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Synthesis of dense brush polymers with cleavable grafts[☆]

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Abstract

We report the synthesis and characterization of dense brush polymers with hydrophobic core and cleavable hydrophobic/hydrophilic grafts. Crosslinked PMMA microspheres, nearly monodisperse were synthesized by dispersion polymerization. Acryloyl groups were generated on the surface by a two-step process of transamidation of the ester group of PMMA with ethanolamine and subsequent coupling of the hydroxyl moiety with acryloyl chloride. These surface acryloyl groups functioned as the initiation sites for graft copolymerization with desired monomer (methyl methacrylate, styrene, and acrylamide). The complete structural characterization of the brush polymers with respect to the dimensions of the core, percentage grafting and molecular weight of grafted chains and grafting density has been carried out. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Systems in which polymer chains are terminally anchored onto a surface or at an interface by chemical or physical forces are classified as polymer brushes. The geometrical shape of the anchoring surface gives rise to planar, cylindrical or spherical brushes. Terminal anchorage imposes restrictions on the free movement of the chain leading to a variety of solvent dependent conformations [1,2]. This has generated considerable theoretical interest [3–7] because of its far-reaching technological implications in diverse fields such as colloidal stabilization [8,9], chromatography, adhesion [10], lubrication, microelectronics, chromatography and biocompatibility of artificial organs in medicine [11] and rheology [12].

Brush polymers have two essential structural components: the anchoring surface and the anchored chains. This work focuses on spherical brushes. Qualitatively a spherical brush polymer has the same morphology as a core-shell polymer [13,14]. Reacting end functionalized polymers with appropriate surface sites is one way to synthesize brush polymers [15,16]. Though this method has the inherent advantage of pre selecting macromolecules of desired chain length, there is a severe limitation on the number of chains that can be anchored on the surface. Because of their random coil conformation, the first few chains effectively block the accessibility of further polymer chains to the surface reaction site. Hence the grafting density remains very low. Indeed we adopted this method to synthesize brush polymers with uniform bristle length [17] where surface amino groups of polystyrene microspheres were coupled to hydroxy terminated polyethyleneoxide of desired molecular weight using TDI, (toluene 2,4-diisocyanate) as the coupling agent. Though clean and fast, the number of PEG chains linked decreased with increasing molecular weight of the PEO. For example,

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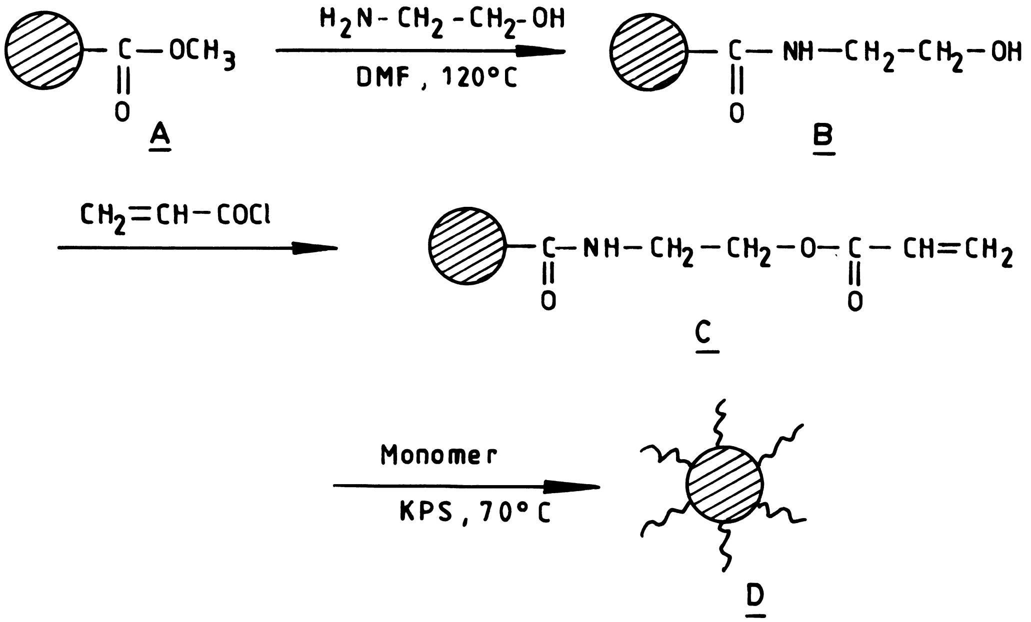
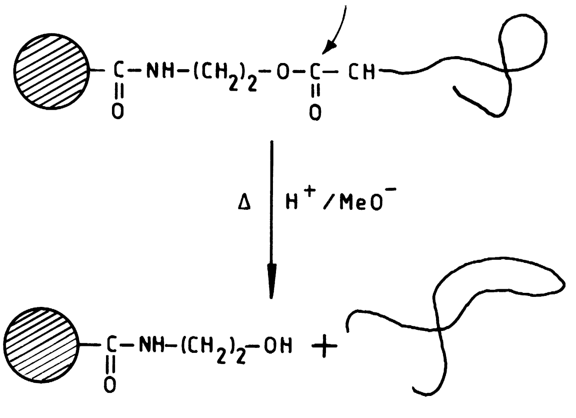


Scheme 1. Synthetic route for the brush polymers: (A) PMMA core, (B) ethanolamine modified PMMA, (C) acryloyl chloride modified PMMA, (D) brush polymer.

the grafting density for PEG 750 was four times that of PEG 5000.

Hence, if dense surface coverage is desired the best technique is free radical graft copolymerization because the chain initiation and propagation are done by monomer units [18–21]. But except in rare cases [19,20] the grafted chains are not easily cleavable from the surface because the linkage is through a C–C bond. This makes it impossible to determine the dimensions of grafted chain, which is an essential structural parameter of the brush polymer. We felt a method, which promised high surface coverage with the concomitant cleavability of the grafted chains for structural evaluation would solve multiple issues.



Scheme 2. Cleaving the grafts from the anchoring surface.

Our approach to achieve high surface coverage with cleavability of the grafts is shown in Scheme 1. This surface modification method allows the grafting of any desired vinylic monomer. PMMA microspheres were functionalized by transamidation with ethanolamine, which replaces the ester methoxy group with amide and provide free hydroxyl groups on the other end. Acryloyl chloride reacts with the free hydroxyl group forming an ester group. The terminal double bond formed is the initiation site for the graft polymerization. Substituted amides (–CONRR′) are not easily hydrolyzed by acid or alkali [22]. On the other hand, the double bond is linked through an ester bond which is susceptible to acid/alkaline hydrolysis [23]. The chemistry for cleaving the long polymer chain from the microsphere surface is shown in Scheme 2.

2. Experimental

2.1. Materials

The chemicals used were methylmethacrylate (MMA), polyvinylpyrrolidone (PVP) and azobisisobutyronitile (AIBN) (Fluka), ethanolamine, styrene, acrylic acid, hydroquinone, Tetrahydrofuran (HPLC grade) (Merck), potassium persulphate, benzoyl chloride, triethylamine, sodium hydrogen carbonate, acrylamide, (Loba Chem, Mumbai). Styrene and MMA were first washed with 5% sodium hydroxide solution and then with water, dried over calcium hydride (Aldrich) and distilled under reduced pressure. Acryloyl chloride was prepared by known procedure [24]. The solvents used were of reagent grade and distilled just before use. Doubly distilled water was used for all the experiments.

2.2. Synthetic procedures

The following steps are involved: synthesis of crosslinked microspheres of PMMA (the core), modification of the microspheres with ethanolamine and acryloyl chloride, in order to create a cleavable group and finally surface grafting with desired monomers.

2.2.1. Synthesis of the crosslinked PMMA microspheres

Crosslinked PMMA microspheres were prepared by the dispersion polymerization of MMA. In a typical experiment MMA (50 g), methanol (495 ml), water (49.5 ml), PVP (11.0 g), divinyl benzene (0.200 g), and AIBN (0.750 g) were used. Reaction was carried out in nitrogen atmosphere at 60°C for 48 h under continuous stirring. The product obtained was washed repeatedly by sedimentation/redispersion process in methanol to remove any PVP adhered to the surface of the microspheres and finally dried in vacuum at 50°C. SEM photographs of the microspheres were taken.

2.2.2. Modification of microspheres

2.2.2.1. Transamidation with ethanolamine. Crosslinked PMMA microspheres (20 g) were swollen in excess DMF (100 ml) at room temperature for 12 h. Transamidation reaction with ethanolamine (25 g) was carried out at 120°C for 4 h with efficient stirring. The microspheres were washed with generous volumes of water first and later with methanol and filtered. The product was then subjected to soxhlet extraction with methanol for 48 h, finally dried in vacuum at 50°C. IR spectra of the modified microspheres were recorded. Hydroxyl groups generated were estimated according to ASTM procedures [25].

2.2.2.2. Derivatization with acryloyl chloride. Ethanolamine modified PMMA microspheres (5 g) were swollen in dry dichloromethane (25 ml) and cooled to 0°C. Acryloyl chloride (3.5 g) and triethylamine (5.8 g) were added drop wise under stirring. The reaction was allowed to go on for 6 h at 0°C and then for further 6 h at room temperature. The product was washed in sequence with 0.1 N HCl, saturated sodium hydrogen carbonate solution and then with water followed by methanol and finally dried in vacuum at room temperature (30°C). IR spectrum of the modified product was recorded. The hydroxyl content of the sample was again determined as above.

2.2.3. Synthesis of brush polymers

Polymerization was carried out in a three-necked flask under nitrogen atmosphere. Acryloyl modified PMMA microspheres (1.0 g) together with the desired monomer (MMA or styrene) were dispersed in double distilled water (80 ml), with potassium persulphate (0.64 g) as initiator. Reaction was carried out at 70°C for 6 h then quenched with hydroquinone and cooled to ambient temperature. The product was filtered, washed with water and then with methanol and dried. It was then subjected to soxhlet extraction with benzene for 48 h to remove homopolymer formed during the reaction. Soxhlet extraction was continued until the product registered constant weight.

The procedure for PMMA-g-PAam was essentially the same except that the solvent system used was benzene/water (3:1) and initiator AIBN. The product was subjected to soxhlet extraction with water for 48 h to remove homopolymer PAam, then rinsed with acetone and dried in vacuum at 50°C.

2.2.4. Analysis of brush polymers

PMMA-g-PMMA, PMMA-g-PS were hydrolyzed by refluxing in 10% methanolic KOH for 96 h. The product was filtered, washed with water, dried and subsequently subjected to soxhlet extraction with benzene for 48 h. The extract was concentrated and the graft precipitated with methanol and dried in vacuum at 50°C. The PMMA-g-PAam brush was hydrolyzed by refluxing in 5 M sulfuric acid for 96 h. This could hydrolyze the amide groups in polyacrylamide to acid groups. After cooling, the reaction mixture was filtered and extracted the residue with water for 48 h. The insoluble part was rinsed with acetone and dried in vacuum at 50°C and weight recorded. The aqueous extract was concentrated in rotary evaporator, and poured into acetone to precipitate partially hydrolyzed polyacrylamide. The dissolution and precipitation was done twice and the product dried in vacuum at 50°C.

The molecular weights of PMMA and PS were determined by gel permeation chromatography using waters microstyragel columns in series (10^2, 10^3, 10^4, 10^5 Å). Tetrahydrofuran was used as eluent with a flow rate of 1 ml/min. The molecular weight of partially hydrolyzed polyacrylamide was determined by dilute solution viscosity in 1 M NaCl [26].

3. Results and discussion

3.1. Core

Crosslinked PMMA microspheres of uniform size were prepared by the dispersion polymerization of MMA in methanol using divinyl benzene as the crosslinker by the procedure reported in literature [27]. Average size of the microspheres was estimated from the SEM photographs (Fig. 1) using the equations [28]

$$d_n = \sum_{i=1}^{N} \frac{d_i}{N}$$

$$d_w = \frac{\sum_{i=1}^{N} d_i^4}{\sum_{i=1}^{N} d_i^3}$$

$$\mathrm{PDI} = \frac{d_n}{d_w}$$

where d_n is number average diameter and d_w is weight average diameter, N is the number of particles, d_i is diameter of the ith particle and PDI is polydispersity index. Diameters of about 300 particles were measured and used for the calculation. The number average diameter of the particle obtained is 0.81 μm. Polydispersity index of the microspheres was calculated to be 1.07. The density of the microspheres obtained from the measurements is 1.170 g/cm^3. The IR spectrum of the synthesized PMMA microspheres is shown in the Fig. 2a.

Microspheres were functionalized by transamidation with ethanolamine, which replaces ester methoxy

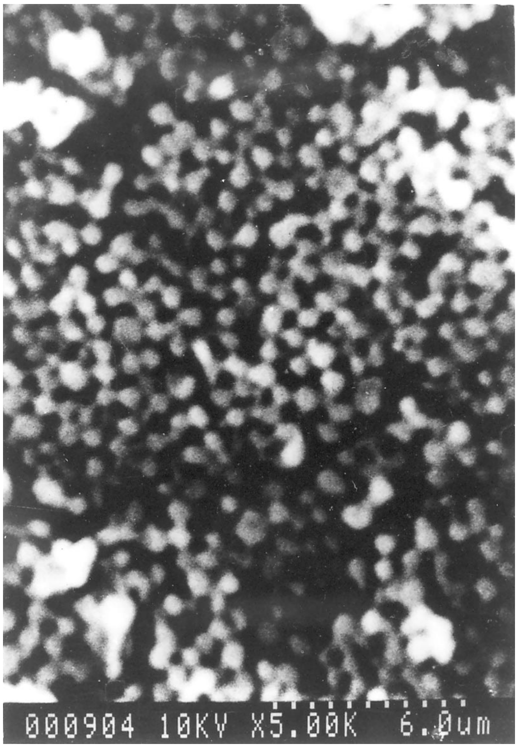


Fig. 1. SEM Photographs of PMMA microspheres

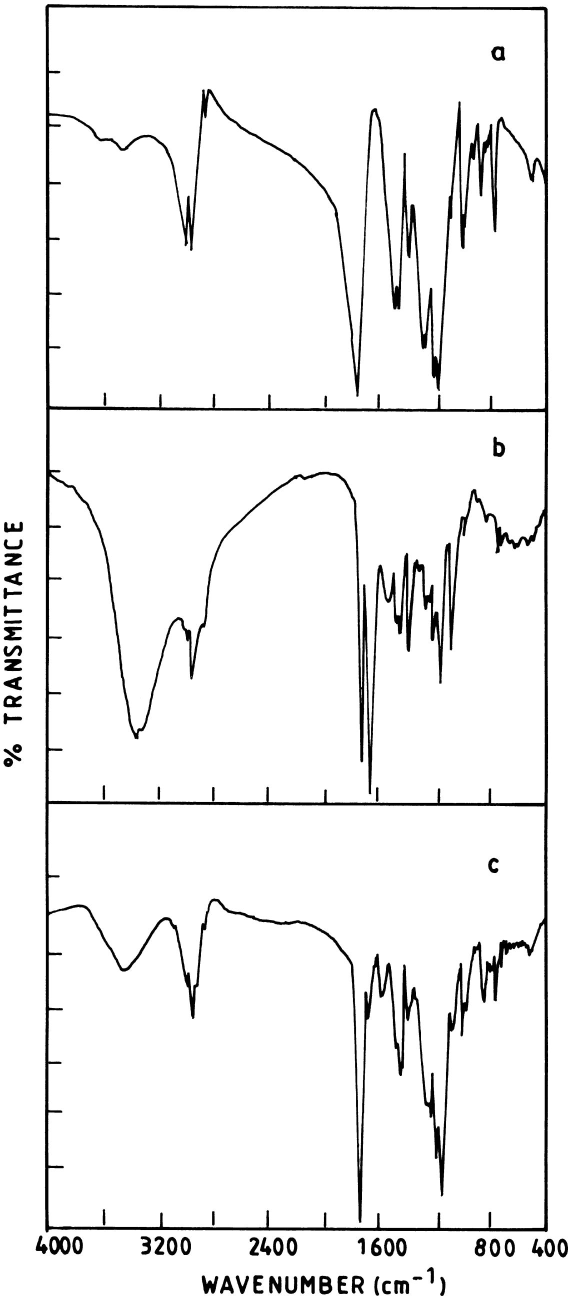


Fig. 2. IR spectra of (a) PMMA, (b) ethanolamine modified PMMA and (c) acryloyl chloride modified PMMA.

Table 1
Structural details of the brush polymers

Brush polymer system	Percentage grafting (wt%)	Average M_w of grafts	Grafting density (σ)		
			μmole/g	μmole/m^2	Area/site (A sq/site)
PMMA-g-PMMA	131	1.08×10^5 (2.54)[a]	12	2.0	90
PMMA-g-PS	78	2.66×10^5 (2.68)	3.0	0.5	380
PMMA-g-PAam	45	5.16×10^3[b]	87	13	13

[a] Polydispersity M_w/M_n from GPC.
[b] M_v by viscosity.

group with amide and provide free hydroxyl groups on the other end [29].

$$-COOCH_3 + H_2N-R-OH \rightarrow -CONHR-OH + CH_3OH$$

Broad absorption in the region 3200–3600 cm^{-1} for hydroxyl group and amide hydrogen stretching and a strong absorption at 1670 cm^{-1} for amide I band in IR spectrum of ethanolamine modified microspheres are indicative of the presence of amide and hydroxyl groups (Fig. 2b). The hydroxyl content of the modified core determined by ASTM methods yielded a value 3.3 mmol/g. This value is comparable with that of Yu et al. [30] who recorded 2.5 mmol of amide groups per gram of the sample for a transamidation experiment of polymethylacrylate with *n*-hexylamine at 118°C in DMF for 4 h.

Acryloyl chloride reacts with the free hydroxyl group forming an ester group. The terminal double bond formed is the initiation site for the graft polymerization. We used excess of acryloyl chloride for this reaction to ensure maximum coupling. IR spectrum of the acryloyl derivatized microspheres shows absorption for double bond stretching at 1623 cm^{-1} and an additional peak at 3027 cm^{-1} for ethylinic proton stretching (Fig. 2c)

From the hydroxyl content of the final product and reactant, we estimated the amount of acryloyl groups introduced on the PMMA microspheres to be 2.3×10^{-3} mol/g indicating 70% of the hydroxyl groups has been derivatized with acryloyl chloride.

3.2. Bristles

Surface acryloyl groups permitted the graft copolymerization of a wide variety of unsaturated monomers. We adopted suspension polymerization technique for graft copolymerizing styrene and methyl methacrylate onto the microspheres as reported in the literature [18,31].

Percentage of grafting was calculated as follows (Table 1)

$$\text{Percentage of grafting} = \frac{W_f - W_i}{W_i}$$

where W_f is the weight of the sample after grafting and W_i is the weight of the sample before grafting. In an earlier study, we had reported that desired percentage of grafting can be obtained by controlling the initiator and monomer concentrations in the initial feed. In the present study, the weight percent of St and MMA in the feed with respect to the matrix were roughly the same about 3:1. Under the conditions of this experiment, the PMMA microspheres are in the glassy state, since the temperature is only 70°C and water is a nonplasticizing solvent for PMMA. This, together with the fact that KPS, a water soluble initiator is used, would keep the internal polymerization relatively small. We repeat our earlier observation that hydrophobic monomers yield higher percentages of grafting than hydrophilic monomers [32]. The lower percentage of grafting of acrylamide could also be due to lesser amount of the monomer in the feed (1:1)

Substituted amides (–CONRR′) are not easily hydrolyzed by acid or alkali [22]. This is because, the initial step is the nucleophilic addition to carbonyl group and amines or amine anions are poor leaving groups. On the other hand, the double bond is linked through an ester bond which is susceptible to acid/alkaline hydrolysis [23]. To prove this point we modified the PMMA microspheres, first with 1,6-diamino hexane and then with acryloyl chloride and then subjected

Table 2
Cleavage results

Brush system	Efficiency of cleaving (%)	
	A[a]	B[b]
PMMA-g-PMMA	92	71
PMMA-g-PS	86	84
PMMA-g-PAam	89	Not determined

[a] Using alkali/acid.
[b] Transesterification.

them to graft copolymerization with MMA and St to get PMMA-g-PMMA and PMMA-g-PS, respectively. Here both the linkages formed were amide group. Even after 6 days of refluxing in methanolic KOH the percentage of cleavage was less than 10%.

With ethanolamine as the spacer group between the surface and the acrylic group, more than 90% of grafted polymer chains could be cleaved from the core. We have also done the cleavage of bristles of PMMA-g-PMMA and PMMA-g-PS brushes using a trans esterification method reported by Prucker et al. [19] using methanol and *p*-toluene sulphonic acid as catalyst in toluene for 48 h. The cleavage details are given in the Table 2.

The average molecular weights of the cleaved PMMA and PS chains determined by GPC were high ($M_w > 10^5$). GPC profiles show polydispersity of 2.54 for PMMA and 2.68 for PS. This observation has been made by others earlier [19,20]. In any case free radical polymerizations yield dispersity values ranging from 1.5 to 3.0. A recent study by Wittmer et al. [33] highlights the differences in the growth pattern of chains formed at interfaces as against those generated in solution. It is possible that polymer chains formed at the surface could have a much higher polydispersity compared to the same reaction occurring in solution. In conventional solution polymerization all the chains are uniformly distributed throughout the solution. The terminally anchored growing chains experience mobility constraints because they are confined to a small volume in close proximity to the surface. This could hamper the frequency with which the growing terminal encounters a monomer unit resulting in a broad distribution of molecular weight.

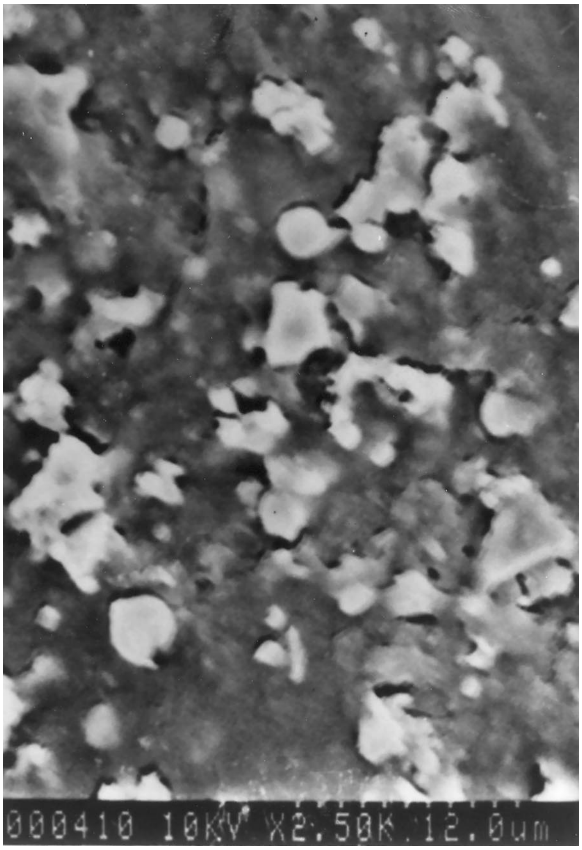


Fig. 3. SEM photograph of PMMA-g-PMMA brush polymer.

For any brush polymer system grafting density (σ) is an important factor which determines the properties of the system. Grafting density can be defined as μmoles of polymer grafted per gram (μmol/g) or per square meter (μmol/m^2) of the matrix. From the size and density of the core, percentage of grafting, molecular weight of the grafts we calculated the grafting density (μmol/g). Results are given in Table 1. Grafting density is high for all three brushes synthesized consistent with the values reported in the literature for similar systems [19,21]. In an earlier comprehensive study, we had shown that the number of chains anchored and their chain length somehow depended on the chemistry of the monomer [32]. Hydrophobic monomers tend to give lesser no of grafting sites with high molecular weight. Whereas the reverse is true with hydrophilic monomers. We repeat this observation in the present study too.

The SEM pictures of the grafted sample indicate the microspheres have lost their initial spherical shape and have a matted appearance (Fig. 3). This is a natural consequence of grafting. At high grafting densities the system will assume a brush like structure, at lower graft densities the chains will collapse on the anchoring surface; in either case the microspheres would lose shape.

4. Conclusions

We demonstrate that it is possible to synthesize cleavable brush polymers with desired chemistry and high surface coverage.

Acknowledgements

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