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GRAFTED POLYMERIC MICROSPHERES: A SYNTHETIC APPROACH TO STRUCTURALLY WELL-DEFINED BRUSH POLYMERS†

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ABSTRACT

A simple method for the surface grafting of crosslinked polystyrene latex particles of narrow size distribution as core is described. Amino groups were generated on the surface of these microspheres by a two-step process of nitration and subsequent reduction. Polyethylene glycol chain of desired molecular weight was covalently linked to the surface amino group using diisocyanate-coupling reaction. The method is appropriate for designing brush polymers.

INTRODUCTION

Brush polymers are novel macromolecular systems in which polymer chains are terminally anchored onto a surface by chemical or physical forces [1-7]. Because of the steric constraints at the anchored terminal, the polymer chains tend to stretch along the direction normal to the surface. Consequently,

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they exhibit properties quite different from the typical behavior of free, flexible chains in solution [8-12]. Such colloidal particles repel one another hence they have technological applications in diverse fields such as colloidal stabilization, modification of interfacial and surface properties etc. These inter particle interactions are sensitive to the size of the grafted chains, grafting density and also solvent quality and composition [3, 9, 11, 13, 14].

Because of their structure and the unusual dynamics of the anchored chains, such systems have attracted both theoretical and experimental attention [1-14]. Theoretical treatments generally focus on idealized systems, where the anchored chains have the same chemistry and uniform dimension. In practice, while the first assumption is easily achieved, the second is rather difficult. Synthetic macromolecules do not possess narrow molecular weight distribution unless stringent reaction conditions are employed.

Very few methods are available in the literature for the synthesis of brush polymers per se and none for well-defined systems. The most commonly reported methods include terminal preferential adsorption [10, 11, 15, 16] and grafting of polymer chains on various solid surfaces [6, 7, 17-19]. Both methods suffer from major drawbacks: assorted chain sizes and low surface coverage.

A brush polymer can also be considered as a special case of core-shell (also called core-corona) polymers [20-29]. A well-defined interface between the anchoring surface and the anchored chains distinguishes a brush polymer from a polymer with core-shell morphology. Suitable modifications of the synthetic strategies for core-shell polymers such as seeded emulsion polymerization or dispersion polymerization can also yield brush polymers. However, it is impossible to determine the molecular weight of the grafted chains since the grafts cannot be easily cleaved off the surface. The recent method reported by Sukhishvili *et al.* [7] for polyelectrolyte brushes calls for rigorous reaction conditions.

Here, we report a simple synthetic route for well-defined brush polymers with spherical geometry. The core is crosslinked polystyrene microsphere. Polyethylene glycol (PEG) chains of desired molecular weight are anchored onto the surface of these microspheres through covalent linkages. The merit of our system lies in the fact that the structural parameters of both the core and bristles can be completely evaluated. SEM measurements provide the necessary data to detennine. the surface area of the core. Gravimetric estimation of percentage of PEG incorporated and the GPC profile of the mol wt of PEG lead to more accurate grafting density σ (no. chains per unit area) which is essential for the thermodynamic calculations.

EXPERIMENTAL

Materials and Methods

Styrene and divinylbenzene (Merck) were purified according to the standard methods available in the literature [30]. Polyethylene glycols and their mono derivatives (Aldrich and Fluka), toluene-2,4-diisocyanate (Fluka) and polyvinypyrrolidone (PVP) (Loba Chemicals, Mumbai) were used as received. (α,α'-Azobisisobutyronitrile (AIBN)was recrystallized from ethanol before use. All solvents were distilled before use. All other chemicals used were of the highest purity available.

Molecular weight and polydispersity of the PEG samples were determined by Gel Permeation Chromatography in a Shimadzu. unit equipped with R.1 detector, in an Asahipak amphiphilic column against PEG standards using water as eluent.

Synthetic strategy includes preparation of monodisperse polystyrene microspheres, surface modification and covalent coupling of PEG chains. Schematic representations of reactions are shown in the Scheme 1.

Preparation of Crosslinked Polystyrene Microspheres

Crosslinked microspheres were prepared by the dispersion polymerization of styrene in isopropanol [31-33]. A typical recipe consists of styrene (60 g), divinylbenzene (0.24 g), PVP (13.0 g), cetyl alcohol (3.6 g), AIBN (0.800 g), water (60 ml), cyclohexane (60 ml) and isopropanol (600 ml). Polymerization was carried out at 70°C in nitrogen atmosphere for 24 hours in a three-necked flask fitted with a mechanical stirrer, condenser and nitrogen inlet. After the reaction, the mixture was cooled and the microspheres were separated by centrifugation. The product was washed free of PVP by repeated dispersion and dried in vacuum oven at 50°C for 24 hours.

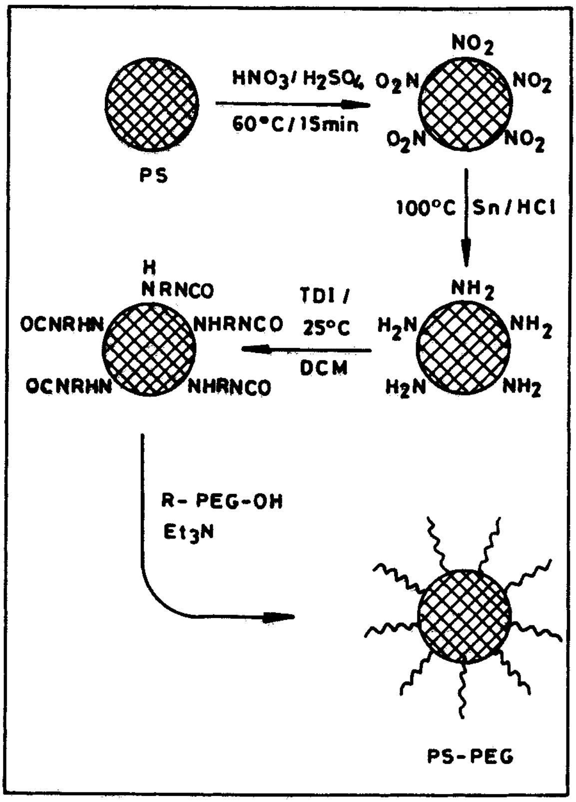
Polystyrene microspheres were characterized by SEM studies. A dispersion of microspheres in methanol was kept on the sample carrier, dried for 24 hours, and then coated with a thin layer of gold before viewing.

Surface Modification of the Microspheres

Surface modification of the microspheres was done in two steps: nitration and subsequent reduction.

Nitration

Polystyrene microspheres (20 g), were treated under constant stirring with nitrating mixture (60 ml of 36N H_2SO_4 and 52.5 ml 1 1N $HN0_3$) at 60°C for 15



Scheme 1. Synthesis of PS-g-PEG brush polymer

minutes in 250 ml R.B flask. The mixture was then poured into ice cold water with stirring. The nitrated polymer was washed free of acid, separated by centrifugation and dried in vacuum oven for 24 hours at 50°C. IR spectrum in KBr and SEM photographs of the nitrated microspheres were recorded.

Reduction

Nitro groups were reduced using Tin/HCl. For this nitrated PS, microspheres (15 g) were dispersed in HCl (12N, 150 ml) and heated to 100°C with stirring.

Granulated Tin metal (30 g) was added slowly over a period of one hour. Reaction was continued for another hour at the same temperature and then cooled to room temperature. Aminated polystyrene microspheres were washed free of acid and dried in vacuum oven at 50°C for 24 hours IR. spectrum and SEM of the aminated microspheres were recorded.

TABLE 1. Recipe for Coupling Reactions

Reactants	Amount (g)
PS-NH_2	0.500
TDI	0.174
DCM	20 ml
*R-PEG-OH	3.50
Triethyl amine	0.075

*R= $OCOCH_3$ or OCH_3

Estimation of Surface Amino Groups

Quantitative estimation of the amino groups on the surface of the polystyrene microspheres was done by acetylation method [34]. A known amount of aminated microspheres was refluxed with acetylating mixture (1:3 v/v acetic anhydride/pyridine) for one hour and excess of acetic anhydride was determined by back titration method. Results were compared with those obtained by spectrophotometric method [35].

Coupling the PEG chains

Monoacetyl ester of the desired PEG was prepared by a minor modification of the previously reported [36] method of borate complexing and subsequent esterification with acetic acid in toluene using PTSA as catalyst. The product was isolated and characterized with respect to its hydroxyl values [34].

Monoacetylated PEG chains were covalently linked to the surface amino groups of the polystyrene microspheres using TDI as the coupling agent. The general procedure is described below and a typical recipe is given in Table 1.

Stoichiometric amounts of amino polystyrene and TDI were allowed to react in dry dichloromethane in nitrogen atmosphere at room temperature for 1 hour under constant stirring. Monoacetylated PEG together with a small amount of triethyl amine as catalyst was added to this reaction mixture. The reaction was continued for another hour, then quenched with methanol. The solvent was removed in a rotary evaporator.

The product was subjected to soxhlet extraction with water to remove unreacted PEG. The PEG linked microspheres were rinsed with acetone several times and then dried in vacuum at 50°C. IR spectrum in KBr and SEM photographs of the product were taken. The amount of PEG incorporated was determined gravimetrically and estimated as percentage grafting from the initial and final weights of the sample.

RESULTS AND DISCUSSION

Functionalized polystyrene microspheres have been synthesized by copolymerizing styrene with small amounts of functionalized monomers [37-39]. Chemical routes for surface functionalization include oxidation, sulfonation, and chloromethylation [40-42]. Plasma sensitized reactions have also been employed to functionalize polymer surfaces. [43-44]. In comparison, we have used a simpler method to generate a more reactive - NH_2 group predominantly on the surface by nitration and subsequent reduction. These reactions might not affect the bulk properties of the polystyrene microspheres because the reaction time for nitration is too short (15 minutes) and the acid doesn't wet and penetrate the microspheres. By controlling the reaction time extent of nitration/amination could be controlled.

Dispersion polymerization gave more than 75% yield of polystyrene microspheres. SEM photographs (Figure la) indicate that the microspheres have narrow size distribution and smooth surface with an average diameter of 1.4 μm.

The SEM photographs of PS-$N0_2$, and PS-NH_2 (Figure lb, c) show no appreciable change in the surface morphology. The IR spectra of PS, PS-$N0_2$ and PS-NH_2 and PS-PEG are shown in Figure 2. PS-$N0_2$ shows strong absorptions at 1520 cm-^{1} (asymmetric aromatic N — 0 stretch) and 1345cm-^{1} (symmetric N — 0 stretch) and absorption at 850 cm-^{1} (C — N stretch). A broad absorption span-ning 3200-3400 cm-^{1} and another one at 1265 crn^1 (C — N stretch) confirm the identity of PS-NH_2. Nitration imparts a slight yellow color to the microspheres. The PS-NH_2 samples turn brown during storage which is characteristic of aromatic -NH_2 group. The characteristic C-H stretch of ethyleneoxide, group at 2840-2910 cm-^{1} and C=O (carbonyl) stretching of urethane linkage at 1705 cm-^{1} confirm the PEG linkage in the final product.

A semiquantitative estimation of the nitro group absorption against the main chain CH2 absorption from the IR spectra yields a value of 5.7 mmols of nitro group per gram of the sample. It is indeed worth mentioning that Merrifield

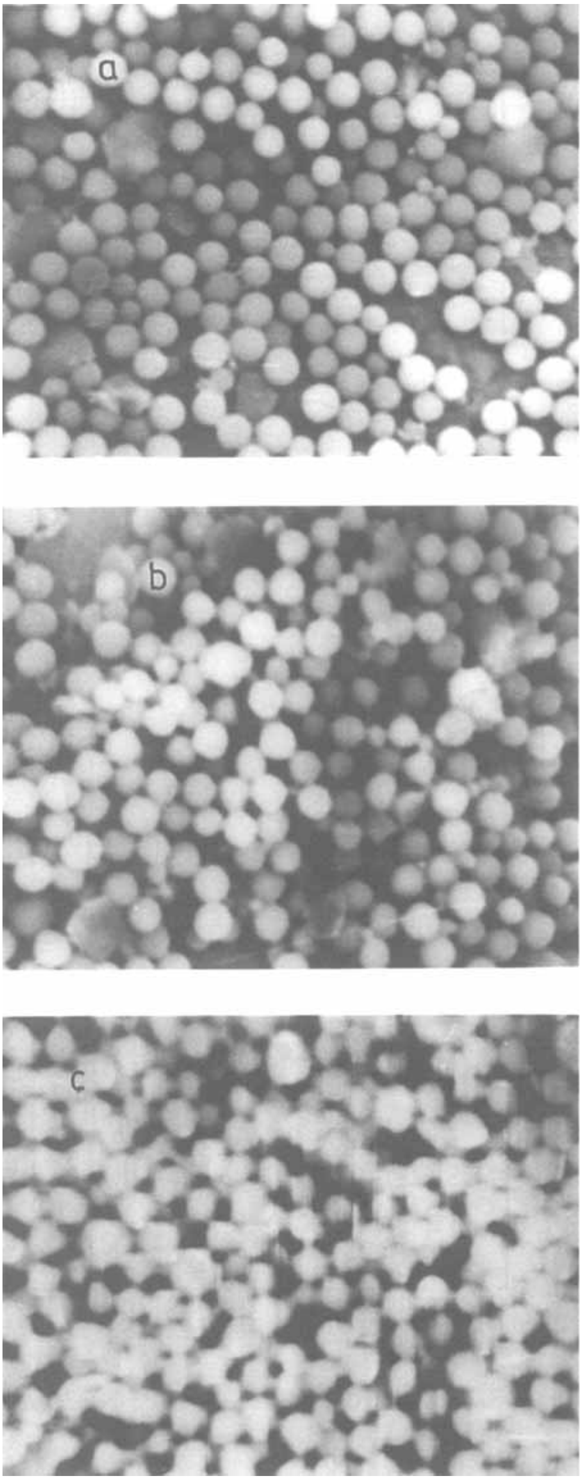


Figure 1. SEM Photographs of microspheres a) PS b) PS-N02 c) PS-NH2.

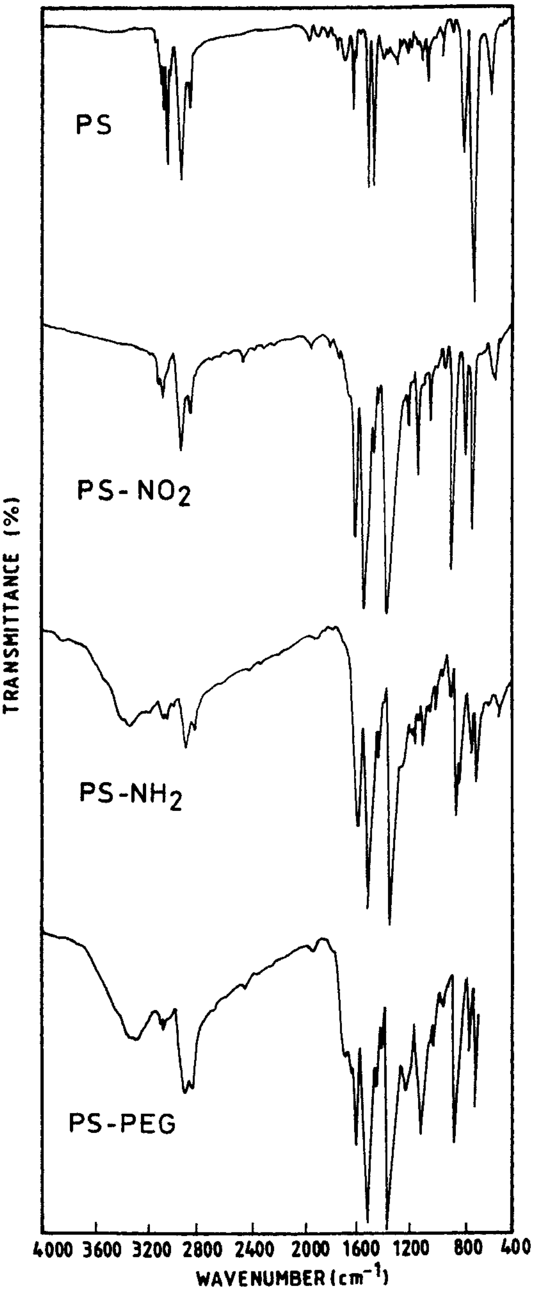


Figure 2. IR. spectrum of PS , PS-NO 2, PS-NH2, and PS-PEG.

[41] reports a value of 6.38 mmoles/gm for nitration of chloromethylated polystyrene.

Instead of the usual method, [45] we chose to estimate the surface amino group by acetylation. Because PS being in the crosslinked state, PS-NH_2 was insoluble in the recommended solvent toluene. Acetylation method is more efficient because in presence of a base, amino group readily forms acetyl derivative. Excess acetic anhydride used was determined by the back titration method. From the difference in the titration value of blank experiment and the sample we calculated the amount of amino group formed on the PS microspheres. The value of 2.04 mmols of amino group per gram compares very well with that of 1.95 mmols per gram obtained by Gisin's method [35].

Quantitative estimations suggest that only -35% of nitro groups have been reduced. This is rather surprising considering the efficeiency of Sn/HCl as a reducing agent. In the literature, values ranging from 35-70% have been reported for the reduction of nitrated polystyrene [46, 47]. Rafikov et al. [47] could reduce 70% of the nitrogroups with tin and HCl, when the polystyrene samples were preswollen in pyridine and the reduction carried out for 7-8 hours at 80-150°C. They observed that nonswollen samples registered a very low efficiency of reduction. In the present study, we did not preswell the samples. The polymeric microspheres were directly dispersed in 12N con. HCl. Moreover, reactions were restricted to 2 hours.

The primary reason for choosing TDI as the coupling agent has been its flat rigid geometry with isocyanate groups positioned at 2 and 4 on a benzene ring. This prevents coupling between two surface amino groups due to steric factors. The reaction between isocyanate and amino group proceeds at room temperature even without the intervention of a catalyst [48]. In the coupling reaction, TDI forms two urethane linkages, one with the surface amino group, and the other with the terminal hydroxyl group of monoacetylated or monomethyl ether of PEG. Reaction between isocyanate and hydroxyl group is comparatively slower at room temperature than with amine, hence we used a small amount of catalyst triethylamine (0.075 g) for this reaction. A correction factor for the weight of TDI was calculated in a blank reaction and was deducted form increase in the weight of final brush polymer in order to estimate the amount of PEG grafted. This is necessary only for lower PEGs and is negligible for higher PEGs. The final product, a fine powder, disperses well in lower alcohols and water just as PS microspheres. Representative SEM photographs of the brushes are shown in Figure 3(a-d). Brush samples retain the shape of original PS microspheres.

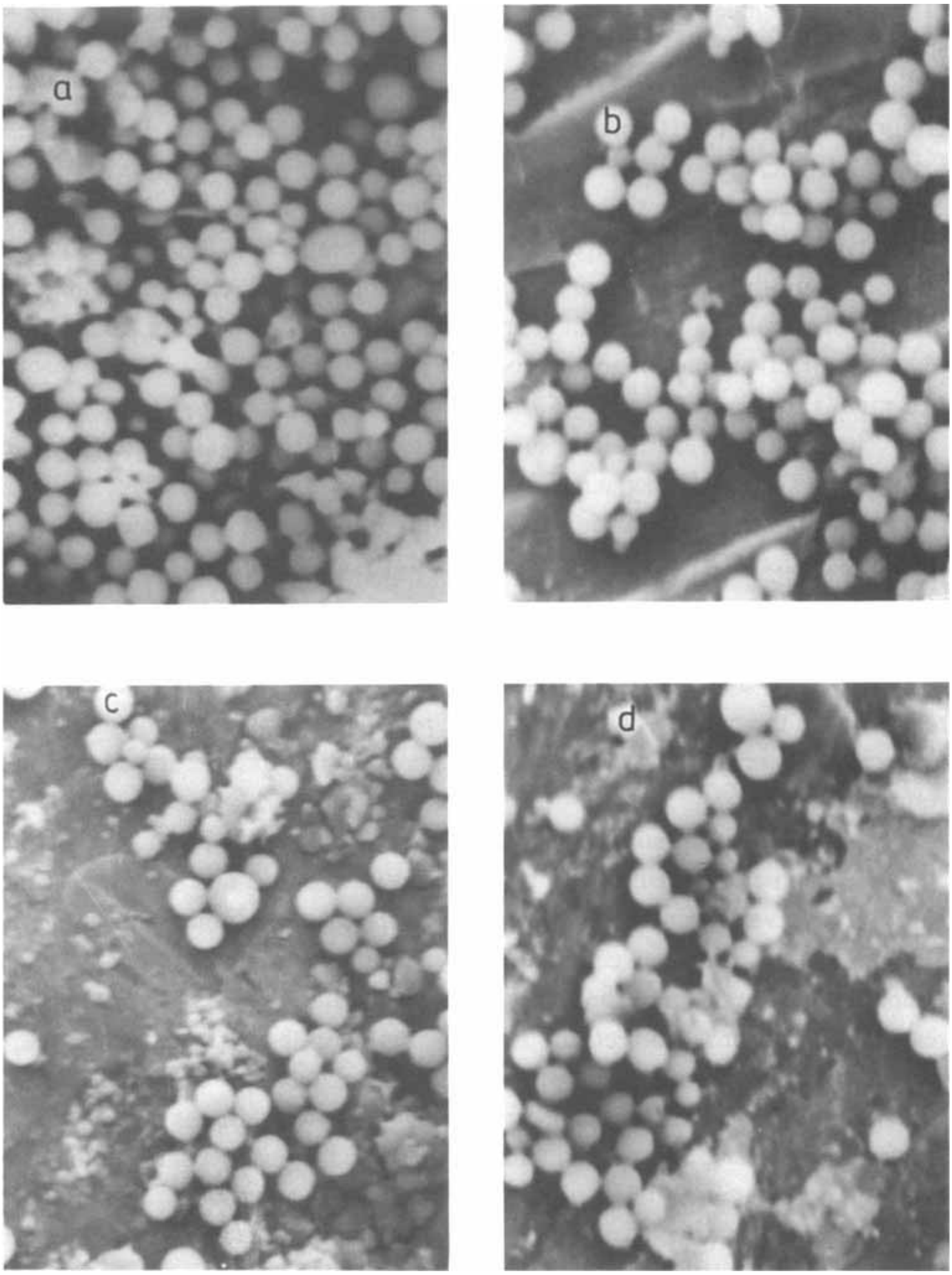


Figure 3. SEM photographs of brush polymers
a) PS-PEG750(A,) b) PS-PEG2500(A2) c)PS-PEG14000 (A4) d) PS-PEG48000 (A5).

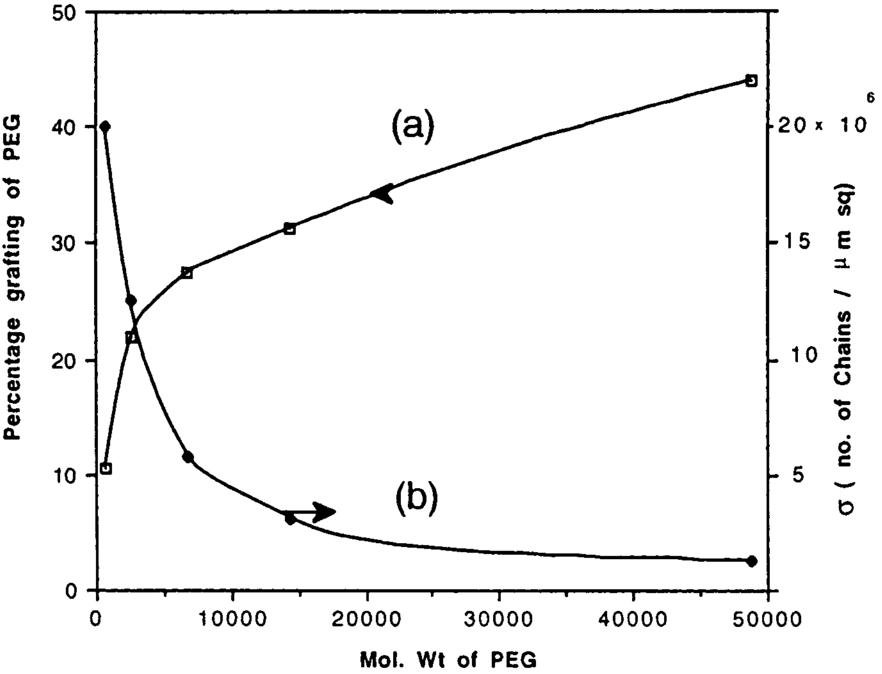


Figure 4. a) Molecular weight of PEG vs. no. of μ moles of PEG grafted b) Dependence of grafting density on molecular weight of PEG.

Figure 4a shows the moles of PEG grafted and 4b number of chains per unit area (σ, the grafting density) as a function of PEG molecular weight. The detailed calculation for σ is given in the Appendix. As the molecular weight of PEG increases, the number of chains grafted onto surface decreases. There could be two equally valid reasons for this, and both may be operative. The terminal hydroxyl group of lower molecular weight PEGs is more reactive because there is less sterical intervention by the ethylene oxide chain. With higher PEGs, the tendency to self-coil increases and the terminal -OH group could get buried inside. Moreover, longer PEG chains could occupy larger areas on the microsphere surface thus masking the surface amino groups. Indeed, Wu *et al.* [28] and Kawaguchi *et al.* [49] have observed that higher PEG's occupy larger surface area on polystyrene microspheres. We observed that the steep decrease in grafting density, with higher PEGs, is in conformity with these reports (Table 2). Grafting poly(dimethyl siloxane) chains onto silica surfaces Auroy *et al.* [10,

TABLE 2.

Sample code	PEG grafted (%)	Molecular weights of PEG's Mw	Mw /Mn	μmoles of PEG grafted per gram of polystyrene	Grafting density σ chains/ [μm]^2
A_1	10.6	750	1.06	140	20x 10^6
A_2	22.0	2500	1.04	86	12.5x 10^6
A_3	27.4	6700	1.02	41	5.8x 10^6
A_4	31.2	14000	1.08	22	3.1x10^6
A_5	44.0	48000	1.04	9	1.3x10^6

11] made a similar observation that, in general, as the molecular weight of the graft increases, distance between the chains also increases. They recorded chain spacing ranging from 29 Å (for M_W= 26,000) to 50 Å (for M_W= 282,000). In the present study values range from 2.5 Å (M_W=750) to 5 Å (for M_W=48000).

We would like to make an observation here. Grafting density σ, of the brush polymer, has been calculated assuming the surface of the microspheres to be smooth and free from pits and crevices. This exercise yields a value of 4.25 m^2/g. However, this may not exactly be the case and the actual surface area available could be several times higher; consequently the actual grafting density could be much lower than envisaged here. Surface area measurements have been reported by several investigators for polystyrene ryficrospheres of varying sizes and porosities. Thus, Lewandowski *et al.* [50] report a value less than 5 m^2/g for slightly porous polystyrene microspheres of 5 μm diameter. Discussing monodisperse porous polymer particles, Cheng *et al.* [51] refer to a value of 0.7m^2/g for polystyrene latex particles of 10 μm diameter. We attempted to determine the surface area of the microspheres from BET isotherm by single point methodin a Micromeritics Pulse Chemisorb unit, model 2700 by nitrogen adsorption at 77K. However due to low resolving power of the instrument we could not obtain a precise value. At present, we don't have the tools to elucidate the fractal geometry of the microsphere surface. Hence, it is more appropriate to treat σ as the apparent grafting density.

CONCLUSION

A simple and efficient method for synthesizing well-defined brush where PEG chains are anchored onto polystyrene microspheres is described. Grafting density σ, can be varied by adjusting the amount of PEG in the reaction medium. It is presumed that the specificity of the reactions between isocyanate and amine is responsible for high surface coverage.

APPENDIX

Calculation of grafting density (σ)

Diameter of the core = $1.4\ \mu m$
Radius of the core = $0.7\ \mu m$
Volume of the core = $4/3\ \pi r^3 = 4/3 \times 3.14(0.7)^3 = 1.436\ \mu m^3$
Density = $11.01 \times 10^{-6}\ \mu g/\mu m^3$
Mass of the core = $1.45 \times 10^{-6}\ \mu g = 1.45 \times 10^{-12} g$
Surface area of the core = $6.154\ \mu m^2$
Surface area for 19 of PS microspheres = $6.154/1.45 \times 10^{-12} = 4.2 \times 10^{-12}\ \mu m^2$

For sample A,

Percentage of PEG 600 grafted = 10.6
No. of moles of PEG grafted = 1.4×10^{-4}
No. of chains of PEG grafted per gram of the core = 8.4×10^{19}
No. of chains per $(\mu m)^2$ = 2×10^{7}
Area per chain in $(\mu m)^2$ = 5×10^{-8}
Area per chain in $(Å)^2$ = 5

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