8766 *J. Am. Chem. Soc.* **1999,** *121,* 8766−8770

Photochemical Attachment of Polymer Films to Solid Surfaces via Monolayers of Benzophenone Derivatives

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Received March 23, 1999

Abstract: We report a simple and yet effective way to photochemically attach thin polymeric layers to solid surfaces. The system is based on a photoreactive benzophenone derivative that is bound to SiO_2 surfaces via a silane anchor. This substrate is then covered with a polymer film that is reacted with the benzophenone moieties by illumination with UV light ($\lambda > 340$ nm). As a result of the photochemical reaction, a thin layer of the polymer is covalently bound to the surface. Nonattached polymer is removed by extraction. As examples, we have successfully attached thin layers of poly(styrene) and poly(ethyloxazoline). The thickness of the layer is a function of the illumination time and the molecular weight of the polymer. The film thickness increases linearly with the radius of gyration of the polymers used for attachment. Using this system, we were able to photochemically attach up to 16 nm thick films of poly(styrene).

Introduction

The covalent attachment of ultrathin films of polymers to a solid substrate is often desirable to enhance the stability of the films against solvents and displacement reagents (e.g., water for hydrophilic surfaces). As a consequence of this need, numerous *grafting* protocols have been developed.[1−13] The most common procedures use polymers that carry functional groups at one or both chain ends or as pendent side groups that are suitable for binding to the surface. All these strategies, however, sometimes require extensive synthetic efforts as the preparation of functionalized polymers is not an easy task. Also, one cannot easily introduce other functional groups to the polymer film because these groups must be inert against the often very reactive anchor groups.

Based on these observations, we were looking for a fast and simple way to covalently attach ultrathin physisorbed layers of polymers by subsequent chemical reactions. The procedure of choice would ideally be independent of the chemical nature of the polymer. This goal rules out any chemistry based on functional groups as these procedures would inherently restrict the number of polymers suitable for attachment. Hence, we designed a system that is based on a light-induced reaction between a photoreactive group on a surface and C−H bonds in the backbone or in side groups of a polymeric overcoat. Our system is schematically depicted in Figure 1. The photoreactive group used here is the benzophenone moiety. This system was chosen because the photochemistry of this compound is well-known and because it attaches to C−H bonds in a wide range of different chemical environments.[14−20] Another advantage of this and other photoreactive groups is the chemical inertness of these materials in the absence of light. A detailed description of the photochemistry of benzophenone can be found in the general literature on photochemistry,[20] but the reader is also referred to a review article by Dormán and Prestwich[19] where its use for biochemical problems is also discussed. To our knowledge, only two comparable systems exist in the literature. One uses monolayers of nitrene that can be photochemically linked to the hydroxyl groups of dextrans.[21] The other one uses benzophenone modified polymers for the photochemical attachment of these materials to polymeric substrates.[22] Although this technique might be considered the "reversed approach" as

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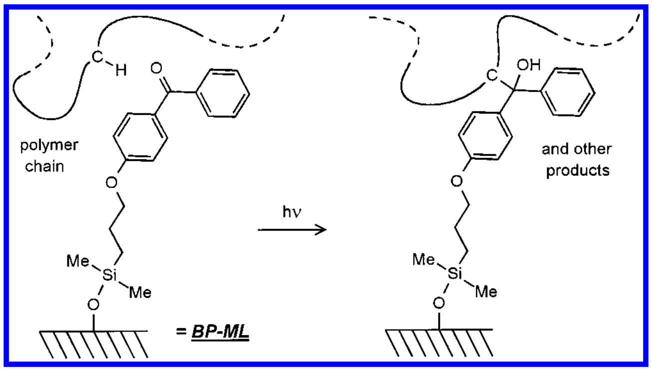

Figure 1. Schematic representation of the photochemical attachment of polymer chains to solid surfaces via illumination of polymer-covered monolayers of a benzophenone derivative (BP-ML).

compared to our system, it also differs significantly as the method with the benzophenone-modified polymer yields surface-attached polymer networks: Many photoreactive groups of the polymer do not bind to the surface but to other chains of the film-forming material.

This paper describes the synthesis of the photocoupling agent, its immobilization on SiO_2 surfaces, and the subsequent attachment of poly(styrene) (PS) and poly(ethyloxazoline) (PEOX) by illumination of spin-cast layers of these polymers on benzophenone-modified surfaces followed by thorough extraction of nonbound chains. The two polymers were chosen because they represent examples of very hydrophobic (PS) and hydrophilic (PEOX) polymers and, therefore, demonstrate the versatility of the system. In addition, we describe a number of reference experiments that support the reaction pathway proposed in Figure 1.

Experimental Section

Materials. Toluene was distilled from molten sodium using benzophenone as indicator and triethylamine was distilled from calcium hydride. Both were stored under a nitrogen atmosphere. Dimethyl chlorosilane was distilled and then immediately used for hydrosilation. All other chemicals and solvents (HPLC grade) were used as received. All reactions that involved chlorosilanes were performed under an atmosphere of dry argon.

Synthesis of 4-Allyloxybenzophenone (1). This compound was synthesized by standard procedures.[23] In a typical run, 39.6 g (0.2 mol) 4-hydroxybenzophenone and 26.6 g (0.22 mol) allyl bromide were dissolved in 120 mL of acetone and 28 g of potassium carbonate was added. The mixture was heated to reflux for 8 h and then cooled to room temperature. Water (80 mL) was added and the resulting solution was extracted twice with 100 mL of diethyl ether. The combined organic phases were washed twice with 100 mL of aqueous NaOH (10%) and dried over Na_2SO_4, and the solvent was evaporated. The resulting, slightly yellowish raw product was recrystallized from methanol to yield 42 g (90%) of **1**. FTIR (KBr): 3081, 3059, 3022, 2939, 2865, 1650, 1600 cm^{-1}. ^1H NMR ($CDCl_3$, δ in ppm): 4.6 (m, 2H, $OC\mathit{H}_2$), 5.3−5.5 (m, 2H, $C\mathit{H}_2{=}$), 6.1 (m, 1H, $={C}\mathit{H}-$), 6.9−7.9 (various m, 9H, $C-H_{arom.}$). ^{13}C NMR ($CDCl_3$, δ in ppm): 69 ($O\mathit{C}H_2$), 162 ($O\mathit{C}_{arom}$), 195 ($\mathit{C}{=}O$), 110−140 (9 peaks, remaining C_{arom} and $-\mathit{C}H{=}$).

Synthesis of 4-(3′-Chlorodimethylsilyl)propyloxybenzophenone (2). Standard hydrosilation procedures[24,25] were employed for the synthesis of this compound. Typically, 2 g of **1** was suspended in ca. 20 mL of freshly distilled dimethyl chlorosilane. Pt−C (10 mg, 10% Pt) was added and the mixture was refluxed for 5 h. The excess chlorosilane was removed in vacuo yielding the desired product **2** in quantitative yields as an oil. FTIR (film): 3059, 3024, 2940, 2875, 1651, 1600 cm^{-1}. ^1H NMR ($CDCl_3$, δ in ppm): 0.3 (s, 6H, $SiC\mathit{H}_3$), 0.9 (m, 2H, $SiC\mathit{H}_2$), 1.9 (m, 2H, $CH_2\ C\mathit{H}_2\ CH_2$), 3.9 (t, 2H, $OC\mathit{H}_2$), 6.9−7.9 (various m, 9H, $C-H_{arom}$). ^{13}C NMR ($CDCl_3$, δ in ppm): 1 ($Si\mathit{C}H_3$), 13 ($Si\mathit{C}H_2$), 21 ($CH_2\mathit{C}H_2\ CH_2$), 68 ($O\mathit{C}H_2$), 112−137 (6 peaks, C_{arom}), 161 ($O\mathit{C}_{arom}$), 194 ($\mathit{C}{=}O$). The catalyst was removed by filtration of a solution of **2** in toluene. This solution was then directly used for the surface modification.

Immobilization of 2 on SiO_2 Surfaces. The silane **2** was immobilized on the SiO_2 surface of a silicon wafer at room temperature from toluene solutions using Et_3N as catalyst and acid scavenger. The solutions with the substrates were left to stand overnight. The samples were then cleaned by rinsing extensively with chloroform. Film thicknesses were determined by ellipsometry. Typically, values of 1.0 ± 0.1 nm were obtained when a refractive index of the layer of $n = 1.5$ was assumed.

Preparation of the Polymer Layers. Thick overcoats (>100 nm) of the polymers were prepared by spin-casting solutions of the polymers at a typical spin speed of 2000 rpm for 1 min. Typical solvents were toluene for PS and methanol for PEOX, and concentrations of 10 mg mL^{-1} were employed. The samples were dried in air and used directly for illumination experiments. These experiments were performed at room temperature using a high-pressure mercury UV lamp (500W, Oriel). A water filter (8 cm) was used to remove IR light from the beam, and a dichroic mirror eliminated short wavelengths with $\lambda <$ 340 nm. The integral light intensity at the sample location was 100 mW cm^{-2}. After illumination for the desired period of time, we extracted the samples in a Soxhlet apparatus with good solvent (PS: toluene; PEOX: methanol) for at least 10 h to remove nonbonded polymer. The thicknesses of the resulting polymer layers were again determined by ellipsometry assuming the respective bulk refractive indices of the polymers (PS: $n = 1.59$; PEOX: $n = 1.52$).

Results and Discussion

The benzophenone silane **2** can be synthesized in high yields following simple procedures as in Figure 2. The first step is a Williamson ether synthesis of 4-allyloxybenzophenone **1** from 4-hydroxybenzophenone and allyl bromide. Compound **1** can then be hydrosilated with dimethyl chlorosilane using platinum on charcoal (Pt−C, 10% Pt) as catalyst.[24,25] The more commonly used catalyst for hydrosilation reactions, hexachloroplatinic acid (H_2PtCl_6), is not suitable for this compound as it also leads to the reduction of the benzophenone carbonyl unit to a methylene moiety. Such reactions of carbonyl groups are known in the literature.[24]

The silane **2** can be immobilized on SiO_2 surfaces by immersing an appropriate substrate into a dilute (typically 10^{-3} M) solution of **2** in toluene. A few drops of dry Et_3N are added to bind the resulting HCl and to act as a catalyst.[26−28] This procedure yields monolayers of the benzophenone silane (BP-ML) of a typical thickness of ca. 1 nm.

The polymer overcoats were then deposited by spin-coating. We typically coat rather thick films of $h > 100$ nm to avoid any influence of the thickness of this film on the final thickness of the covalently bound layer. Also, it is obvious that thick overcoats should be more homogeneous and essentially pinhole free. These layers were then illuminated with UV light. Benzophenone and many of its derivatives show an absorption of UV light around 345 nm caused by a n,π^* transition in the

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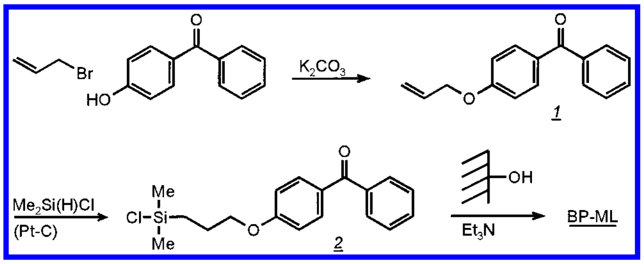

Figure 2. Synthesis of the benzophenone silane **2** and its immobilization on SiO_2 surfaces.

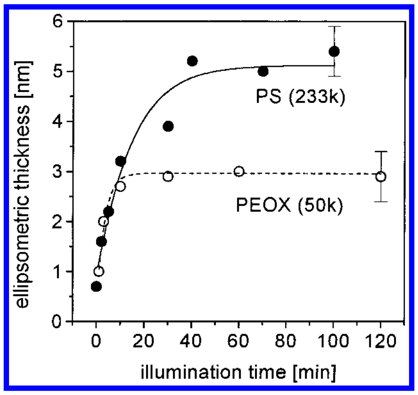

Figure 3. Influence of the illumination time on the photochemical attachment of PS and PEOX to benzophenone monolayers (BP-ML). The integral light intensity was adjusted to 100 mW cm^{-2}.

carbonyl group. The resulting triplet is biradical in nature and will therefore react with groups in its vicinity or return to the electronic ground state mainly by phosphorescence.[20] The most prominent reaction of a benzophenone triplet is schematically depicted in Figure 1. In the first step of this reaction the oxygen of the carbonyl group abstracts a hydrogen atom from the reaction partner leaving behind two radicals , at the previous carbonyl carbon and the carbon of the other molecule, that eventually recombine. Figure 1 demonstrates that, in our case, the attachment of the benzophenone or its carbonyl group to a polymer chain also leads to the covalent attachment of this chain to the surface.

We have performed various sets of experiments each for PS and PEOX to study this procedure for the photochemical attachment of thin polymer coatings to solid surfaces. All experiments were carried out at comparable light intensities. In the first set of experiments, we varied the illumination times of PS and PEOX layers deposited on benzophenone-modified silicon wafers. The molecular weights of the polymers used in these studies were 233000 g mol^{-1} (PS) and 50000 g mol^{-1} (PEOX). The illumination times were varied between 5 min and 2 h. After that the samples were rigorously extracted with toluene (PS) or methanol (PEOX) in a Soxhlet apparatus for at least 10 h to remove nonbonded chains. We found that the extractions were necessary because simple rinsing procedures are not sufficient to wash away all nonbound chains. The thicknesses determined after only a few minutes of rinsing were higher than the respective values obtained after extraction. Also, the scattering of the data was much more pronounced if the samples were only rinsed. This observation may essentially be due to entanglements of nonbound chains with those that are attached to the surfaces.

Figure 3 shows the results of the ellipsometric measurements of the film thicknesses after extraction as a function of illumination time. For each polymer the thickness of the bound layer first increases and then levels off to reach a constant value of 5 nm for PS and 3 nm for PEOX. In both cases these saturation values are reached after about 10−20 min of illumination under the described conditions. The differences between the polymers may be due to the different molecular weights used in this study, although other factors may also be of some importance. One could, for example, envisage different conformations of the two types of polymers directly at the interface with the substrate due to different interactions between the benzophenone layers and the polymers. Also, there could be differences in the photochemistry for these polymers, as it is known, for example, that hydrogen atoms on aromatic rings (as those of the phenyl rings of PS) are less easily abstracted by benzophenone than those in aliphatic environments.[18] Additionally, in the case of PEOX it should be noted that electron-transfer reactions of the benzophenone triplet often occur in the presence of nitrogen atoms.[19,20] These reactions will not necessarily lead to the attachment of the polymer chain to the benzophenone monolayer.

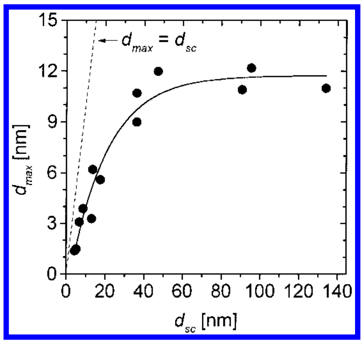

Figure 4. Influence of the thickness, d_{sc}, of the spin-cast layer on the saturation thickness d_{max} after 30 min of illumination followed by extraction; PS, $M_w = 1.3 \times 10^6$ g mol^{-1}, integral light intensity 100 mW cm^{-2}. The dotted line indicates the reference case of complete attachment.

To ensure that this film formation is indeed due to the light-induced coupling of the surface benzophenone groups to the polymer chains of the physisorbed films, we performed two sets of reference experiments. In the first set, we simply illuminated spin-cast PS and PEOX layers deposited directly on unmodified silicon wafers. In the absence of the benzophenone layer, no coupling should occur. Indeed, even after prolonged illumination times (2 h) we were able to wash all polymer off the surfaces by means of Soxhlet extraction with good solvent (toluene for PS and methanol for PEOX). In most cases, even simple rinsing procedures were sufficient to remove the polymer layers from the surfaces. This clearly demonstrates that the observed film formation based on this benzophenone attachment chemistry is due to the light-induced coupling between the two layers and cannot be caused by side reactions such as cross-linking. Also, spin-cast layers of both polymers could be easily washed away from benzophenone modified silicon wafers that were *not* illuminated.

In another set of experiments, we investigated the influence of the thickness of the spin-cast layer on the thickness of the resulting bound layer after illumination and extraction. Here, we used poly(styrene) with $M_w = 1.3 \times 10^6$ g mol^{-1} and prepared spin-cast layers with thicknesses ranging from 6 to 140 nm. The results are shown in Figure 4, where d_{sc} denotes the thickness of the spin-cast layer and d_{max} stands for the thickness of the covalently attached PS layer after 30 min of illumination followed by Soxhlet extraction. The dotted line indicates the reference case of complete attachment of the film which is not expected. The thickness of the attached layer is always smaller than the starting thickness after spin-coating even for very thin films. Initially about half of the polymer overcoat

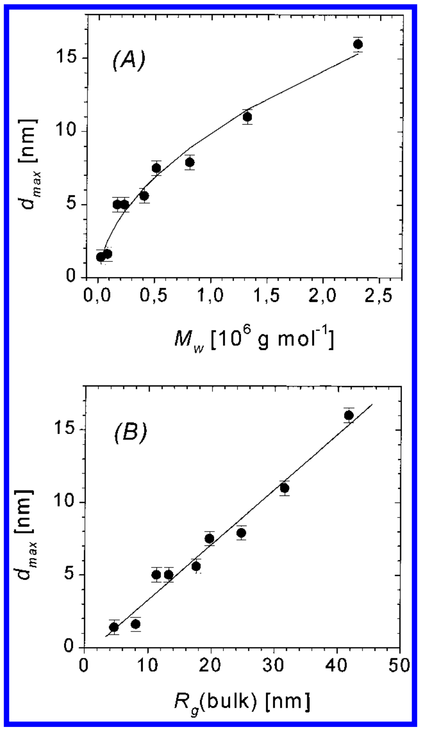

Figure 5. Influence of the chain dimensions on the photochemical attachment of PS to benzophenone monolayers. Plot A shows the dependency of the maximum film thickness on the molecular weight of the polymers. Plot B shows the same data as in plot A but recalculated for the bulk radii of gyration, R_g, according to eq 1. The samples were illuminated for 30 min at an integral light intensity of 100 mW cm^{-2}.

can be attached via the benzophenone units on the surface. Soon, however, the curve levels off at about 11.5 nm for this particular poly(styrene) with a rather high molecular weight.

It is rather obvious from the experiments described so far that the molecular weight of the polymers used for film preformation is a crucial parameter for this attachment chemistry. Therefore, we studied this influence and again selected an illumination time of 30 min which was found to be fully sufficient to reach the saturation thickness d_{max}. For PS we varied the molecular weight over a range from 30000 to 1500000 g mol^{-1}; for PEOX two samples with 50000 and 500000 g mol^{-1} were used. Again, the samples were extracted after illumination, and the thicknesses were determined by ellipsometry.

The results for PS are plotted in Figure 5A. The values clearly indicate that the thickness d_{max} that can be obtained by this method increases with increasing molecular weight of the polymers used for film formation. This becomes even more obvious if the data are plotted as a function of the bulk radius of gyration (R_g) of the polymers, as shown in Figure 5B. Here, we find a linear relationship between d_{max} and R_g. The R_g values given there were calculated from the weight average molecular weight M_w according to eq 1:[29,30]

$$R_g = 0.0275\sqrt{M_w}\ (\text{in nm}) \qquad (1)$$

For the two PEOX molecular weights that we tested, we qualitatively observed a similar molecular weight dependence; films prepared from $M_n = 50000$ g mol^{-1} yielded saturation thicknesses of 3 nm whereas 7.2 nm was obtained from samples made from PEOX with $M_n = 500000$ g mol^{-1}.

The linear relationship between the obtained thickness and the coil dimensions of the polymers is, of course, not surprising as it is entirely consistent with most of the polymer coils being in their unperturbed Gaussian conformation. The bound thickness will be restricted to coils having contact with the benzophenone-modified substrate and, hence, chains with their center of gravity being further away from the surface than R_g will not be attached. This argument is further substantiated if we reinvestigate the dependence of the bound thickness d_{max} on the thickness d_{sc} of the spun-cast layer as presented earlier in Figure 4. For the PS used for these experiments with $M_w = 1.3 \times 10^6$ g mol^{-1} we found that d_{max} no longer increases when spun-cast films with thicknesses of d_{sc} higher than about 30−40 nm are illuminated. This range compares rather well with the $R_g = 31$ nm of this particular PS. Again, we recognize that chains inside the spun-cast layer that are not in contact with the surface cannot be attached. Hence, it is not surprising that the curve shown in Figure 4 levels off at a value for d_{sc} that is related to the coil dimensions of the polymer used for attachment.

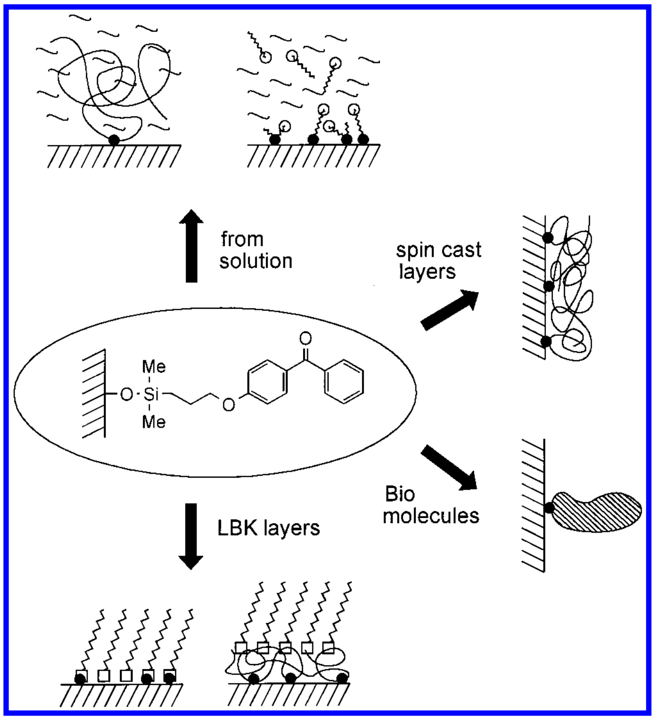

Figure 6. Possible methods for the photochemical immobilization of ultrathin organic or polymeric films using monolayers of benzophenone derivatives.

Conclusions

In this paper we introduce a new way to stabilize thin polymer films by photochemical attachment via monolayers of a photoreactive group. The silane that carries this group can be readily synthesized from simple chemicals and forms monolayers that are typical for structurally comparable compounds. Molecules of subsequently deposited layers of polymers, which are in direct contact with the surface, can be bound to the benzophenone-modified substrate by illumination with UV light of appropriate wavelength. Typically, several nanometers of the polymeric overcoat can be attached. The thickness d_{max} is a function of the molecular weight or, more precisely, of the chain dimensions of the polymer used for film formation: d_{max} increases linearly with the bulk radius of gyration of the polymer. Other factors

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that influence the conformation of polymer chains near interfaces may also be of some importance, e.g., attractive forces between the polymer and the surface like hydrogen bonding, but were not checked explicitly in this study. As first examples, we have chosen PS and PEOX, the first being a rather hydrophobic and the latter a hydrophilic polymer, to demonstrate the versatility of the system.

Altogether, the thicknesses that can be realized with this type of chemistry are of the same order or even higher as for other "grafting-to" techniques.[1−13] The advantage of this photochemical route to covalently attached polymer films clearly is the simplicity of the silane synthesis and the versatility with regard to the polymers that can be used for attachment. If, however, thicker films are to be prepared, one has to use a different approach where the polymers are formed in situ on the surface by means of monolayers of initiators ("grafting-from" technique).[31−34]

Finally, we want to point out that this approach is not limited to the attachment of spin-cast layers of polymers. Other methods of film preformation are also suitable. A clear advantage of this photochemical mode of attachment is the chemical inertness of the benzophenone moiety in the absence of light. This makes it suitable for the subsequent attachment of Langmuir−Blodgett−Kuhn (LBK) layers deposited onto benzophenone-modified surfaces as the contact with the subphase water during the dipping process will not cause any side reactions in the benzophenone monolayer. Besides that, one can also envisage direct chemisorption processes from solutions of polymers or low molecular weight compounds that can otherwise not easily be immobilized. Figure 6 summarizes this outlook. Some of these examples are currently being investigated in our groups.

Acknowledgment. Oswald Prucker and Christoph A. Naumann want to thank the Deutsche Forschungsgemeinschaft (DFG) for their fellowships ("Forschungsstipendien"). We would also like to thank Martina Knecht for valuable technical support. This work was supported in part by the Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA) through the NSF-MRSEC program under DMR 94-00354.

JA990962+

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