Macromolecules

Volume 40, Number 11 May 29, 2007

Communications to the Editor

Synthesis and Chemistry of a Monotethered-POSS Bis(cyanate) Ester: Thermal Curing of Micellar Aggregates Leads to Discrete Nanoparticles

Michael E. Wright,* Brian J. Petteys,
Andrew J. Guenthner,* Gregory R. Yandek,[†]
Lawrence C. Baldwin, Conrad Jones,[‡] and
M. Joseph Roberts

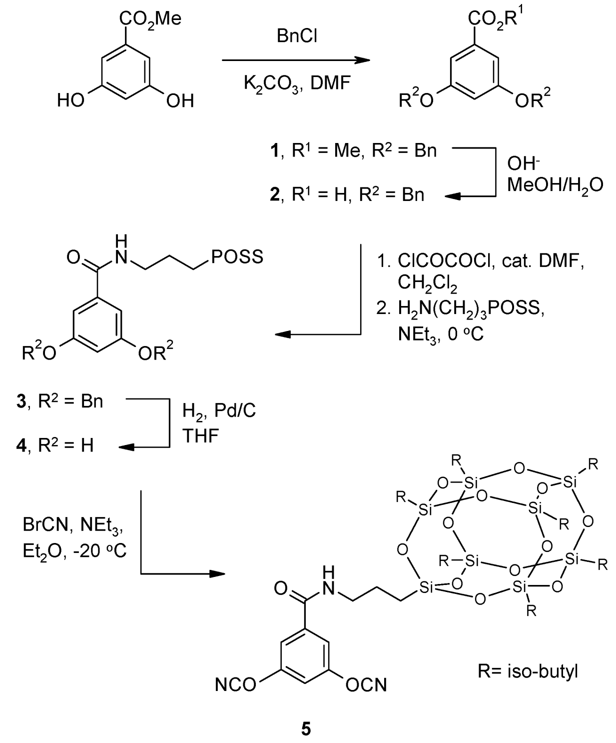
NAVAIR Research Department, Chemistry
Division-NAWCWD, China Lake, California 93555

Received February 9, 2007
Revised Manuscript Received March 23, 2007

Polyhedral oligomeric silsesquioxanes (POSS) are a family of nanoscale chemical structures that contain a silicon/oxygen core based on $(SiO_{1.5})_n$ and have each apex (i.e., silicon atom) connected to some organic group.[1] It is this combination of an inorganic core covered with an organic shell at the molecular level that has led POSS structures to being labeled as hybrid materials.[2] The most easily prepared, commercially available, and widely studied POSS structures have a core unit of eight silicon atoms: $(RSiO_{1.5})_8$ with R being a wide variety of neutral[3] and charged[4] organic functionalities. Thus, the chemical nature of the R group that modifies a POSS cage controls the solubility and hence compatibility of the hybrid material with solvents and in many cases, a host polymeric material.[5]

Early in the development of POSS chemistry Feher and co-workers[6] discovered that incompletely condensed cages of the formula $R_7Si_7O_9(OH)_3$ could be isolated and then capped with an organosilane (R^1SiX_3) reagent to produce a wide variety of POSS molecules with one apex uniquely modified.[7] Over the past two decades research groups have utilized monotethered-POSS molecules for the covalent attachment to a variety of host materials.[8] More recently several groups have recognized that the amphiphilic nature of monotethered-POSS molecules can be utilized to assemble three- and two-dimensional nano- and microstructures.[9,10] In this communication we present the synthesis of a new monotethered-POSS molecule that will form micellar aggregates that undergo a thermally induced polymerization/cure reaction to afford very stable and discrete nanosized macromolecular structures.

Scheme 1



Starting from methyl 3,5-dihydroxybenzoate, the bis-benzyl-protected benzoic acid (**2**) is produced in essentially quantitative yield in two steps (Scheme 1).[11] Formation of amide **3** is subsequently achieved in high yield by treatment of **2** with oxalyl chloride (catalytic DMF) followed by reaction with 3-aminopropyl-hepta(isobutyl)POSS. The benzyl-protecting groups

---

* Corresponding author. E-mail: michael.wright@navy.mil.

[†] Current address: ERC Incorporated, Materials Applications Branch, Air Force Research Laboratory, 10 East Saturn Blvd, Edwards AFB, CA 93524.

[‡] Current address: Southern University, Department of Chemistry, Harding Blvd, rm 108 Lee Hall, Baton Rouge, LA 70813.

10.1021/ma0703507

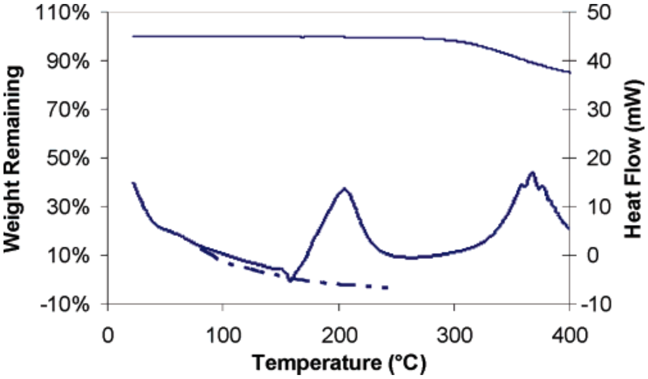


Figure 1. Simultaneous TGA (upper curve) and DSC (lower curves) of monomer **5**, heated at 10 °C/min under nitrogen. The dashed curve is the DSC signal from the second heating of a separate sample of monomer **5** thermally cycled to 250 °C (i.e., a completely cured sample).

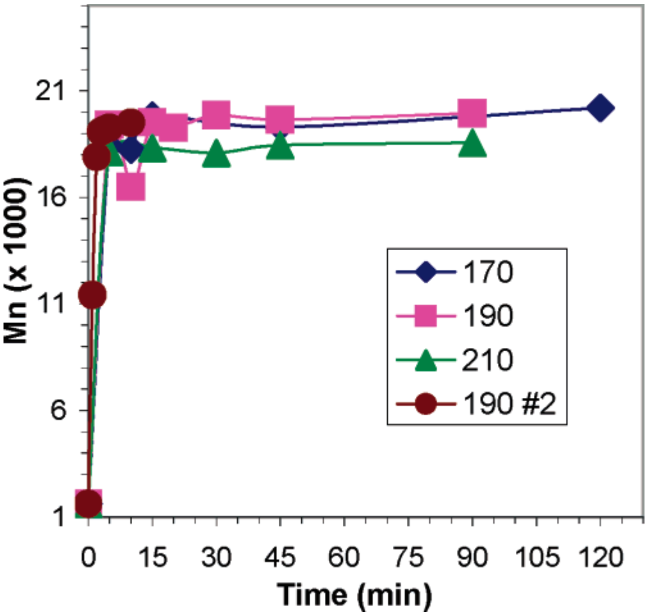


Figure 2. SEC analysis for the curing reaction of **5** carried out at selected temperatures. Each data point represents a unique sample that was quenched at the reported time and then analyzed by SEC. Results are relative to polystyrene standards using THF as solvent. Polydispersity values were typically in the range of 1.4−1.6 for samples.

are readily removed under mild conditions using hydrogen and Pd/C as catalyst[12] to afford the dihydroxy benzamide **4**.[13] A chilled (−20 °C) ether solution containing **4** and a slight excess of cyanogen bromide is treated with triethylamine to afford after workup, monomer **5** in excellent yield and purity.[14] It is noteworthy to mention that the only purification steps required to provide pure intermediates and the target monomer are either simple aqueous workups or filtration through Celite.

A cure profile obtained in a differential scanning calorimeter (DSC) for cyanate monomer **5** is displayed in Figure 1. As anticipated, we find an exothermic cure event; however, this usually does not occur until well over 220 °C for most aromatic cyanate ester resins.[15] The reason for the lower temperature cure is unclear at this time. In Figure 1, we also show that when the ramp is halted at 250 °C and then cooled, the second heating cycle shows no exothermic cure event. Thermogravimetric analysis (TGA) of monomer **5** under nitrogen (Figure 1) confirms no weight loss during the cure reaction as expected in the formation of the triazine rings. Treatment of a sample in the TGA under a purge of air shows an intermediate weight reduction of ∼34% at ∼300 °C that is consistent with loss of the POSS-alkyl groups, and then after ∼2 h at 600 °C, complete conversion to SiO_2 is nearly quantitative.[16] Both infrared and NMR spectroscopic analysis of the cured materials show a complete disappearance of the signals associated with the cyanate ester group.[17] Furthermore, silicon-29 NMR spectroscopic data of the thermally cured material reveals two very sharp and strong signals at δ 67.5 and 67.8 ppm that are virtually identical to the starting monomer **5**.

We have carried out the thermal curing of **5** at a variety of temperatures and monitored progress of the reaction using size exclusion chromatography (SEC). A plot of the data for reaction time vs M_n is shown in Figure 2. Although at higher temperature the cure is discernibly faster, it is evident that in a matter of minutes even at 170 °C the reaction is nearly complete and the molecular weight becomes quite stable in a short time period. Furthermore, the polydispersity (1.4−1.6) we measure is quite narrow at the higher reaction temperatures (230 and 250 °C), especially for a polymerization reaction that is well-known to form extensive 3-dimensional hyper-cross-linked networks.[15]

Further support for a compact and discrete nanostructure of limited molecular weight for the thermally cured **5** is revealed by viscosity measurements.[18] Plots of relative viscosity (η_{rel}) for the POSS cyanate ester monomer **5** and the thermally cured polymer as a function of concentration in hexanes are shown in Figure 3. Despite the relatively high concentrations used, the relative viscosities measured remain low, even for the polym-

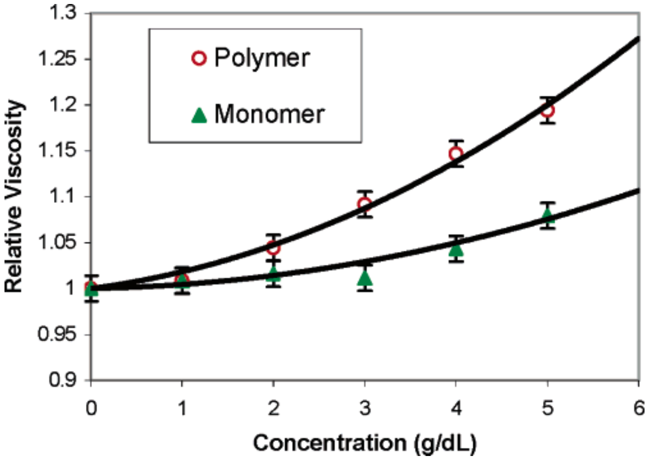


Figure 3. Relative viscosity of monomer **5** and cured polymer (i.e., *POSS-nanoplanets*, formed at 210 °C) in hexanes at 19.5 °C.

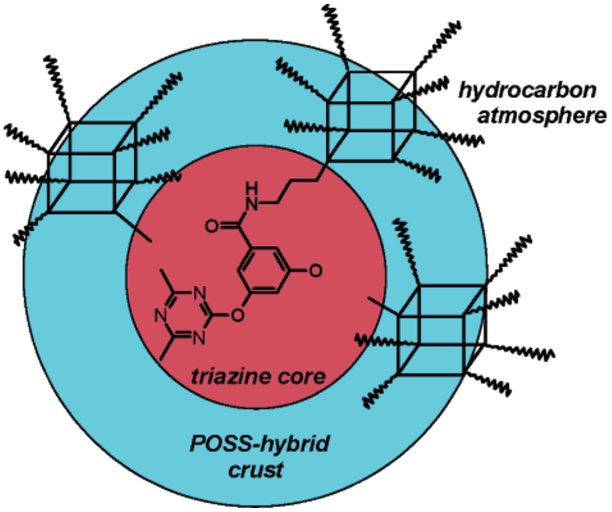


Figure 4. Drawing that illustrates the chemical makeup for *POSS-nanoplanets*.

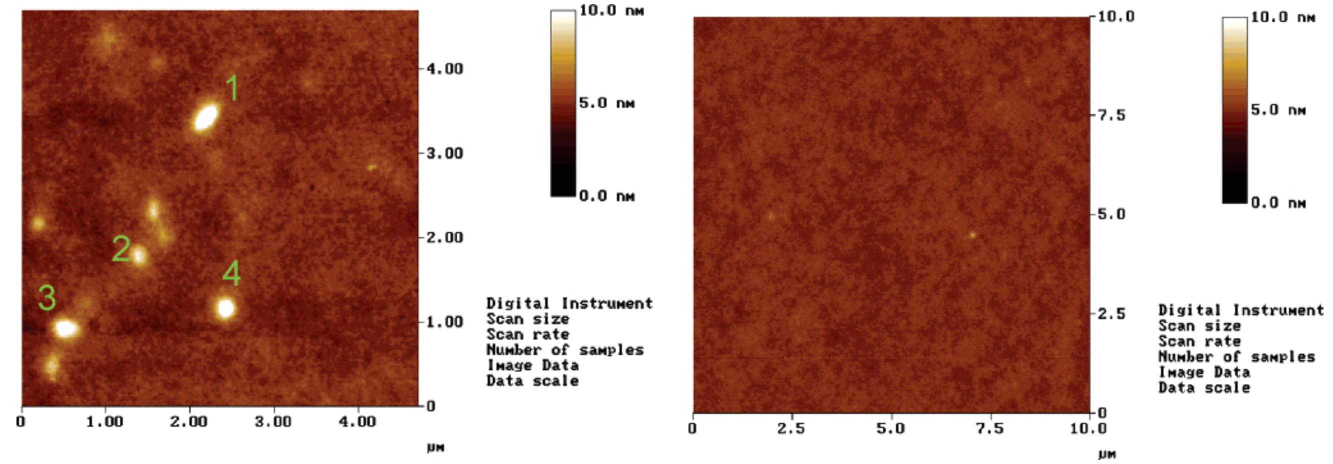


Figure 5. Physical characterization of the *POSS-nanoplanets* by tapping mode AFM on the left. Picture on the right is a scan of a prepared blank slide.

erized system. The extrapolated intrinsic viscosities were 0.012 ± 0.003 and 0.005 ± 0.002 dL/g for polymer and monomer **5**, respectively. Using the universal constant Φ at a value of 2.5 $\times$ 10^{21} (dL/mol) cm^3,[19] the observed intrinsic viscosities are consistent with a size on the order of ~1 nm for the monomer **5** and ~5 nm (for a hypothetical polymerization of 18) for the cured material in hexanes.

For POSS-systems that are substituted at one corner, that is monotethered, there exist a number of examples where distinct phase separation has been noted.[8a,9] For monomer **5**, it appears to favor a micellar-like structure that is thermodynamically driven by the very distinctive (i.e., amphiphilic) chemical nature of the dipolar cyanate ester−benzamide group and the very hydrocarbon-like character of the seven isobutyl groups. The difference in size of the groups dictates that the cyanate esters will be directed to the core of a micelle. This results in a very high effective concentration of the cyanate ester groups and may also provide some degree of preorganization for the subsequent trimerization reaction. This may account for the accelerated cure that was mentioned above. A theoretical reaction of 18 units of **5** can produce a core with reasonable geometry and complete reaction of the cyanate ester groups. Using an amorphous density of 20 Å^3 for non-hydrogen atoms, an 18-mer would have a cyanate ester resin core diameter of ~2.4 nm and a surface area of ~16 nm^2 (Figure 4). The core surface area can easily accommodate the "footprint" of 18 POSS molecules to form a hybrid "crust." The surface of the spherical structure is dominated by the iso-butyl groups. With this unique three-layer architecture we are proposing to call these new macromolecular structures *POSS-nanoplanets.* Our SEC data with a polydispersity of 1.4−1.6 for the samples clearly show we do not prepare a monodisperse *POSS-nanoplanet*, but rather, we in fact do isolate systems that contain more and less POSS units. Having a spherical-like structure also makes SEC polydispersity data less sensitive to changes in molecular weight. Hence, it is very likely we have an array of similar spherical-like architectures that are induced by the strong amphiphilic nature of monomer **5**.

To provide further physical characterization of the *POSS-nanoplanets* we have examined the structures using atomic force microscopy (AFM) in the tapping mode.[20] A cyclohexane solution of the *POSS-nanoplanets* was placed on a glass slide and the solvent evaporated by spinning at 1000 rpm. The slide surface is analyzed using AFM and the results are shown in Figure 5.[20] The AFM in the tapping mode shows the *POSS-nanoplanets* form aggregates on the surface. The height of these islands is measured at ~5 nm. These data are consistent with the proposed structure for the *POSS-nanoplanet*. The image on the right side of Figure 5 shows a background check for the slide preparation and AFM operation.

In conclusion, we have prepared a new mono-tethered and functionalized POSS monomer that reacts under thermal curing to afford robust and discrete micelle-like structures that we have denoted as *POSS-nanoplanets*. The unique structures have a defined core of cured cyanate ester resin, a "crust" largely consisting of the Si_8O_{12} inorganic cages, and an "atmosphere" that is dominated by the hydrocarbon isobutyl chains. Although similar types of nanospherelike structures have been reported using block polymers[21] and dendrimeric structures,[22] the simplicity and thermal processing for creating the hybrid *POSS-nanoplanets* is quite unique. Work continues to uncover how one can control the size of the *POSS-nanoplanets*, and we are exploring the inclusion of guest molecules of interest in the core during the thermal cure cycle.

Acknowledgment. M.E.W. and A.J.G. would like to thank the Office of Naval Research for funding of this work through the ILIR program. The authors would also like to thank Mr. Dan Bliss for his work in collecting the SEC data.

Supporting Information Available: Text giving complete experimental details and spectroscopic data and figures showing tapping-mode AFM, FT-IR of a film showing the loss of the cyanate ester peak, and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199−235. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409−1430. Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−2236. Lichtenhan, J. In *Polymeric Materials Encyclopedia*; Salomone, J. C., Ed.; CRC Press: New York, 1996; Vol. 10; pp 7768−7777. Provatas, A.; Matisons, J. G. *Trends Polym. Sci.* **1997**, *5*, 327−333. Laine, R. M. *J. Mater. Chem.* **2005**, *15*, 3725−3744 and references cited therein.

(2) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422 and references cited therein.

(3) For a compilation of papers that provide a broad overview of activity in the area of POSS materials see: *Inorganic Hybrid Materials*; Klein, L., De Guire, M., Lorraine, F., Mark, J., Eds.; MRS Symposium Series 576; Materials Research Society: Warrendale, PA, 1999. Neumann, D.; Fisher, M.; Tran, L.; Matisons, J. G. *J. Am. Chem. Soc.* **2002**, *124*, 13998−13999.

(4) For a recent application of such highly charged POSS-materials, see: Frankamp, B. L.; Fischer, N. O.; Hong, R.; Srivastava, S.; Rotello, V. M. *Chem. Mater.* **2006**, *18*, 956−959.

(5) Fu, B. X.; Hsiao, B. S.; White, H.; Rafailovich, M.; Mather, P.; Joen, H. G.; Phillips, S.; Lichtenhan, J.; Schwab, J. *Polym. Int.* **2000**, *49*, 437−440. Fu, B. X.; Zhang, W.; Hsiao, B. S.; Rafailovich, M.; Sokolov, J.; Johansson, G.; Sauer, B. B.; Phillips, S.; Blanski, R. *High Performance Polym.* **2001**, *12*, 565−571 and references cited therein.

(6) Feher, F. J.; Budzichowski, T. A.; Blanski, R. L.; Weller, K. J.; Ziller, J. W. *Organometallics* **1991**, *10*, 2526.

(7) Chandrasekhar, V.; Boomishankar, R.; Nagendran, S. *Chem.. Rev.* **2004**, *104*, 5847−5910 and references cited therein.

(8) (a) Kim, K.-M.; Keum, D.-K.; Chujo, Y. *Macromolecules* **2003**, *36*, 867−875. (b) Baker, E. S.; Gidden, J.; Anderson, S. E.; Haddad, T. S.; Bowers, M. T. *Nano. Lett.* **2004**, *4*, 779−785. (c) Kopesky, E. T.; Haddad, T. S.; Cohen, R. E.; McKinley, G. H. *Macromolecules* **2004**, *37*, 8992−9004. (d) Wright, M. E.; Petteys, B. J.; Guenthner, A. J.; Fallis, S.; Yandek, G. R.; Tomczak, S. J.; Minton, T. K.; Brunsvold, A. *Macromolecules* **2006**, *39*, 4710 and references cited therein.

(9) For selected examples of polymeric materials, see: Zheng, L.; Hong, S.; Cardoen, G.; Burgaz, E.; Gido, S. P.; Coughlin, E. B. *Macromolecules*, **2004**, *37*, 8606−8611. Cardoen, G.; Coughlin, E. B. *Macromolecules*, **2004**, *37*, 5123−5126 and references cited therein. Also see ref 8a of this paper.

(10) Jeoung, E.; Carroll, J. B.; Rotello, V. M. *Chem. Commun.* **2002**, 1510−1511. Carroll, J. B.; Frankamp, B. J.; Rotello, V. M. *Chem. Commun.* **2002**, 1892−1893.

(11) A similar sequence to prepare compound **2** has been reported: Tetsuji, K.; Shinzo, K. *Yakugaku Zasshi* **1962**, *82*, 1059−1062; *Chem. Abs.* **1962**, *58*, 4537f). Yields obtained in the present procedure are much higher (98% for both steps), simplified, and afford analytically pure material (mp 211−212 °C, lit. mp 209−211 °C).

(12) Typically 10 wt % of catalyst (5 wt % of palladium on carbon) is employed using THF as solvent and ∼2 psig of a hydrogen atmosphere.

(13) Selected data for **4**: mp 192 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 6.82 (br s, 2H), 6.49 (br s, 1H), 6.20 (br t, 1H, NH), 3.51−3.35 (m, 2H), 1.91−1.75 (septant, 7H), 1.73−1.62 (m, 2H), 0.94 (d, 42H), 0.71−0.62 (m, 2H), 0.60 (dd, 14H).

(14) Selected data for **5**: ^{1}H NMR ($CDCl_3$) 7.70 (d, $J = 2.4$ Hz, 2H, $H_{aromatic}$), 7.40 (t, $J = 2.4$ Hz, 1H, $H_{aromatic}$), 6.16 (broad t, $J = 5.1$ Hz,1H, NH), 3.47 (m, 2H, $NCH_2CH_2CH_2$), 1.85 (m, 7H, $SiCH_2CH(CH_3)_2$), 1.74 (m, 2H, $NCH_2CH_2CH_2$), 0.95 (d, $J = 6.7$ Hz, 42H, $SiCH_2CH(CH_3)_2$), 0.67 (m, 2H, $NCH_2CH_2CH_2$), 0.60 (m, 14H, $SiCH_2CH(CH_3)_2$; ^{29}Si NMR ($CDCl_3$) -67.5, -67.8, -68.1. Anal. Calcd for $C_{40}H_{73}N_3O_{15}Si_8$: C, 45.29; H, 6.94. Found: C, 45.01; H, 6.99.

(15) Hamerton, I. *Chemistry and Technology of Cyanate Ester Resins*; Blackie Academic, Glasgow, Scotland, 1994.

(16) Thermogravimetric analysis of cured *nanoplanet* samples under an atmosphere of air showed a distinct weight loss/cleavage of the organic groups (i.e. atmosphere) at ∼300 °C and then a higher temperature (∼400−500 °C) event the cyanate ester core depolymerized/decomposed. After the sample is heated to 800 °C, a pure white solid is obtained that contains virtually no carbon (elemental analysis showed less than 0.1%), and the residue weight is always consistent with formation of SiO_2.

(17) The infrared absorption peak for the cyanate ester groups at ∼2250 cm^{-1} disappear (FT-IR in Supporting Information) and are replaced by absorbance bands corresponding to the triazine ring near 1370 and 1505 cm^{-1} after cure.

(18) Macosko, C. W. *Rheology: Principles, Measurements, and Applications*; Wiley-VCH, Inc.: New York, 1994; Chapter 11.

(19) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley & Sons: New York, 1992.

(20) TM-AFM images were obtained with a Digital Instruments Model DI3100 AFM operating in the tapping mode.

(21) Iijima, M.; Nagasaki, Y.; Okada, T.; Kato, M.; Kataoka, K. *Macromelecules* **1999**, *32*, 1140−1146.

(22) Joralemon, M. J.; O'Reilly, R. K.; Hawker, C. J.; Wooley, K. L *J. Am. Chem. Soc.* **2005**, *127*, 16892−16899 and references cited therein.

MA0703507