260 units of monomer. The weight average molecular weight (M_w) was 227400 g mol⁻¹, for a polydispersity of 3.5. The reaction mixture was evaporated to drvness and the remaining solid was triturated with pentane, and collected by filtration. δ_H (400 MHz, CDCl₃) 1.38–1.70 (2H, br, CH₂ backbone), 2.25 (1H, br, CH backbone), 3.69 (3H, s, OMe), 3.85 (3H, br, cubane CH), 4.13 (3H, br, cubane CH), 4.21 (2H, br s, OCH₂). v_{max}(KBr)/cm⁻¹ 2964, 1721, 1441, 1325, 1223, 1183, 1092.

Cyclooctatetraene Polyacrylate 5

A solution of polymethyl 4-(acryloyloxymethyl)cubane carboxylate (**poly-4**) (200 mg, 0.81 mmol cubane equivalents) and [Rh(norbornadiene)Cl]₂ (30 mg, 0.07 mmol) in anhydrous toluene (10 mL) was heated to 60°C for 2 h and a precipitate formed. TLC analysis (Et₂O/hexane, 1:1) of the solution indicated complete consumption of the starting material. The resulting orange solid was collected by filtration and washed with toluene (2 × 10 mL). The solid was insoluble in organic solvents, water, and trifluoroacetic acid. v_{max} (KBr)/cm⁻¹ 3434 (H₂O), 2987 (C=CH), 2950, 1724 (C=O), 1634 (C=C), 1437, 1256, 1212, 1157, 1087, 967, 732.

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References

- F. S. Nichols, R. G. Flowers, Ind. Eng. Chem. 1950, 42, 292. doi:10.1021/IE50482A024
- [2] R. F. Brady, Jr, J. Macromol. Sci. Rev. Macromol. Chem. Phys. 1992, C32, 135.
- [3] Expanding Monomers: Synthesis, Characterization, and Applications (Eds R. K. Sadhir, R. M. Luck) 1992 (CRC Press: Boca Raton, FL).
- [4] W. J. Bailey, R. L. Sun, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 1972, 13, 281.
- [5] T. Endo, W. J. Bailey, J. Polym. Sci. Pol. Lett. 1980, 18, 25. doi:10.1002/POL.1980.130180106
- [6] T. Endo, M. Okawara, N. Yamazaki, W. J. Bailey, J. Polym. Sci. Polym. Chem. Ed. 1981, 19, 1283. doi:10.1002/POL.1981.170190526

- [7] K. Tanigaki, K. Saigo, Y. Ohnishi, H. Kato, K. Mizutani, T. Ogasawara, T. Endo, J. Appl. Polym. Sci. 1985, 30, 1419. doi:10.1002/APP.1985.070300409
- [8] I. Fukuchi, F. Sanda, T. Endo, Macromolecules 2001, 34, 4296. doi:10.1021/MA001993O
- [9] R. Schaefer, D. Heindl, D. Schöde, O. Nuyken, R. Böhner, C. Erdmann, US Patent 5,750,590 1998.
- [10] A. J. Holder, D. A. White, C. D. Harris, J. D. Eick, C. C. Chappelow, J. Mol. Struct. – Theochem. 2001, 541, 159. doi:10.1016/S0166-1280(00)00763-6
- [11] W. J. Bailey, US Patent 4,387,215 1983.
- [12] C. C. Chappelow, C. S. Pinzino, L. Jeang, C. D. Harris, A. J. Holder, J. D. Eick, *J. Appl. Polym. Sci.* 2000, 76, 1715. doi:10.1002/(SICI)1097-4628(20000613)76:11<1715::AID-APP13>3.0.CO;2-R
- [13] C. S. Wang, J. Mater. Sci. Lett. 1999, 18, 1259. doi:10.1023/ A:1006668117964
- [14] Y. J. Park, K. H. No, J. H. Kim, I. H. Suh, Bull. Korean Chem. Soc. 1992, 13, 375.
- [15] R. A. Evans, E. Rizzardo, Macromolecules 1996, 29, 6983. doi:10.1021/MA960573P
- [16] T. Yildirim, P. M. Gehring, D. A. Neumann, P. E. Eaton, T. Emrick, *Carbon* 1998, *36*, 809. doi:10.1016/S0008-6223(98)00009-8
- [17] V. M. Carroll, D. N. Harpp, R. Priefer, *Tetrahedron Lett.* 2008, 49, 2677. doi:10.1016/J.TETLET.2008.02.161
- [18] L. Cassar, P. E. Eaton, J. Halpern, J. Am. Chem. Soc. 1970, 92, 3515. doi:10.1021/JA00714A075
- [19] G. W. Griffin, A. P. Marchand, Chem. Rev. 1989, 89, 997. doi:10.1021/CR00095A003
- [20] P. E. Eaton, Angew. Chem. Int. Ed. Engl. 1992, 31, 1421. doi:10.1002/ANIE.199214211

- [21] Y. Chauvin, L. Saussine, *Macromolecules* 1996, 29, 1163. doi:10.1021/MA9511715
- [22] T. Kakuchi, W. Hirata, S. Yano, H. Kaga, Polym. Bull. 1997, 38, 651. doi:10.1007/S002890050101
- [23] M. Mahkam, N. S. Sanjani, *Polym. Int.* 2000, 49, 260. doi:10.1002/(SICI)1097-0126(200003)49:3<260::AID-PI347>3.0. CO;2-B
- [24] M. Mahkam, N. S. Sanjani, Polym. Degrad. Stabil. 2003, 80, 199. doi:10.1016/S0141-3910(02)00388-9
- [25] R. Priefer, S. Nguyen, P. Farrell, D. N. Harpp, *Macromolecules* 2003, 36, 5435. doi:10.1021/MA025906Z
- [26] R. H. Grubbs, S. H. Pine, in *Comprehensive Organic Synthesis* 1991, Vol. 5, Ch. 9.3 (Pergamon: New York, NY).
- [27] M. Bliese, J. Tsanaktsidis, Aust. J. Chem. 1997, 50, 189. doi:10.1071/C97021
- [28] P. E. Eaton, N. Nordari, J. Tsanaktsidis, S. P. Upadhyaya, Synthesis 1995, 501. doi:10.1055/S-1995-3961
- [29] M. A. Bennett, J. D. Saxby, Inorg. Chem. 1968, 7, 321. doi:10.1021/IC50060A031
- [30] E. H. White, H. C. Dunathan, J. Am. Chem. Soc. 1964, 86, 453. doi:10.1021/JA01057A033
- [31] J. Sugiyama, K. Ohashi, M. Ueda, *Macromolecules* 1994, 27, 5543. doi:10.1021/MA00098A005
- [32] G. P. Savage, G. T. Wernert, Aust. J. Chem. 2005, 58, 877. doi:10.1071/CH05189
- [33] P. E. Eaton, Y. Xiong, J. P. Zhou, J. Org. Chem. 1992, 57, 4277. doi:10.1021/JO00041A038
- [34] J. T. Edward, P. G. Farrell, G. E. Langford, J. Am. Chem. Soc. 1976, 98, 3075. doi:10.1021/JA00427A003