ELSEVIER

Polymer 42 (2001) 6811–6815

polymer

www.elsevier.nl/locate/polymer

Controlled grafting of a well-defined polymer on a porous glass filter by surface-initiated atom transfer radical polymerization

M. Ejaz, Y. Tsujii, T. Fukuda*

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Received 29 January 2001; received in revised form 19 February 2001; accepted 2 March 2001

Abstract

The atom transfer radical polymerization (ATRP) technique using the copper halide/sparteine complexes was applied to the graft polymerization of methyl methacrylate on a porous glass filter on which the initiator, 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane, was immobilized by chemisorption. The graft chains were cleaved from the glass filter by the HF treatment in the presence of a phase transfer catalyst. Gel permeation chromatographic and infrared absorption spectroscopic measurements confirmed that the polymerization carried out in the presence of the free (sacrificing) initiator, *p*-toluenesulfonyl chloride, afforded a graft layer of well-controlled, low-polydispersity polymer on the inner surface of the porous glass filter. The number-average molecular weight (M_n) of the graft polymer increased with reaction time, and it was nearly equal to the M_n of the free polymer produced in the solution. The graft density on the inner surface of the porous glass filter was as high as those formed on a silicon wafer and a silica particle under similar conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; Polymer brush; Porous glass filter

---

1. Introduction

Due to a high surface area, porous materials are of specific interest in a wide range of applications for, e.g. adsorbents, solid supports for sensors and catalysts, low-dielectric materials for microelectronics devices, and membranes for separation and purification [1–7]. Porous materials equipped with responsibilities to chemical and physical stimuli such as pH, temperature, light and chemicals can provide a basis for the design and development of intelligent materials with such functions as ‘chemical gate’ [8–15]. Attempts have been made of grafting stimuli-responsive polymers and hence preparing a polymer-brush layer on the inner surface of porous materials. However, it is difficult to achieve, by conventional surface-initiated graft polymerization techniques, a high-density uniform graft layer (brush) of well-defined polymers on solid surfaces [16–21]. Recently, some living polymerization techniques were successfully applied to the surface-initiated graft polymerization to prepare a uniform dense polymer brush [22–33].

We succeeded in achieving a dense polymer brush on the surfaces of silicon wafer and silica particle by applying atom transfer radical polymerization (ATRP), one of living radical polymerization techniques see for example [34]: well-defined polymers successfully grafted by this surface-initiated ATRP include poly(methyl methacrylate) (PMMA) [24], polystyrene [25], and a glycopolymer [26] with a bulky side group. In addition to control of chain length and chain length distribution, this technique afforded exceptionally high graft densities. The properties of these high-density polymer brushes were quite different and unpredictable from those of the ‘moderately dense’ polymer brushes previously studied [35,36]. Thus, the application of this novel technique to porous materials would give a new route to the development of materials with sophisticatedly designed functions. The key question to be asked is whether the catalytic system governing the ATRP process effectively works even on the surfaces of small pores in these materials.

As a model system to study this, we attempt to carry out the graft polymerization of methyl methacrylate (MMA) on a porous glass filter with the ATRP initiator, 2-(4-chlorosulfonylphenyl) ethyltrichlorosilane (CTCS), immobilized on its inner surfaces (see Fig. 1). After the polymerization, the grafted polymers were cleaved from the surface by the HF treatment and directly characterized by gel permeation chromatography (GPC) to examine the degree of control achieved by this process.

---

* Corresponding author. Tel.: +81-774-38-3161; fax: +81-774-38-3170.
E-mail address: fukuda@scl.kyoto-u.ac.jp (T. Fukuda).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00192-6

2. Experimental

2.1. Materials

A porous glass filter disc (diameter, 65 mm; thickness, 5 mm; average pore diameter, 5 μm) was purchased from Sogo Laboratory Glass Works Japan. The scanning electron micrograph (Fig. 1) of the crashed surface of the glass filter suggests a broad distribution of pore size. Fig. 2 shows the pore size distribution as measured by Hg porosimetry (Poresizer 9310, Micromeritics Instrument, USA): it can be seen that the pore size ranges from one to a few tens of μm. The inner surface area as measured on a BET surface area analyzer (NOVA 1200, Quanta Chrome Instruments, USA) was $1 \pm 0.5\ \mathrm{m^2\,g^{-1}}$. A 50 wt% CTCS solution in dichloromethane was obtained from Gelest, USA and used as received. *p*-Toluenesulfonyl chloride (TsCl), copper bromide (CuBr, 99.0%), L-(−)-sparteine (Sp), aqueous HF solution (46%) and trioctylmethylammonium chloride (TOC) were purchased from Nacalai Tesque, Japan and used without further purification. MMA was obtained from Nacalai Tesque, Japan and distilled under reduced pressure over CaH_2 before use. Toluene (Nacalai Tesque, Japan) was distilled over CaH_2.

Unless otherwise specified, all other reagents were purchased from commercially available sources and used without purification.

2.2. Immobilization of initiator and graft polymerization

The glass filter was cut into small blocks measuring about $5 \times 5 \times 30\ \mathrm{mm^3}$, and treated with 0.1 M HNO_3 at 70°C for 3 h, washed with distilled water several times, and then dried in vacuum oven at 140°C for 6 h [13]. CTCS with a chlorosulfonylphenyl group, which is one of the best initiating groups for ATRP [37–39], was immobilized on the surface of the glass filter blocks by the self-assembled monolayer-deposition method; namely, the blocks were dipped in dry toluene containing ca. 6 wt% CTCS for 18 h, washed several times with toluene and finally with tetrahydrofuran (THF), and dried in vacuum.

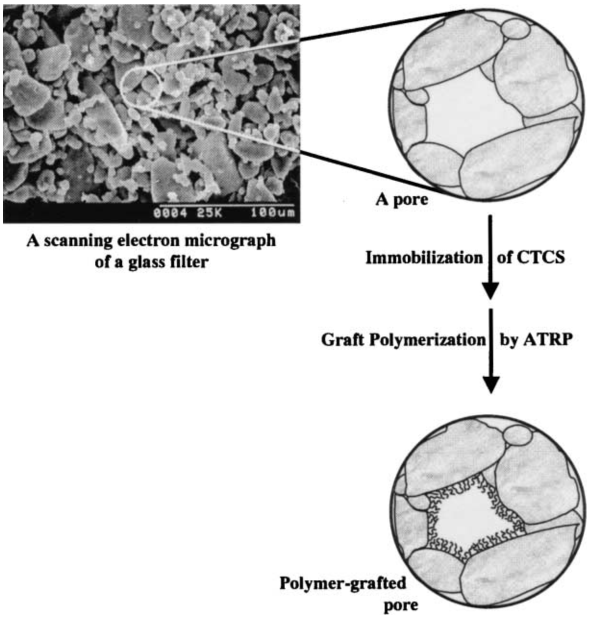

Fig. 1. Schematic illustration showing the control graft polymerization of MMA on the pore surfaces of a glass filter.

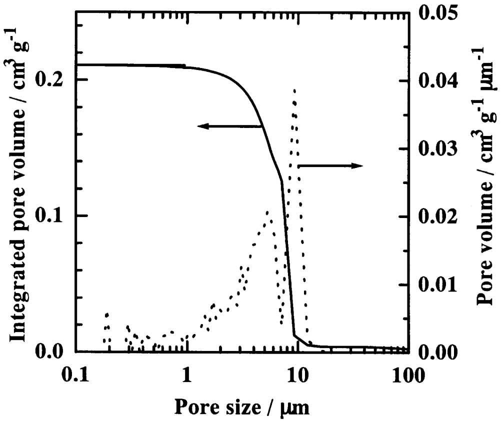

Fig. 2. Pore size distribution of glass filter estimated by Hg porosimetry.

The graft polymerization was carried out as follows; a degassed diphenyl ether solution of CuBr (0.03 M), Sp (0.06 M), MMA (5.0 M) and free initiator (TsCl, 5.0 mM), in which the CTCS-fixed glass filter block was dipped, was sealed in a glass tube under vacuum and heated for a prescribed period of time at 70°C. Sp is a ligand coordinating with Cu, providing a homogeneous ATRP system for MMA [40]. The free initiator was added to self-adjust the concentration of the Cu^{II} complex and to control the polymerization [24]. After polymerization, in order to efficiently remove ungrafted, physically adsorbed (free) polymers, the glass filter blocks were hammered into small pieces and washed by ultrasonication in toluene followed by centrifugation. This washing process was repeated until no free polymer was detectable in the supernatant solution by GPC.

2.3. Cleavage of the graft polymer from the glass filter

PMMA chains grafted on the glass filter were cleaved as follows; 500 mg of the solid (the washed glass filter pieces) was vigorously stirred in a poly(ethylene) flask containing 3.5 ml of toluene, 3.5 ml of 20 wt% aqueous HF solution and 2 wt% TOC as a phase transfer catalyst [31]. After ca. 4 h, the aqueous layer was removed, and 3.5 ml of 5% aqueous HF solution containing 1.6 wt% of TOC was added and stirred for further 2 h. The organic layer containing cleaved polymers was washed with aqueous $NaHCO_3$ solution and water, filtered to remove solid impurities, and then subjected to the GPC measurements.

2.4. Measurements

Monomer conversion and the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the free polymer produced in the solution and those of the graft polymer cleaved from the glass filter were determined by PMMA-calibrated GPC (8010 high-speed liquid chromatograph, Tosoh, Japan). THF was used as eluent, and the temperature was maintained at 40°C. Sample detection and quantification were made with a Tosoh refractive-index detector, RI-8020. For Fourier transform infrared absorption (IR) spectroscopy (KBr pellet), a BioRad FTS 6000 Fourier transform Infrared Spectrometer (BioRad Laboratories, USA) was used. The cross-sectional view of the glass filter was obtained by a scanning electron microscope (SEM, S-510, Hitachi, Japan) with an accelerating voltage of 50 kV.

3. Result and discussion

The addition of an appropriate amount of TsCl as a free initiator brought about a well-controlled polymerization; the M_n of the free polymer increased proportionally to the monomer conversion, and the M_w/M_n ratio remained small, as will be discussed later. The supernatant solution obtained in the washing process (see Section 2), which should contain the free polymer produced in the pores of the glass filter, was subjected to the GPC analysis. It gave a GPC curve nearly the same as that of the free polymer sampled from the bulk solution just after the polymerization. This suggests that the polymerization conditions, e.g. the concentrations of the free initiator, the monomer, and the Cu/ligand complexes, were almost the same in the pores of the glass filter and in the bulk solution.

In order to estimate the amount of PMMA grafted on the glass filter, the IR spectra were measured. As Fig. 3 shows, a sharp absorption band characteristic of the ester group of PMMA is clearly observed at a wavenumber of 1735 cm^{-1}. By referring to the absorption band characteristic of silica at around 800 cm^{-1}, the amount of the graft polymer per 1 g of glass filter (w_g) can be evaluated. In order for this analysis to be correct, no free polymer should remain in the pores of the glass filter. To check this, graft polymerization was carried out with the glass filter on which phenylethyl trimethoxysilane with no ATRP initiating group had been immobilized. The IR measurements detected no PMMA in the sample after the washing process described in Section 2. This confirms the appropriateness of the used washing procedure. Fig. 4 shows the relationship between w_g and monomer conversion. Within the (admittedly large) experimental error, a proportionality exists between these two quantities.

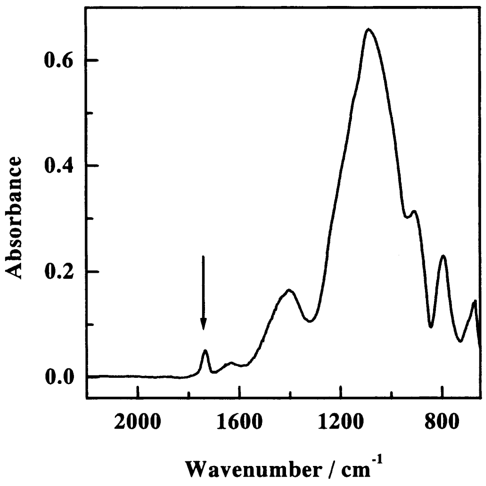

Fig. 3. IR spectrum of the glass filter after graft polymerization for 9 h.

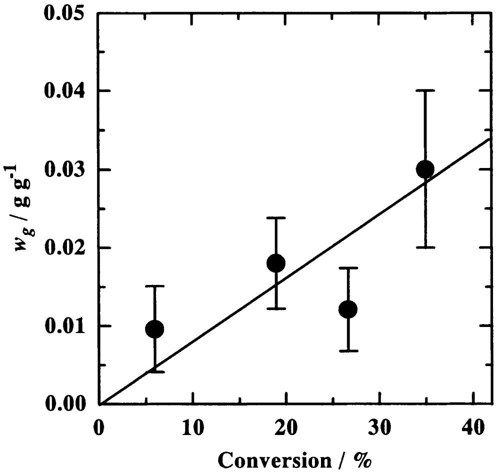

Fig. 4. Relationship between w_g and monomer conversion.

For direct characterization of the graft polymer, it was cleaved from the surface at their point of attachment

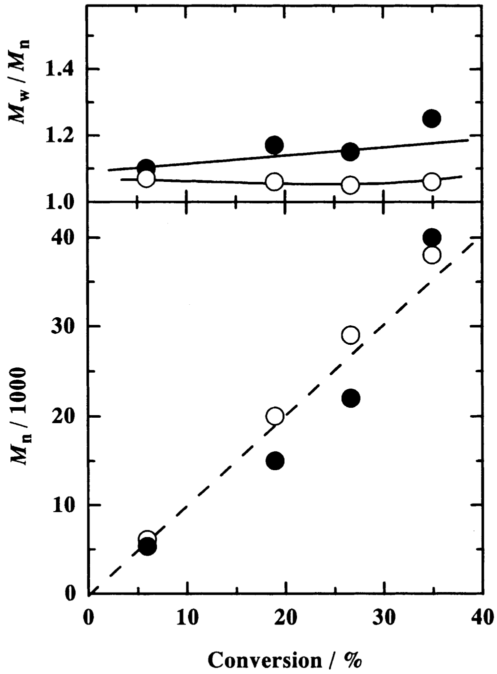

Fig. 5. Plots of M_n and M_w/M_n of the cleaved (●) and free (○) polymers vs. monomer conversion. The broken line is the theoretical prediction calculated from the conversion/[TsCl]$_0$ ratio, and the solid curves are an aid for the eye.

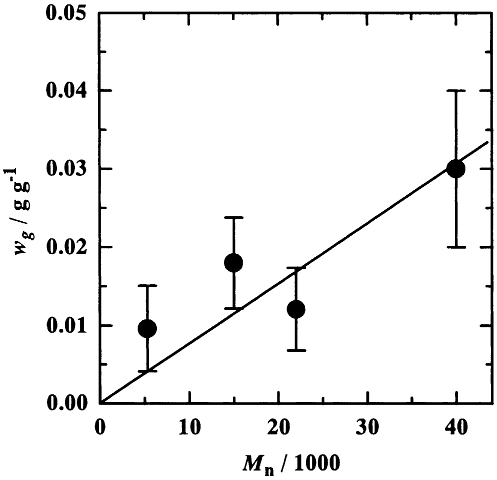

Fig. 6. Relationship between w_g and M_n of graft polymers.

according to the procedure described in Section 2. By using a standard PMMA sample, it was confirmed that the cleavage process including the two-step addition of HF and TOC gave no damage on the PMMA chain. In Fig. 5, the M_n and M_w/M_n of the cleaved (graft) and free polymers are plotted as a function of monomer conversion. For both polymers, M_n increased proportionally to the monomer conversion, in good agreement with the theoretical value (shown by the broken line in the figure) calculated from the conversion/$[TsCl]_0$ ratio, where $[TsCl]_0$ is the initial concentration of TsCl (the contribution of the fixed initiator to the monomer consumption was negligibly small under the polymerization condition adopted in this study). In addition to this, the polydispersity remained low in all cases. These results confirm that the graft polymerization process is as well controlled as the free ATRP of MMA in solution. Fig. 5 also shows that the M_n and M_w/M_n values of the graft polymer are nearly the same as those of the free polymer. This means that the free polymer gives a good measure of the M_n and M_w/M_n of the graft polymer, as was the case with the graft polymerization on the silica particle [24,25]. Fig. 6 shows that the w_g value is approximately proportional to M_n of the graft polymer. This indicates that the graft density, the number of graft chains per unit area, is constant during the course of polymerization. From the slope of the line, the graft density is estimated to be 0.6 ± 0.3 chains nm^{-2} on the basis of the BET-estimated surface area of 1 ± 0.5 m^2 g^{-1}. This value is comparable to the value obtained for the silicon wafer and the silica particle [24,25]. All these results suggest that all the inner (and outer) surfaces of the porous glass filter were uniformly covered by a high-density polymer brush, an ultrathin polymer layer.

4. Conclusions

We have succeeded in achieving a homogeneous and dense graft layer of a low-polydispersity PMMA on the inner (and outer) surface of a glass filter with a large distribution of pore size in a μm range. The ATRP of MMA initiated with a free initiator proceeded in a controlled way in the small pores of the glass filter as well as in the bulk solution, giving free polymers with the same M_n and M_w/M_n. The graft polymer was successfully cleaved from the glass filter by the HF treatment and analyzed by GPC. IR and GPC analyses revealed the following points: (i) the M_n of the graft polymer increased linearly with increasing monomer conversion, keeping the polydispersity low ($M_w/M_n < 1.2$). (ii) The M_n and M_w/M_n values of the graft polymer were nearly equal to those of the free polymer throughout the course of polymerization. (iii) The amount of grafted polymer increased proportionally to monomer conversion and hence the M_n of the graft polymer. The proportionality suggests a constant and high graft density of 0.6 ± 0.3 chains nm^{-2}. Since living radical polymerization can be applied not only to homopolymerizations but also to block and/or random copolymerizations of a variety of monomers, this success will open up a new and wide route to 'precision' surface modification of various porous materials including organic and inorganic membranes.

Acknowledgements

The authors gratefully acknowledge Mr T. Nakano and Mr M. Sato (Kyoto Municipal Institute of Industrial Research, Kyoto, Japan) for the measurements of the BET specific surface area and pore size distribution of a porous glass filter. This work was supported by a Grant-in-Aid for Scientific Research, the Ministry of Education, Science, Sports, and Culture, Japan (Grant-in-Aid 12450385) and Industrial Technology Research Grant Program in 2000 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

[1] Lake R. Science 1987;235:1038.
[2] Bhave RR. Inorganic membranes. Synthesis, characteristics and applications. New York: Van Nostrand Reinhold, 1991.
[3] Fain DE. MRS Bull 1994;19(4):40.
[4] Prakash SS, Brinker CJ, Hurd AJ, Rao SM. Nature 1995;374:439.
[5] Keizer K, Verweij H. Chemtech 1996;January:37.
[6] Lin VSY, Motesharei K, Dancil KPS, Sailor MJ, Ghadiri MR. Science 1997;278:840.
[7] Hedrick JL, Miller RD, Hawker CJ, Carter KR, Volksen W, Yoon DY, Trollsås M. Adv Mater 1998;10:1049.
[8] Okahata Y, Noguchi H, Seki T. Macromolecules 1987;20:15.
[9] Barbucci R, Casolaro M, Magnani A, Roncolini C, Ferruti P. Polymer 1989;30:1751.
[10] Aoyama M, Watanabe J, Inoue S. J Am Chem Soc 1990;112:5542.
[11] Ito Y, Inaba M, Chung DJ, Imanishi Y. Macromolecules 1992;25:7313.
[12] Israels R, Gersappe D, Fasolka M, Roberts VA, Balazs AC. Macromolecules 1994;27:6679.
[13] Park YS, Ito Y, Imanishi Y. Macromolecules 1998;31:2606.
[14] Ito Y, Park YS. Polym Adv Technol 2000;11:136.

[15] Kawai T, Sugita K, Saito K, Sugo T. Macromolecules 2000;33:1306.

[16] Dekking HGG. J Appl Polym Sci 1967;11:23.

[17] Spange S, Simon F, Heublein GJ. Macromol Sci 1991;A28:373.

[18] Boven G, Oosterling MLCM, Challa G, Jan A. Polymer 1990;31:2377.

[19] Tsubokawa N, Maruyama K, Sone Y, Shimomura M. Polym J 1989;21:475.

[20] Prucker O, Rühe J. Macromolecules 1998;31:592.

[21] Liu Y, Zhao M, Bergbreiter DE, Crooks RM, Wells M. J Am Chem Soc 1997;119:8720.

[22] Jordan R, Ulman A. J Am Chem Soc 1998;120:243.

[23] Jordan R, Ulman A, Kang JF, Rafailovich MH, Sokolov J. J Am Chem Soc 1999;121:1016.

[24] Ejaz M, Yamamoto S, Ohno K, Tsujii Y, Fukuda T. Macromolecules 1998;31:5934.

[25] Marumoto Y, Ejaz M, Ohno K, Tsujii Y, Fukuda T, Miyamoto T. Polym Prepr Jpn 1999;48:139.

[26] Ejaz M, Ohno K, Tsujii Y, Fukuda T. Macromolecules 2000;33:2870.

[27] Huang X, Wirth MJ. Macromolecules 1999;32:1694.

[28] Zhao B, Brittain WJ. J Am Chem Soc 1999;121:3557.

[29] Husseman M, Malmström EE, McNamara M, Mate M, Mecerreyes D, Benoit DG, Hedrick JL, Mansky P, Huang E, Russell TP, Hawker CJ. Macromolecules 1999;32:1424.

[30] Matyjaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelman A, Luokala BB, Siclovan TM, Kickelbick G, Vallant T, Hoffmann H, Pakula T. Macromolecules 1999;32:8716.

[31] von Werne T, Patten TE. J Am Chem Soc 1999;121:7409.

[32] de Boer B, Simon HK, Werts MPL, van der Vegte EW, Hadziioannou G. Macromolecules 2000;33:349.

[33] Kim JB, Bruening ML, Baker GL. J Am Chem Soc 2000;122:7616.

[34] Fukuda T, Goto A, Ohno K. Macromol Rapid Commun 2000;21:151.

[35] Yamamoto S, Ejaz M, Tsujii Y, Matsumoto M, Fukuda T. Macromolecules 2000;33:5602.

[36] Yamamoto S, Ejaz M, Tsujii Y, Fukuda T. Macromolecules 2000;33:5608.

[37] Grimaud T, Matyjaszewski K. Macromolecules 1997;30:2216.

[38] Percec V, Barboiu B. Macromolecules 1995;28:7970.

[39] Percec V, Barboiu B, Kim HJ. J Am Chem Soc 1998;120:305.

[40] Yu B, Ruckenstein E. J Polym Sci Part A: Polym Chem 1999;37:4191.