JOURNAL OF
Materials
CHEMISTRY

Grafting of dendritic polyethers onto nanometre silica surface

Zhao-Xia Guo and Jian Yu*

Institute of Polymer Science and Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. E-mail: yujian@chemeng.tsinghua.edu.cn

Received 3rd August 2001, Accepted 18th December 2001
First published as an Advance Article on the web 25th January 2002

Frechet-type polyether dendrons bearing COOH groups at the focal points have been grafted onto nanometre silica premodified with 3-aminopropyltriethoxysilane by *N*,*N*′-dicyclohexylcarbodiimide mediated amidation. The dendron grafted silicas have been characterized by FTIR spectroscopy, elemental analysis and thermogravimetric analysis (TGA). The percentages of net grafting were 4–16% (thus the percentages of total grafting were 11–23%), as determined by TGA and elemental analysis, suggesting that 4–19% of the total amino groups were involved in amidation. The effects of solvent, catalyst and generation number have also been studied.

Introduction

Nanometre silica has attracted increasing attention for its superior properties over conventional micrometre particles.[1] It has been widely used as a filler in the manufacture of paints, rubber, plastics, binders, functional fibers, anti-virus materials and so on. However, its agglomeration and incompatibility with the organic matrix are impeding problems which limit its efficient use. It is known that surface modification by grafting of polymers or other organic molecules onto nanometre silica is an effective way to improve its dispersibility in an organic matrix or solvents and its compatibility with the matrix, thus enhancing the properties of the composite materials.[2,3]

Because of the wide use of functionalized silica materials in chromatographic applications, as support for heterogeneous catalysts, and for immobilization of bioactive compounds *etc.*, surface modification of silica has been extensively studied.[4–6] Most procedures are based on the use of the reaction of silanol groups, involving mainly treatments with silane reagents and graft polymerizations.[4]

Dendrimers have a well controlled three-dimensional structure with a high degree of branching and a large number of functional groups on the surface that can be easily designed according to need. These unique topological features make dendrimers good candidates for the surface designing of inorganic nanometre silica. Polyamidoamine (PAMMA) dendrimer has been grafted onto a nanometre silica surface using the divergent approach leading to improved dispersibility in methanol.[7] Studies[8,9] have shown that PAMMA grafted silicas could be complexed to rhodium and palladium, being useful as effective catalysts for hydroformylation and Heck reaction. When PAMMA dendrimer was used to modify porous silica,[10] the pore-size distribution could be controlled by the generation number. As to the convergent approach, first and second generation polyether dendrons have been used to modify the inner wall of fused silica capillary columns using 3-(triethoxysilyl)propyl isocyanate as the anchoring agent,[11] and the dendritic coatings have shown to be more effective than linear alkane coatings for suppressing the electroosmotic flow. Other related work[12–14] concerning covalent bonding of dendrimers to inorganic surfaces involved different types of reactions and first generation dendrons only. Recently, it has been reported that chiral dendrimers with peptide linkages have been immobilized on silica,[15] forming a new class of chiral stationary phases for use in HPLC.

The present study deals with grafting of Frechet-type polyether dendrimers[16,17] onto a nanometre silica surface using the convergent approach. As *N*,*N*′-dicyclohexylcarbodiimide (DCC) mediated esterification and amidation are common reactions in organic synthesis, and have been successfully used for grafting of active groups and polymers bearing OH and NH_2 groups at the chain ends onto a carbon black surface (which has carboxy groups),[18,19] and there are a large number of silanol groups on the silica surface, we thus considered grafting dendritic polyether using DCC as the condensing agent. Model studies[20] with stearic acid have shown that no reaction occurred when bare silica was used, but significant grafting was obtained with 3-aminopropyltriethoxysilane (APS) modified silica. This indicates that the reactivity of surface groups was increased by converting silanol groups into amino groups. Therefore, in this study, DCC mediated amidation is used to couple polyether dendrons bearing COOH groups at their focal points[21,22] to the multifunctional inorganic APS functionalized silica core (Scheme 1).

Experimental

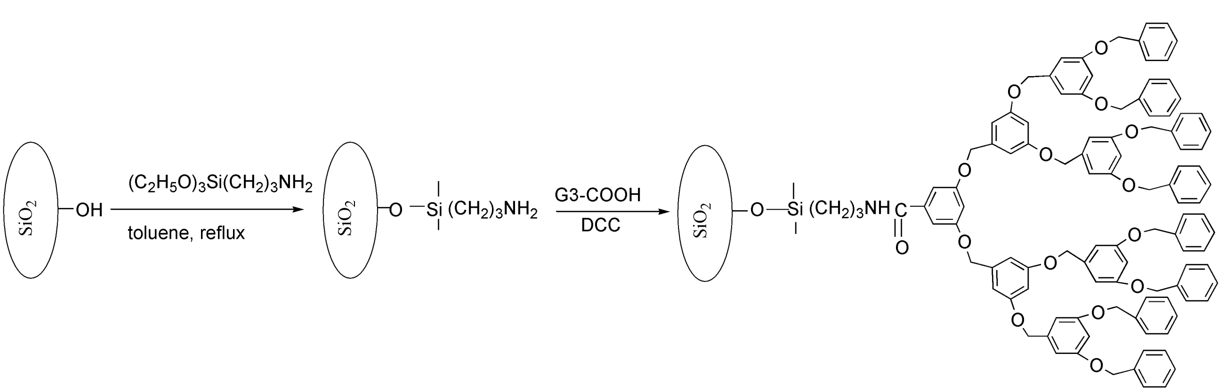
Materials and reagents

Nanometre silica (type MN1S) was from Zhoushan-Mingri company (China) with a mean particle size of 15 nm and a specific surface area of 160 $m^2\ g^{-1}$. It was dried *in vacuo* at 110 °C for 6 h before use. DCC and APS were used as received. Toluene and dichloromethane were dried over 4 Å molecular sieves and distilled. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Polyether dendrons (G1, G2 and G3) bearing COOH groups at the focal points were synthesized according to published procedures[21–23] with some modifications as shown in Scheme 2.

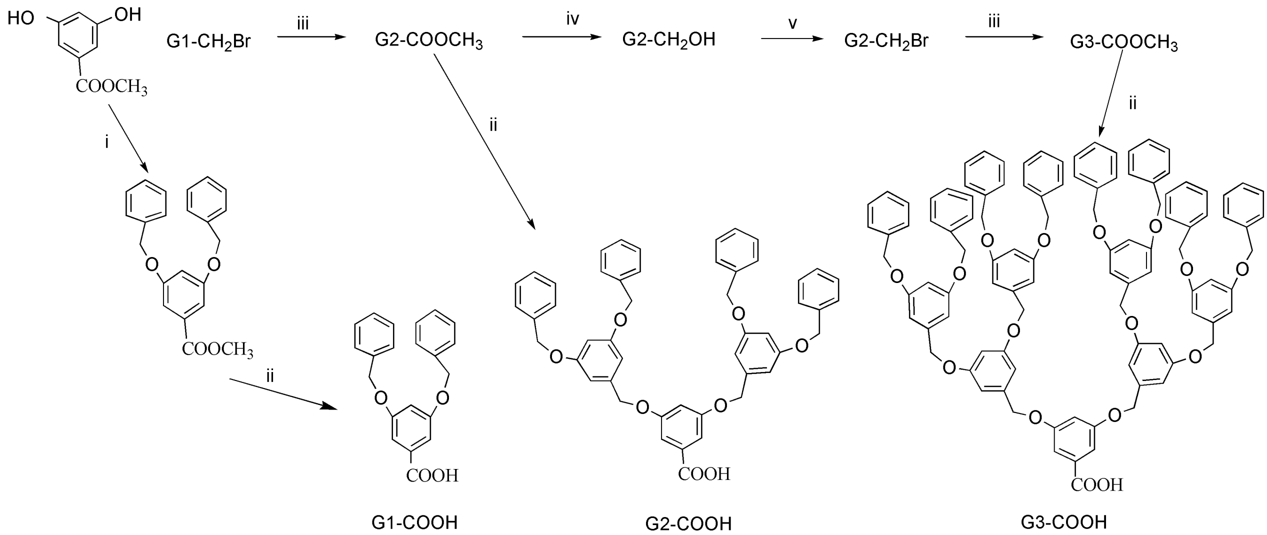
Functionalization of silica with APS

Functionalization of silica by converting most of the surface silanol groups into amino groups was carried out following a slightly modified literature procedure[7] as follows. To a stirred suspension of dried silica (5 g) in dry toluene (100 ml) under nitrogen was added dropwise over 25 min a solution of APS (7.5 g) in dry toluene (30 ml). The mixture was refluxed for 8 h under nitrogen. After cooling to room temperature, it was suction filtered and washed with toluene, then extracted with toluene in a Soxhlet apparatus for 8 h. The functionalized silica

DOI: 10.1039/b107032k



Scheme 1 Illustration of the grafting of polyether dendron G3 onto APS functionalized silica surface.



Scheme 2 The synthesis of polyether dendrons. *Reagents and conditions*: (i) BnBr, acetone, K_2CO_3, reflux; (ii) KOH, 18-crown-6, 95% ethanol, reflux; (iii) methyl 3,5-dihydroxybenzoate, K_2CO_3, 18-crown-6, acetone, reflux; (iv) KBH_4, LiCl, THF, reflux; (v) CBr_4, PPh_3, CH_2Cl_2, 0 °C.

was dried *in vacuo* at 100 °C for 6 h and stored in a desiccator over P_2O_5.

The amount of amino groups introduced onto the silica surface was 1.08 mmol g^{-1} (functionalized silica), as determined by elemental (nitrogen) analysis, corresponding to 1.17 mmol g^{-1} (bare silica). The percentage of grafting contributed by this functionalization step was described as silane grafting and defined as follows:

$$\text{Silane grafting}(\%) = \frac{\text{Organic composition/g}}{\text{Bare silica/g}} \times 100$$

The amount of organic composition introduced by APS functionalization was calculated from the TGA weight loss data (6.93%) obtained between 150 °C and 700 °C. Thus, silane grafting was calculated to be 7.4%.

Grafting of dendritic polyether onto silica nanoparticles

For reactions carried out at room temperature (rt): polyether dendron (1 equiv.) was dissolved in dichloromethane (10 ml) under nitrogen. DMAP (26 mg, 1 equiv.) and functionalized silica (200 mg, 0.22 mmol) were added, followed by the addition of DCC (89 mg, 2 equiv.). The mixture was stirred at rt overnight. Then, it was suction filtered and washed with dichloromethane and hot THF. The product was purified by Soxhlet extraction with THF until the amount of grafting was constant, as determined by TGA (50 h usually sufficient).

For reactions performed at reflux: a mixture of polyether dendron (1 equiv.), DMAP (26 mg, 1 equiv.), functionalized silica (200 mg, 0.22 mmol) and DCC (89 mg, 2 equiv.) in dichloromethane (20 ml) was refluxed under nitrogen for 6 h, then worked out and purified as described above.

The percentages of the overall grafting and net grafting of polyether dendrons were calculated by the following equations:

$$\text{Overall grafting}(\%) = \frac{\text{Overall Organic composition/g}}{\text{Bare silica/g}} \times 100$$

$$\text{Net grafting}(\%) = \text{Overall grafting}(\%) - \text{Silane grafting}(\%)$$

The amount of overall organic composition was calculated from TGA data similarly to the functionalization step mentioned above on taking into account that polyether dendrons G2 and G3 were not fully thermalized at 700 °C (as shown in Fig. 4).

Grafted G*n* (mmol g^{-1}) was defined as the number of grafted G*n* (in mmol) per gram of bare silica, and calculated from the net grafting and the molecular weight of G*n* as follows:

$$\text{Grafted G}n/(\text{mmol}\,\text{g}^{-1}) = \frac{\text{Net grafting}}{\text{M} - 17} \times 1000$$

where 17 is the weight of OH which the acid loses during amidation.

The percentage of reacted NH_2 was defined as the number of amino groups reacted in the amidation step to the initial amino group of APS functionalized silica (1.17 mmol g^{-1}), and calculated by the following equation:

$$\text{Reacted NH}_2(\%) = \frac{\text{Grafted G}n}{1.17} \times 100$$

For comparative study, the percentage of net grafting was also calculated from elemental (carbon) analyses of the products before and after the grafting of dendritic polyether.

Characterization

FTIR spectra in KBr pellets were recorded on a Nicolet 560 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a TA 2050 instrument with a heating rate of 10 °C min^{-1} in flowing N_2, and a sample of 3–8 mg. Elemental analyses were performed on a Elementar Vario EL (Germany) analyzer.

Results and discussion

Characterization of dendritic polyether grafted silicas by FTIR

Fig. 1 shows FTIR spectra of second generation dendron G2, G2 grafted silica and APS functionalized silica. Compared to the spectrum of APS functionalized silica, G2 grafted silica showed new peaks at 1600, 1450, 3060, 3050 cm^{-1} which are characteristic peaks of aromatics found in the spectrum of G2, indicating grafting of G2 onto APS functionalized silica. The absence of the acid peak at 1700 cm^{-1} indicated that G2 was involved *via* reaction at the acid group. The amino group peak at 1627 cm^{-1} in the spectrum of APS functionalized silica has shifted to 1635 cm^{-1} in the spectrum of G2 grafted silica, implying the formation of an amide group. This shift is clearer (to 1651 cm^{-1}) when an aliphatic carboxylic acid (stearic acid) was used for amidation of APS functionalized silica, as shown in Fig. 2.

It is known that the by-product, *N*,*N*′-dicyclohexylurea, formed by DCC mediated amidation is hardly soluble in common organic solvents. When Tsubokawa *et al.*[19] grafted polymers bearing hydroxy groups onto a carbon black surface (which had carboxy groups) using DCC as the condensing agent, *N*,*N*′-dicyclohexylurea was completely removed by Soxhlet extraction of the crude product with THF, as indicated by the absence of nitrogen from the elemental analysis of the final products. In this work, APS modified silica contained nitrogen, and the nitrogen content usually decreased slightly after grafting of dendritic polyethers. In combination with the results from TGA (constant weight loss) and IR (no obvious increase of the characteristic peaks of CH_2 at 2900, 2950 cm^{-1}), it can be concluded that *N*,*N*′-dicyclohexylurea has been removed by Soxhlet extraction with THF.

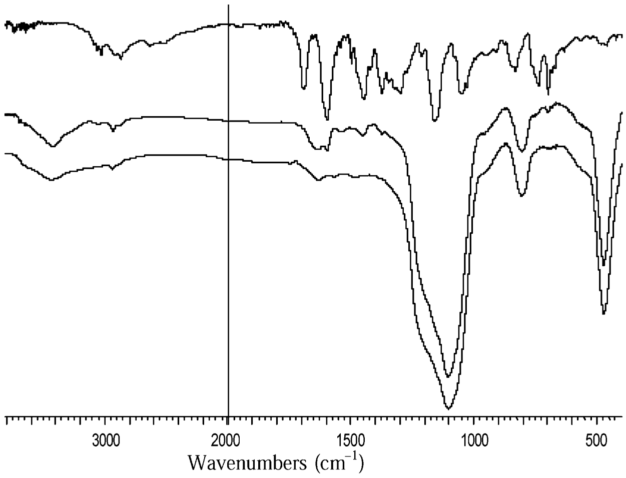


Fig. 1 FTIR spectra of polyether dendron G2 (top line), G2 grafted silica (sample Entry 4, middle line) and APS functionalized silica (bottom line).

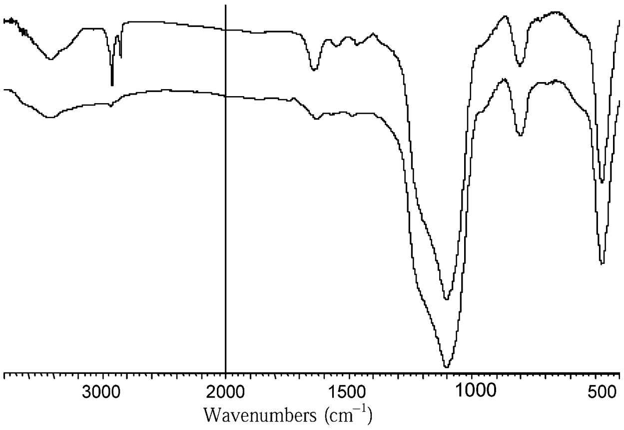


Fig. 2 FTIR spectra of stearic acid grafted silica (top line) and APS functionalized silica (bottom line).

Quantification of overall grafting by TGA

Fig. 3 shows TGA diagrams of original silica, APS functionalized silica and dendritic polyether G2 grafted silica. The weight loss of APS functionalized silica was mainly between 300 °C and 600 °C. The dendritic polyether G2 grafted silica showed two distinct weight loss regions: one rapid decomposition between 300 °C and 400 °C with the maximum rate of weight loss at 369 °C, and one relatively slow weight loss region between 400 °C and 700 °C. The above described thermal behavior of polyether G2 grafted silica was similar to that of polyether G2 (Fig. 4), implying that the weight loss between 300 °C and 700 °C found in TGA diagram of polyether G2

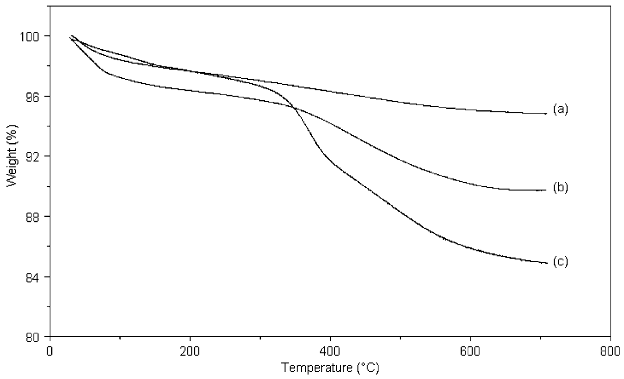


Fig. 3 TGA diagrams of (a) original silica, (b) APS functionalized silica and (c) polyether dendron G2 grafted silica (sample Entry 4).

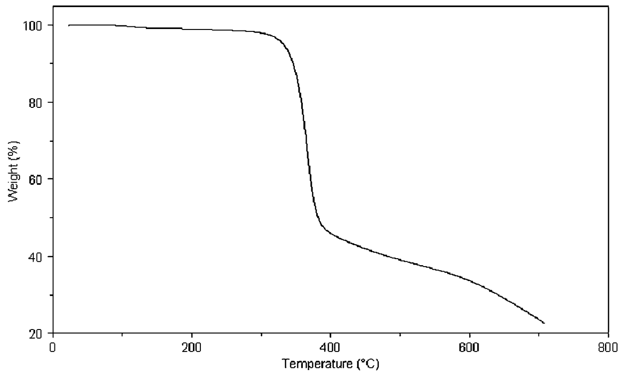


Fig. 4 TGA diagram of polyether dendron G2.

Table 1 Effects of solvent and catalyst on grafting[a]

Entry	Solvent	DMAP (eq)	Grafting (%) overall/net	Grafted G*n*/mmol g^{-1}	Reacted NH_2 (%)	C/Net grafting[b] (%)/(%)
1	THF	0	10.8/3.4	0.05	4	6.86/3.0
2	THF	1	15.0/7.6	0.10	9	10.48/8.8
3	CH_2Cl_2	0	17.0/9.6	0.13	11	11.64/10.8
4	CH_2Cl_2	1	17.9/10.5	0.14	12	11.69/10.9

[a]Reaction conditions: with G2, at rt. [b]Calculated from carbon content.

Table 2 Grafting of three generation dendrons onto APS functionalized silica

Entry	Solvent/temperature	G*n*	Grafting (%)[a] overall/net	Grafted G*n*/ mmol g^{-1}	Reacted NH_2 (%)	C/Net grafting[b] (%)/(%)
5	THF/rt	G1	13.9/6.5	0.20	17	9.62/7.4
2	THF/rt	G2	15.0/7.6	0.10	9	10.48/8.8
6	THF/rt	G3	16.1/8.7	0.05	4	9.51/7.2
7	CH_2Cl_2/rt	SA[c]	19.5/12.1	0.45	38	12.40/11.9
4	CH_2Cl_2/rt	G2	17.9/10.5	0.14	12	11.69/10.9
8	CH_2Cl_2/rt	G3	16.5/9.1	0.06	5	10.18/8.3
9	CH_2Cl_2/reflux	G1	13.3/5.9	0.19	16	10.48/8.8
10	CH_2Cl_2/reflux	G2	23.7/16.3	0.22	19	13.21/13.6
11	CH_2Cl_2/reflux	G3	21.5/14.1	0.09	8	12.71/12.7

[a]Determined by means of TGA. [b]Calculated from carbon content. [c]SA: stearic acid.

grafted silica was originated from the organic composition of APS functionalized silica and grafted G2.

All dendritic polyether grafted silicas showed TGA curves similar to that shown in Fig. 3. As shown in Table 1 and 2, the overall grafting was 11–23%, thus the net grafting was 4–16%, corresponding to 0.05–0.22 mmol of G*n* per g of bare silica, suggesting that 4–19% of total amino groups were involved in amidation.

Characterization of polyether grafted silicas by elemental analyses

The original silica did not contain any carbon. After functionalization with APS, the carbon content was 4.84%, indicating the introduction of an organic composition onto the silica surface. The carbon content increased dramatically after grafting of dendritic polyethers onto the silica surface, as shown in Table 1 and 2. For example, for Entry 4, the polyether grafted sample contained 11.69% of carbon, with an increase of 6.85% compared to APS functionalized silica (4.84%); the net grafting for this amidation step calculated from the carbon content was 10.9%, a value comparable with that calculated from TGA (10.5%). For samples in Table 1 and 2, the net grafting values calculated from the carbon contents of APS functionalized silica and of the polyether grafted silicas were basically in line with the results obtained by TGA. Thus, the elemental analyses provided complementary evidence for the grafting of dendritic polyethers and can serve as an alternative method to TGA for the estimation of net grafting.

Effects of solvent and catalyst

Table 1 shows the results of grafting dendritic polyether G2 onto APS functionalized silica using different solvents (THF or dichloromethane) in the absence or presence of DMAP (catalyst). The amount of grafting was larger in dichloromethane than in THF, especially in the absence of DMAP. The use of DMAP gave slightly better grafting in dichloromethane, but with significant improvement in THF.

Effect of generation number

The effect of generation number under three different sets of reaction conditions is listed in Table 2. It was shown that the percentages of grafting were similar for all three generations (G1, G2 and G3) under the same reaction conditions, with Entry 9 being an exception. The low reactivity found with G1 in Entry 9 was rather surprising, and was probably because G1 was not very soluble in dichloromethane. If the number of reacted G*n* or the percentage of reacted NH_2 was compared, a decreasing tendency was shown as the generation number increased. This implied that the reactivity of higher generation number dendrons was reduced by steric hindrance and larger molecular weight. Compared to the linear aliphatic stearic acid (Entry 7), the reactivity of dendritic acids towards DCC mediated amidation was much lower because of the steric hindrance provided by the branching. This is in agreement with the observation of Woo *et al.*[14] in their work concerning the anchoring of hyperbranched silane coupling agents on the surface of magnetic particles.

It is noteworthy that a rise in temperature to refluxing (in dichloromethane) gave better grafting. Also, the surface properties of the dendron grafted silicas have changed dramatically. Unlike the original silica, the dendritic polyether grafted silicas were completely hydrophobic, they float on water and easily disperse in organic solvents such as THF, dichloromethane *etc.*

Conclusion

Dendritic polyether has been successfully grafted onto nanometre silica under mild conditions using DCC mediated amidation. It was found that dichloromethane gave slightly better grafting than THF, and the use of DMAP increased to some degree the grafting. Refluxing in dichloromethane increased grafting, compared to room temperature reactions. The percentages of net grafting were similar for all three generations studied, but the number of grafted dendritic molecules tended to decrease as the generation number increased. The dendritic polyether grafted silicas were completely hydrophobic, and could be potentially useful, for example, as a functional filler.

Acknowledgement

We are grateful to China Postdoctoral Science Foundation and Tsinghua-Zhongda Postdoctoral Science Foundation for financial support.

References

1 *Handbook of nanostructured materials and nanotechnology*, ed. H. S. Nalwa, Academic Press, San Diego, 2000.

2 E. Bourgeat-Lami, P. Espiard, A. Guyot, C. Gauthier, L. David and G. Vigier, *Angew. Makromol. Chem.*, 1996, **242**, 105.

3 S. Hayashi, Y. Takeuchi, M. Eguchi, T. Iida and N. Tsubokawa, *J. Appl. Polym. Sci.*, 1999, **71**, 1491 and references therein.

4 S. Spange, *Prog. Polym. Sci.*, 2000, **25**, 781.

5 B. R. Guidotti, E. Herzog, F. Bangerter, W. R. Caseri and U. W. Suter, *J. Colloid Interface Sci.*, 1997, **191**, 209.

6 B. Nitzan and S. Margel, *J. Polym. Sci. Part A: Polym. Chem.*, 1997, **35**, 171.

7 N. Tsubokawa, H. Ichioka, T. Satoh, S. Hayashi and K. Fujiki, *React. Funct. Polym.*, 1998, **37**, 75.

8 S. C. Bourque, F. Maltais, W. J. Xiao, O. Tardif, H. Alper, P. Arya and L. E. Manzer, *J. Am. Chem. Soc.*, 1999, **121**, 3035.

9 H. Alper, P. Arya, S. C. Bourque, G. R. Jefferson and L. E. Manzer, *Can. J. Chem.*, 2000, **78**, 920.

10 K. Sakai, T. C. Katada, T. Harada, S. Uemura, Y. Asami, M. Sakata, M. Kunitake and C. Hirayama, *Chem. Lett.*, 2001, 510.

11 H. Chao and J. E. Hanson, *Polym. Mater. Sci. Eng.*, 2000, **83**, 438.

12 R. S. Majerle, C. M. Bambenek and J. A. Rice, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1997, **38**(2), 690.

13 S. A. Henrie, P. F. Molitor and R. S. Majerle, *Polym. Mater. Sci. Eng.*, 1999, **80**, 318.

14 T. Woo, J. Y. Huh and D. E. Nikles, *Polym. Mater. Sci. Eng.*, 2000, **83**, 399.

15 B. T. Mathews, A. E. Beezer, M. J. Snowden, M. J. Hardy and J. C. Mitchell, *New J. Chem.*, 2001, **25**, 807.

16 C. Hawker and J. M. J. Frechet, *Chem. Commun.*, 1990, 1010.

17 C. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

18 N. Tsubokawa and M. Hosoya, *React. Polym.*, 1991, **14**, 95.

19 N. Tsubokawa, M. Hosoya and J. Kurumada, *React. Funct. Polym.*, 1995, **27**, 75.

20 Z. X. Guo, J. Yu and J. Yu, *Chin. Chem. Lett.*, 2001, **12**, 933.

21 M. Kawa and J. M. J. Frechet, *Chem. Mater.*, 1998, **10**, 286.

22 D. C. Tully, A. R. Trimble and J. M. J. Frechet, *Chem. Mater.*, 1999, **11**, 2892.

23 Z. Bo, X. Zhang, X. Yi, M. Yang, J. Shen, Y. Rehn and S. Xi, *Polym. Bull.*, 1997, **38**, 257.