

Surface Modification of Ultra-Flat Polydimethylsiloxane by UV-Grafted Poly(acrylic acid) Brushes

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ABSTRACT: The graft density and surface topography of ultra-flat polydimethylsiloxane films grafted with poly(acrylic acid) brushes by UV irradiation are investigated. The graft density keeps increase with the irradiation time and with the monomer concentration to a maximum, after which it remains unchanged in the former case or drops in the latter. Atomic force microscopy results show that a longer irradiation

time, a higher monomer concentration and the addition of ethanol in the grafting solution are favorable to obtain the grafted polydimethylsiloxane films with flat surface. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2266–2271, 2012

Key words: polydimethylsiloxane (PDMS); UV graft; poly(acrylic acid); brush; AFM

INTRODUCTION

Polydimethylsiloxane (PDMS) has been widely used in the fields of biomedicine,^{1,2} microfluidic chips,^{3,4} and soft lithography^{5–8} for its unique properties, including physiological inertness, good blood compatibility, low toxicity, low modulus, low-temperature polymerization, transparency at UV-visible region, permeability to gases, low cost, and reversible sealing to itself and a range of other materials.^{8–10} However, its applications are limited by the inherent strong hydrophobicity of PDMS. Take biomedical application for example, proteins are prone to accumulate on its surface by hydrophobic interaction and stimulate immunological responses.^{11,12} In membrane application, the adsorption of some organic solvents and some hydrophobic analytes causes fouling of the membrane.^{3,11} In microcontact printing, the weak adsorption of hydrophilic compound limits the “ink” to nonpolar surface.^{13,14} In the application in microfluidic chip for bioanalysis, it is difficult to fill hydrophobic microchannels with aqueous solution.^{3,8,10,15}

There have been a variety of chemical methods for modifying solid surfaces. Among them, surface graft polymerization has been carried out to improve the surface properties such as wettability, the antistatic property, and adhesion without deterioration of the

bulk properties.¹⁶ Moreover, surface-initiated polymerization of polymer brushes, based on initiators bound to surfaces to initiate polymerization and generate tethered polymers, provides a stable modification of surface properties and thus can control the thickness, functionality, and density of polymer brushes with molecular precision.¹⁷ In addition, the grafted-polyelectrolyte brushes have received wide attentions for the possibility in controlling the catalytic selectivity,¹⁸ preventing the adsorption of proteins on surfaces¹⁹ and designing porous filters for pH-controlled gating.²⁰

In this study, UV graft polymerization of acrylic acid brush was used to modify the surface properties of PDMS. UV graft is chosen as the modification method since it follows simple steps and possesses low or no penetration into the bulk polymer.¹⁰ Acrylic acid, as the monomer, can be polymerized to functional films for chemical modification via the formation of amide and ester linkages, whereas the physical properties and biocompatibility of such films can be reversibly modulated as polyelectrolyte brushes.²¹ Although there has been extensive work on tailoring the PDMS surface by introducing poly(acrylic acid) (PAA) chains through UV graft polymerization from the surface adsorbed photoinitiators to modify the hydrophobic channels in PDMS fluidic microchips,^{10,12,21,22} the dependence of surface topography of the grafted PDMS films on the graft conditions were not provided in these studies.

Here, PDMS films with an ultra-flat surface are used for grafting; therefore, any tiny difference of the surface topography at different graft conditions could easily be detected on such a flat surface. To study the surface topography of the grafted PDMS,

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Atomic force microscopy (AFM), which can accurately reproduce the true topography of soft samples and has been used extensively in investigating polymer brushes,²³ was adopted for the high-resolution profiling of surface morphology and nanostructure in tapping mode. The variation in the graft density with the graft conditions was also investigated.

EXPERIMENTAL

Materials

The Sylgard 184TM PDMS kit was purchased from Dow Corning and stored at 4°C. Acrylic acid (AAc) and benzophenone (BP) were obtained commercially from Sinopharm Chemical Reagent Co. (Shanghai, China) and used as received.

Fabrication of PDMS films

Flat PDMS films were fabricated as described previously.²⁴ Sylgard 184TM PDMS prepolymer was mixed thoroughly with its crosslinking agent at 10 : 1 (w/w) and degassed by vacuum. Then the mixture was cast on freshly cleaved mica and degassed again to ensure good replication of the flat surface. Finally, the mixture was cured at 80°C for 4 h. After peeling off from the mica surface, the PDMS films with atomic flatness were obtained.

Surface graft polymerization of PAA brushes

The grafting process was conducted in two steps as previously described²² with some modification. First, the flat PDMS films were immersed in 0.5% wt of acetone solution of BP for 30 s to adsorb BP/acetone solution onto their surfaces. Then, the films were dried in air at ambient temperature, and the dissolved BP was deposited onto their surfaces after the volatilization of the solvent. Second, these films adsorbed with BP on their surfaces were immersed into a monomer solution at the indicated concentration and irradiated under a lamp (1000 W Xe, 190 nm–800 nm wavelength). The distance between the film and the center of the Xe lamp was 5 cm. Uniform UV exposure was ensured by placing the lamp at the focus of a concave mirror. The grafted films were then washed in acetone to remove the remained BP and extracted in a Soxhlet apparatus by water for a week to remove the adsorbed monomers and polymers.

Control of reaction temperature

The temperature of the graft reaction was controlled by immersion the reaction chamber in a water bath. Water with the temperature of 45°C was continu-

ously flushed into the bath then drained to take the heat produced by the lamp away.

For those experiments without water drainage taking the heat away, the temperature of solution gradually increased from 20 to 90°C in 50 min. Since the power of the lamp and the volume of the solution are fixed, we deemed that the temperature increases in proportion to the reacting time, with a heating rate of 1.4°C/min.

Measurement of graft density

Before grafting, PDMS films were cut into pieces with the same size. Then they were dried at 80°C until their weights remain unchanged. After grafting and cleaning, these films were dried at the same condition and the graft density was defined as the difference in the film weight before and after grafting per unit surface area.

Topography of PDMS films

The topography of the dried PDMS films was measured by AFM (SPA 400, Seiko Instruments, Japan) in tapping mode with the setpoint ratio of 0.9. The rectangular silicon cantilever (NSC18/Cr-Au, Mikro-Masch, Russia) used has a nominal constant of 3.5 N/m and a typical resonant frequency of 75 kHz, attaching to that the phosphorus doped silicon probe has a tip radius of about 50 nm.

RESULTS AND DISCUSSIONS

Effects on the surface topography

The surface topography of PDMS films after grafted with PAA brushes was investigated by AFM [shown in Fig. 1A–C)]. As a control, the surface topography of an original PDMS film was also shown in Figure 1D. And the profiles at the selected line in each image were displayed in Figure 1E, which can directly reflect the roughness of these surfaces. From Figure 1D, we can find that the origin PDMS film is ultra-flat, with the highest domains less than 3 nm (profile d in Fig. 1E). Therefore, any tiny surface changes after grafting could be discriminated by AFM. After grafted in AAc aqueous solution of 2% vol, the PDMS surface becomes more and more flat with increasing the irradiation time from 30 min to 50 min [from Fig. 1(A–C)]. The aggregates of grains in Figure 1A may be the PAA brushes grafted in such a high monomer concentration. Additionally, these grains are randomly located on the surface, which may result from the unevenness adsorption of BP in the drying process since the initiator density at the start of the polymerization determines the ultimate “footprint” and hence the density of polymer

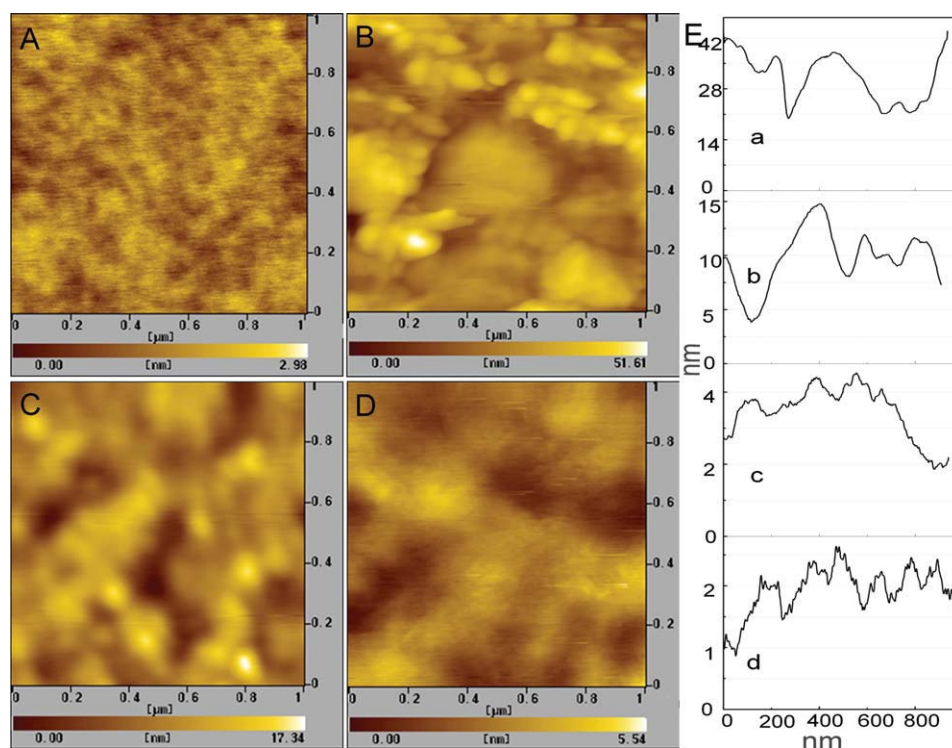


Figure 1 AFM topographical images of grafted PDMS surface after irradiated for variable time in AAC aqueous solution of 2% vol. (A) 30 min, (B) 40 min, (C) 50 min, (D) Original PDMS film, and (E) profiles (a, b, c, and d) corresponding to the selected lines in these images (A, B, C, and D). [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

molecules in polymer brushes.²⁵ Under the irradiation of UV light, the BP absorbed on the surface is excited, which can preferentially abstract the hydrogen near the film surface, resulting in grafting from the surface.²⁶ But due to the uneven adsorption of BP, the grafted chains are unevenly distributed and aggregated into grains in the drying process, as shown in Figure 1A. With the diffusion of monomer into the PDMS substrate, grafting is most likely to take place in the superficial layer of the substrate rather than at the interface between polymer and solution,²⁷ so the grafted surface becomes more and more flat (shown in Fig. 1(A and C)). The unevenness in Figure 1C may be the surface waves formed in the drying process,²⁸ since the topography of graft layers scanned in air can be considered as the conformation of grafted chains in a poor solvent,²⁹ and the surface roughness (profile c) is very close to that of the origin PDMS film (profile d) in Figure 1E.

Monomer concentration can also exert influences on the surface topography of grafted PDMS films (shown in Fig. 2). From Figure 2(A-C), the size of the grains on the grafted surface increases with increasing the monomer concentration. In Figure 2F, the increase of the grains' maximum height from 4 nm (profile a) to 10 nm (profile c) and length from 80 nm (profile a) to 150 nm (profile c) also proved this tendency. These grains are expected to be the

grafted brushes initiated by BP absorbed on the PDMS surface mentioned earlier. With increasing the monomer concentration, the reaction rate and the length of the grafted chains increases; thus, the aggregation of grafted chains in a local area results in a bigger grain size within such a short period of irradiation time. From Figure 2C to Figure 2E, more and more small grains appear on the surface and finally form a continuous layer. It can be easily observed that the grains' maximum length increases from 150 nm (profile c) to more than 300 nm (profile e) in Figure 2F. These small grains can be regarded as the aggregation of the grafted chains from the superficial layer of the PDMS substrate. Due to the impediment of the substrate, the diffusion of monomer into the superficial layer is significantly reduced, so the reaction rate in this area is reduced. Within a short irradiation time, these grafted chains form small grains. Higher monomer concentration indicates quicker monomer diffusion into the substrate and higher probability of the interaction between the PDMS backbone and the AAC monomer. Therefore, with the increase of monomer concentration, more and more chains are grafted from the superficial layer of the substrate and form a continuous layer eventually.

As is known, solvent is the carrier by which monomer molecules are transported to the vicinity

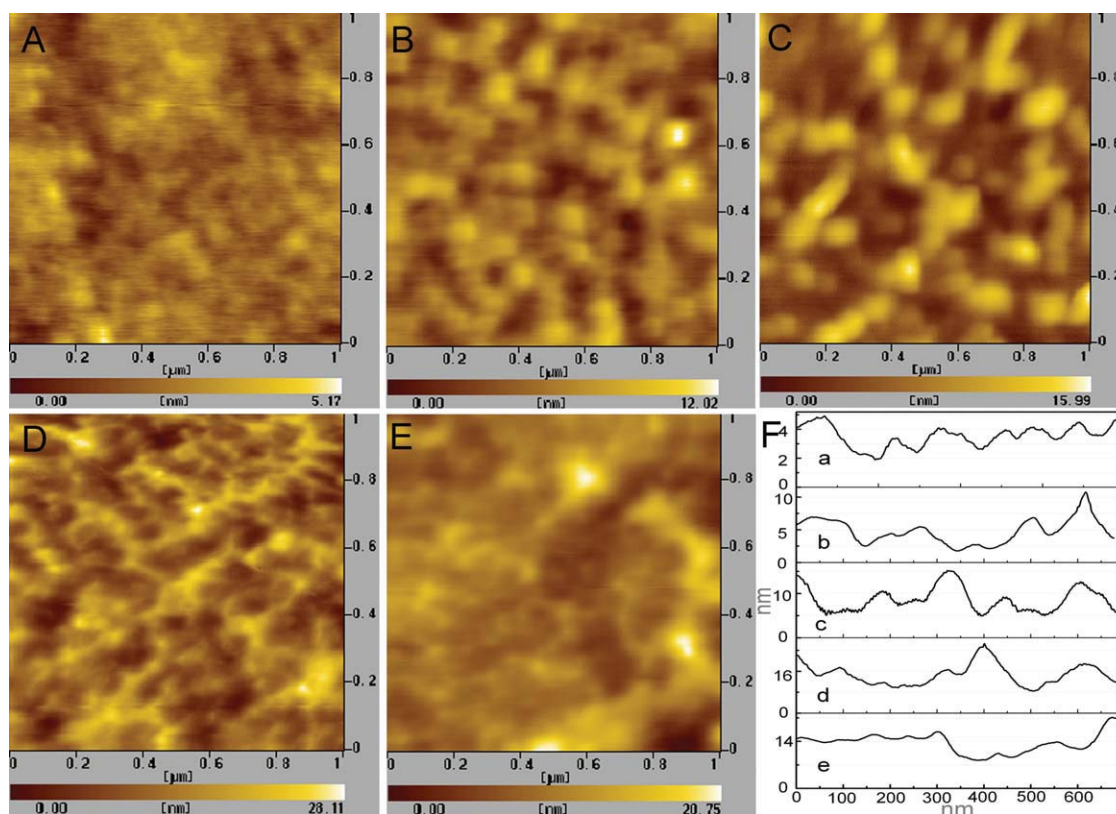


Figure 2 AFM topographical images of grafted PDMS surface in ethanol aqueous solution of 10% vol after irradiated for 30 min with different monomer concentration: (A) 0.75% vol, (B) 1.0% vol, (C) 1.25% vol, (D) 1.5% vol, (E) 2.0% vol, and (F) profiles (a, b, c, d, and e) corresponding to the selected lines in these images (A, B, C, D, and E). [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

of the backbone, while the generation of free radicals of solvent is also very important since the efficiency of grafting in a solution depends upon the relative reactivity of monomer and solvent in competing for the radicals induced on the base polymer.³⁰ Hence, solvent can also influence the topography of grafted PDMS surfaces even at the same polymerization condition. The difference of surface topography in Figure 1A and 2E and Figure 1A can well prove this. The surface of Figure 2E is flatter than that of Figure 1A, which can be attributed to the compatibility and the chain transfer effect of ethanol.³¹ On the one hand, ethanol can slightly swell the PDMS substrate, benefiting the diffusion of monomer into the radical sites in the superficial layer of the substrate and promote grafting.³⁰ As a result, uniform grafting from the superficial layer can be conducted in such a short irradiation time. When the grafted chains would entangle with each other, they form a continuous graft layer in Figure 2E. When grafting in aqueous solution, few monomer molecules can diffuse into the superficial layer of the substrate since water cannot swell PDMS. Graft polymerization mostly takes place at the interface of solution and solid substrate, forming isolated grains in Figure 1A due to the unevenness of the preabsorbed BP on

the PDMS surface. On the other hand, ethanol is an effective chain transfer agent, which could decrease the grafted chain length, whereas water is insensitive to most organic radicals.³² Therefore, the length of chains grafted in ethanol is shorter than that grafted in water. The height of the aggregated chains should be reduced further even if no continuous graft layer is formed.

Effects on the graft density

The variation in the graft density with the irradiation time is revealed in Figure 3. The graft density increases with the reaction time to a maximum value of 3.0 g/m² at 50 min, after which it keeps almost unchanged. But in the first 30 min, the increase is relatively slow, and even no grafting can be detected in the first 10 min. This trend is related to the transfer of initiated radicals to the dissolved oxygen in AAc solution.^{33,34} It is known that photoexcited benzophenone (BP*) can diffuse into the surface and abstract hydrogen atoms from PDMS, producing the radicals required for grafting.³⁰ Since oxygen is a strong inhibitor of radical polymerization, the free radicals formed in the first 10 min were consumed up by the dissolved oxygen, resulting in no grafting

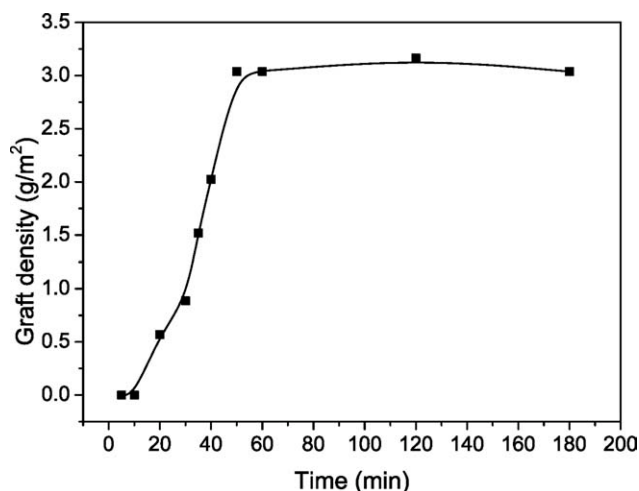


Figure 3 Plot of graft density versus irradiation time in aqueous solution with the monomer concentration of 1.0% vol.

to be initiated. After the consumption of dissolved oxygen, the radicals start to initiate the grafting. The graft density increases linearly with increasing the irradiation time until the highest graft density is reached. Yamamoto et al.²⁶ explained that this linear increase in graft density with increasing irradiation time contributes to the extension of grafted chains like "living" radical polymerization: the propagating radicals are capped with pinacol radicals, and the BP-terminated AAc extends through the breakage of the BP-AAc bond by UV-irradiation and consumption of AAc monomer. As shown in Figure 1, we deemed that this linear increase results from gradually increased graft areas with increasing irradiation time, because more monomer molecules diffuse into the superficial layer of PDMS and take part in graft polymerization. Gradually, the PDMS surface is spread with the grafted chains. After BP is consumed up, no more PAA chains can be grafted onto the surface, so the graft density keeps unchanged at 3.0 g/m² with further irradiation.

Figure 4 illustrates the dependence of graft density on the monomer concentration at different temperature. These two curves display the same trend: the graft density increases with increasing the monomer concentration up to a certain level and then descends with further increase in the monomer concentration. It is well known that higher monomer concentration results in faster chain propagation, longer graft chains, and quicker monomer diffusion into the superficial layer of substrate. Thus, with the increase of the monomer concentration in close proximity to the PDMS substrate, the graft density increases. After the monomer concentration reaches a certain level, further increase will accelerate the homopolymerization reaction rather than grafting.³⁰ Moreover, intensive homopolymerization leads to

not only a significant reduction in monomer for grafting but also a high viscosity of the grafting solution.³² Therefore, less monomer can diffuse into the graft layer, so the graft density decreases.

Figure 4 also demonstrates the noticeable effect of graft temperature on the grafting process. The graft density of samples grafted at a heating rate of 1.4°C/min is higher than that of samples grafted at 45 ± 5°C, which may be ascribed to the high temperature (about 90°C) at the end of reaction. Compared with preirradiation grafting,³¹ the grafting temperature may have same effects on the grafting reaction, including quicker decay and formation of radical sites on the PDMS surface, faster diffusion of monomer molecules to the matrix, and higher grafting rate. For the existence of excess photoinitiator on the substrate, the effect of temperature on the decay and formation of free radicals will counteract each other and have little influence on the graft density. The last two factors may dominate the reaction, resulting in higher graft density at high temperature. Additionally, increasing the temperature can facilitate the decomposition of peroxides formed as a result of irradiation of PDMS in oxygen-contained solution, which enhances the graft density further.³⁰ From Figure 4, we can also find that the inflection of curves shifts to higher monomer concentration at higher graft temperature. This trend is largely due to the Tromasdorff effect: at higher temperatures, monomer molecules have a higher mobility which favors grafting; otherwise they will most probably become embedded in the swollen hydrogels, which leads to homopolymerization. Moreover, the viscosity of the grafting solution decreases with temperature rise, consequently the

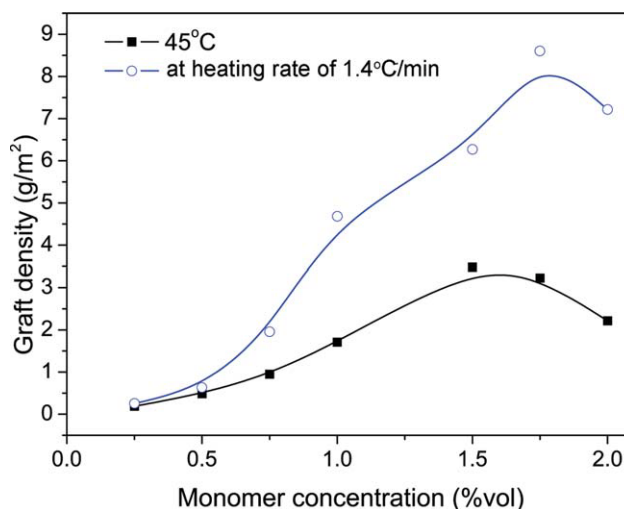


Figure 4 Variation of graft density as a function of monomer concentration in aqueous solution at the irradiation time of 50 min. ■, reaction at 45 ± 5°C; ○, reaction at a heating rate of 1.4°C/min. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

diffusion rate of monomer at a higher temperature is increased further.

CONCLUSIONS

After adsorption of BP from its acetone solution, PDMS films with ultra-flat surface are grafted with PAA through UV initiation. The irradiation and reaction conditions influence the graft density significantly. The graft density increases with the increase in the reaction time to a maximum at 50 min and then keeps unchanged. The rise in monomer concentration increases the graft density to a certain level, beyond which the graft density decreases. Higher reaction temperatures also promote graft density. As to the surface topography of the grafted films, the films are flat if grafting is conducted in ethanol/aqueous solution with higher monomer concentration and lasts for a longer irradiation time.

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References

1. Abbasi, F.; Mirzadeh, H.; Katbab, A. A. *Polym Int* 2001, 50, 1279.
2. Chen, H.; Zhang, Z.; Chen, Y.; Brook, M. A.; Sheardown, H. *Biomaterials* 2005, 26, 2391.
3. Makamba, H.; Kim, J. H.; Lim, K.; Park, N.; Hahn, J. H. *Electrophoresis* 2003, 24, 3607.
4. Ng, J. M. K.; Gitlin, I.; Stroock, A. D.; Whitesides, G. M. *Electrophoresis* 2002, 23, 3461.
5. Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem Rev* 1999, 99, 1823.
6. Xia, Y.; Whitesides, G. M. *Annu Rev Mater Sci* 1998, 28, 153.
7. Rogers, J. A.; Paul, K. E.; Jackman, R. J.; Whitesides, G. M. *Appl Phys Lett* 1997, 70, 2658.
8. McDonald, J. C.; Duffy, D. C.; Anderson, J. R.; Chiu, D. T.; Wu, H.; Schueller, O. J. A.; Whitesides, G. M. *Electrophoresis* 2000, 21, 27.
9. Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Willson, C. G.; Whitesides, G. M. *Chem Rev* 2005, 105, 1171.
10. Hu, S.; Ren, X.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. *Anal Chem* 2002, 74, 4117.
11. Lahann, J. R.; Balcells, M.; Lu, H.; Rodon, T.; Jensen, K. F.; Langer, R. *Anal Chem* 2003, 75, 2117.
12. Hu, S.; Ren, X.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L. *Langmuir* 2004, 20, 5569.
13. Sadhu, V. B.; Perl, A. S.; Péter, M. R.; Rozkiewicz, D. I.; Engbers, G.; Ravoo, B. J.; Reinhoudt, D. N.; Huskens, J. *Langmuir* 2004, 23, 6850.
14. Trimbach, D. C.; Al-Husseini, M.; de Jeu, W. H.; Decré, M.; Broer, D. J.; Bastiaansen, C. W. M. *Langmuir* 2004, 20, 4738.
15. Hartman, L. C.; Bessette, R. W.; Baier, R. E.; Meyer, A. E.; Wirth, J. J. *Biomed Mater Res* 1988, 22, 475.
16. Uchida, E.; Uyama, Y.; Ikada, Y. *Langmuir* 1994, 10, 481.
17. Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem Soc Rev* 2004, 33, 14.
18. Ruckenstein, E.; Hong, L. *J Catal* 1992, 136, 378.
19. Carignano, M. A.; Szeleifer, I. *Colloids Surf B* 2000, 18, 169.
20. Ito, Y.; Ochiai, Y.; Park, Y. S.; Imanishi, Y. *J Am Chem Soc* 1997, 119, 1619.
21. Patrito, N.; McCague, C.; Chiang, S.; Norton, P. R.; Petersen, N. O. *Langmuir* 2006, 22, 3453.
22. Hu, S.; Ren, X.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. L. *Anal Chem* 2004, 76, 1865.
23. Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. *Macromolecules* 2000, 33, 8821.
24. Yang, H.; Wang, P.; Wang, H.; Wang, X.; Zhang, F.; Li, B.; Li, H. *Surf Rev Lett* 2008, 15, 763.
25. Jones, D. M.; Brown, A. A.; Huck, W. T. S. *Langmuir* 2002, 18, 1265.
26. Yamamoto, K.; Kyozuka, S. J.; Shimada, S. *Macromolecules* 2004, 37, 86.
27. Ruckert, D.; Geuskens, G. *Eur Polym Mater* 1996, 32, 201.
28. Xi, H.-W.; Milner, S. T. *Macromolecules* 1996, 29, 4772.
29. Uchida, E.; Ikada, Y. *Macromolecules* 1997, 30, 5464.
30. Bhattacharya, A.; Misra, B. N. *Prog Polym Sci* 2004, 29, 767.
31. Lu, J.; Li, J.; Yi, M.; Ha, H. *Radiat Phys Chem* 2001, 60, 625.
32. Hou, Z.; Chen, S.; Sheng, K. *J Appl Polym Sci* 2007, 103, 1570.
33. Albertin, L.; Stenzel, M. H.; Barner-Kowollik, C.; Foster, L. J. R.; Davis, T. P. *Polymer* 2005, 46, 2831.
34. Studer, K.; Decker, C.; Beck, E.; Schwalm, R. *Prog Org Coat* 2003, 48, 92.