# Cosolvency-Induced Switching of the Adhesion between Poly(methyl methacrylate) Brushes

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S *Supporting Information*

ABSTRACT: We present a simple method to reversibly switch the adhesive force between two surfaces that are decorated with poly(methyl methacrylate) (PMMA) graft polymers. By employment of a PMMA/isopropanol/water or a PMMA/ethanol/water cosolvent system, we can tune the swelling of the brushes. In pure isopropanol or ethanol the polymer grafts are collapsed, and the adhesion is high when the contacting brushes are pulled apart. In an 80−20 vol % isopropanol−water or ethanol−water composition, the brushes are swollen. In these systems the adhesion is approximately 5 times smaller compared to the adhesion measured in the pure solvent systems. Moreover, we show that PMMA/isopropanol/water cosolvent systems perform better as switchable adhesives than PMMA/ethanol/water cosolvent systems. In the latter pulling events can arise when the swollen brushes are kept in contact for a longer time, such that the adhesion hysteresis can become large and the surface coating can be damaged due to bond-breaking events.
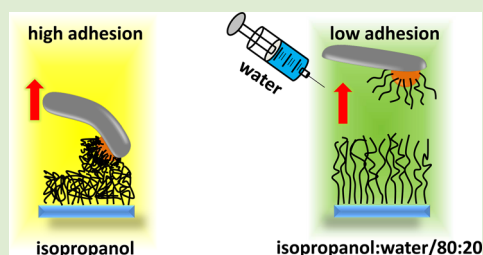
Controlling the magnitude of adhesion between two objects is of crucial importance for a wide variety of applications, which include: "pick-up and place" systems,[1] gecko or mussel inspired tape,[2] and biomedical glues.[3] A versatile method of achieving such adhesion control is the functionalization of surfaces with polymeric materials,[4] for example hydrogels,[5,6] films,[7,8] and especially brushes.[9−11] These polymeric systems allow for reversible switching of the adhesive force between low and high values.

Under good solvent conditions, a polymer has an extended coil conformation, while in poor solvents, polymers are in a collapsed globule state.[12] Switching between the coil and globule state can be achieved by changing the effective solvent quality, for example by directly replacing the solvent,[13] by cononsolvency,[14,15] by UV light,[16] by changing the temperature,[17] by changing the oxidation state,[18] or by adjusting the pH of the solvent.[19] Upon end-anchoring polymers to a surface at a sufficiently high density, a so-called polymer brush is formed.[20,21] When such brushes are in good solvents, the polymers stretch away from the surface, whereas in poor solvents, they form a collapsed, dense film on the surface. Swollen polymer brushes can act as efficient lubricants[22−24] but can also find application in bioengineering[25] or oil recovery.[26]

The adhesion between two contacting, brush-functionalized surfaces depends on the conformational state of the polymers, i.e., whether the brushes are swollen or collapsed. The adhesion between two collapsed polymer brushes is generally high[9−11] and determined by intermolecular interactions between the contacting polymers. In contrast, the adhesion is often observed to be low under good solvent conditions[9−11] because the attractive polymer−polymer interactions are now overshad- owed by more favorable polymer−solvent interactions such that the polymers effectively repel each other.

Keeping in mind potential applications of switchable adhesives, we anticipate that the necessity of a constant energy supply to maintain a constant high or low adhesion, as one would need for thermoresponsive polymers[9−11] or polymers that change their conformation in an external electric field,[27] would not be preferred. Also, removing components from the system (e.g., salt[28] or one of the solvents in a solvent mixture[29]) to trigger switching from the default state would be suboptimal, while this removal is not always practically feasible. Ideally, one would like to have the default adhesive state in pure solvent, while addition of a component triggers the adhesion switch. For example, for a "pick-up and place" system, the default state for pick-up asks for a high adhesive force and thus poor solvent conditions in pure solvent. A component addition should trigger brush swelling resulting in low adhesion and therefore deposition of the picked-up material. Triggering by cosolvency, in which a mixture of two poor solvents becomes a good solvent for a particular type of polymer, meets all demands described above for a "pick-up and place" system. Nevertheless, cosolvency has, to our knowledge, not been explored in the context of smart surface coatings.

Cosolvency is a generic phenomenon that has been observed in a wide variety of polymers with different solvent mixtures[30−33] and is commonly applied in the pharmaceutical industry and environmental engineering.[34] The mechanism can

be qualitatively understood from the Flory−Huggins theory[35,36] using the single liquid approximation of Scott,[37] where the effective Flory−Huggins parameter χ_{PSm} between polymer P and solvent mixture Sm (of solvents S1 and S2 with volume fractions ϕ_1 and ϕ_2) is $\chi_{PSm} = \phi_1\chi_{PS1} + \phi_2\chi_{PS2} - \phi_1\phi_2\chi_{S1S2}$. The effective interaction parameter χ_{PSm} is the weighted average of the independent interactions χ_{PS1} and χ_{PS2}, corrected for the reduction in interaction due to mixing of the two solvents. When the two solvents are poor solvents for the polymer (χ_{PS1} and $\chi_{PS2} > 0.5$, in the limit of infinitely long chains[37]) and the solvents are miscible ($\chi_{S1S2} < 2$, within the regular solution model,[37,38]) χ_{PSm} can be smaller than 0.5 such that the solvent mixture becomes a good solvent for the polymer. The single liquid approximation discussed above only provides a qualitative explanation for cosolvency. To quantitatively reproduce the ternary phase diagrams of polymers in solvent mixtures more detailed models are required.[37,39,40] We note that the mechanism behind the globule−coil−globule transitions upon increasing the cosolvent content is different from the mechanism governing cononsolvency. In the latter, the coil−globule transition in a mixture of good solvents in triggered by preferential adsorbance of the better solvent on the polymer.[41]

In this article we show that adhesion between two opposing poly(methyl methacrylate) (PMMA) brushes can be reversibly switched from high to low using cosolvency of PMMA in isopropanol−water and ethanol−water mixtures. At room temperature, pure alcohols (such as isopropanol and ethanol) and pure water are considered to be poor solvents for PMMA, while mixtures prepared within a particular range of alcohol−water ratios form good solvents for PMMA.[39,42,43] Using atomic force microscopy (AFM), we determine the adhesive force between high density PMMA brushes that are grafted from a flat silicon surface and a gold colloid probe (of diameter 6 μm, spring constant 0.14 N/m) by surface-initiated atom transfer radical polymerization (grafting density 0.25 chains/nm^2 and degree of polymerization 8000) via force versus distance measurements. In the experiments, we monitor the deflection of the cantilever upon approach to and retract from the surface (distance 700 nm and velocity 420 nm/s). We find that the adhesion between PMMA brushes in an 80−20 vol % mixture of isopropanol−water or ethanol−water is approximately a factor 5 lower than that for the brushes in pure isopropanol or ethanol. Therefore, our system would be suitable for "pick-up and place" types of applications. Moreover, we show that the performance of the switchable adhesive is better in isopropanol−water mixtures than in ethanol−water mixtures. In the latter the effective interaction parameter between the polymers and the mixed solvents is higher than in the former, which results in only minor PMMA brush swelling and thus more direct polymer-polymer interaction in ethanol−water mixtures. Transient interdigitation[44] allows for deeper penetration and thus a strong polymer−polymer interaction when the brushes are kept in contact for a longer time. As a consequence, we observe bond-breaking polymer-pulling events in the force−distance measurements such that the adhesion hysteresis per indentation cycle of PMMA brushes in an ethanol−water mixture can be up to a factor of 3 higher than in pure solvent.

Figure 1 shows the swelling ratio of the PMMA brush as determined from AFM images captured under low normal loads (1 nN) in a region where, prior to the experiments, part of the brush was gently removed from the surface by scratching
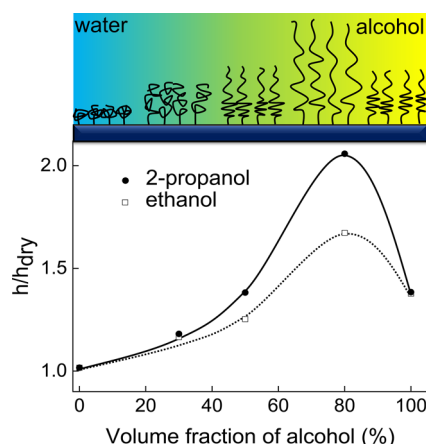

Figure 1. Height h of the PMMA brush on the flat surface for various alcohol−water ratios (isopropanol closed symbols and ethanol open symbols) as measured by AFM using a small normal load (of 1 nN). The measured height is normalized by the height of the brush measured under dry conditions (h_{dry}). The lines are guides to the eye.[45]

using Teflon tweezers. More details on the experimental procedures, sample preparation, and characterization can be found in the Supporting Information. As the alcohol (isopropanol or ethanol) content of the solvent mixture is increased, the brush height increases. The brush height was found to be maximum for the 80−20 vol % alcohol−water mixtures and decreases as the alcohol content is further increased above 80%. In pure water the brush swells by approximately 2%, which is consistent with the low absorption of water (4.5 wt %) in bulk PMMA.[46] In pure isopropanol the brush swells by 38%, which is close to the 46 wt % of isopropanol absorbed in bulk PMMA, measured using a Cahn counterbalance.[47] Though the isopropanol absorbance in PMMA is significant, isopropanol is still considered to be a poor solvent for PMMA because the upper critical solution temperature (UCST) is above room temperature (350 K).[42] The height of the brush solvated in pure ethanol is only slightly smaller than the height measured in isopropanol (<1%), which is in qualitative agreement with the UCST of ethanol/PMMA being only 5 K higher than the UCST of isopropanol/PMMA.[43] The stronger affinity of the alcohols with PMMA compared to water shifts the solubility maximum toward high relative alcohol concentrations and is typically found at an 80−20 vol % alcohol−water mixture.[39,42,43] At the solubility maximum, the brush swells by 67% in the ethanol−water mixture, while it swells by more than a factor of 2 (105%) in isopropanol−water. The reason for this strong difference in brush swelling for the different alcohols is the slightly smaller interaction between ethanol/PMMA compared to isopropanol/PMMA.[43] Due to these reduced interactions, χ_{PSm} will be a bit smaller for isopropanol/water/PMMA than for ethanol/water/PMMA, which can result in relatively large changes in the brush height when χ_{PSm} is close to the θ-point[48] (of $\chi = 0.5$ for infinitely long chains[37]). The latter implies that a mixture of water and ethanol or isopropanol becomes a mediocre, but not a good, solvent for PMMA.[49] In fact, in acetophenon (good solvent for PMMA) our swelling ratio was measured to be much higher (4.3).

Figure 2 shows three typical force versus tip−surface−separation curves upon retract of the PMMA surfaces using either pure isopropanol as a solvent (solid lines) or an 80−20
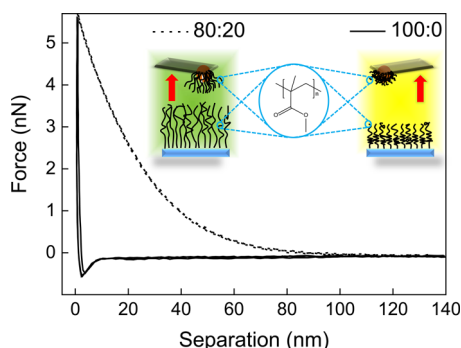
Figure 2. Typical force curves upon retract of the AFM cantilever from the surface in the 80−20 vol % isopropanol−water mixture (three curves, dashed lines) and in 100% isopropanol (three curves, solid lines).

vol % isopropanol−water solvent mixture (dashed lines). The "zero" in Figure 2 is set by the distance at which the slope of the force curve goes to infinity, which happens when the elastic repulsion stiffness is much stronger than the stiffness of the cantilever and should not be confused with colloid−surface contact. The difference between the force traces measured under the same conditions is small (<10%, see Figure 2). However, the force traces measured in pure isopropanol or in the mixture are qualitatively different (dashed lines versus full lines in Figure 2). For the swollen brushes (80−20 vol % mixture), we observe a long-range repulsive interaction, due to the osmotic pressure in the solvent.[50,51] The adhesion hysteresis is small (not shown) and determined by the hydrodynamic resistance of the solvent moving through the brushes.[51,52] Due to this hysteresis, there is a small attractive (adhesive) force (<0.1 nN) upon retract of the surfaces, which would disappear in the limit of retract-velocity $v \rightarrow 0$. However, this limit is difficult to reach experimentally due to noise and drift limitations. For the collapsed brushes in pure isopropanol, the force upon retraction is determined by attractive polymer−polymer interactions. Consequently, we observe a clear adhesive force of more than 0.4 nN.

Figure 3 shows the adhesive force between the PMMA brush covered surfaces, averaged over typically 20 force−distance curves captured on the same position on the sample surface, for four consecutive solvent exchanges from pure isopropanol to the 80−20 vol % isopropanol−water mixture and back. The
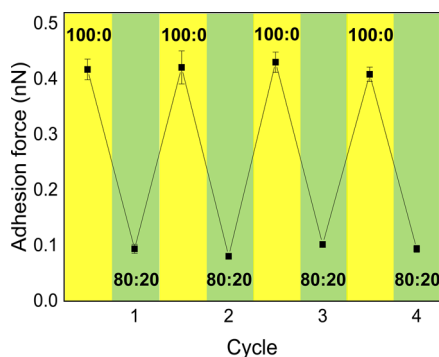

Figure 3. Adhesive force between the PMMA brushes after solvent exchange from 100-0 vol % isopropanol−water to an 80−20 vol % isopropanol−water mixture. The adhesion is typically 5 times higher in pure isopropanol than in the 80−20 solvent mixture. The error bars denote the standard error of the mean with a 95% confidence interval.

adhesive force measured under poor solvent conditions is consistently 5 times higher than the adhesive force between the swollen brushes. The variation in the adhesive force between different cycles is <10% and is most likely caused by small differences in the solvent composition that can occur during evaporation of the solvent. Experiments performed in pure ethanol and an 80−20 vol % ethanol−water mixture show qualitatively the same results, except that we observed pulling events in approximately 40% of the force−distance curves obtained in the ethanol−water mixture. Such pulling events occur when bonds are broken during retraction of the two surfaces.[53,54] For our system we attribute bond breaking to an increase in polymer−polymer interactions due to the less favorable interaction of PMMA with ethanol−water compared to isopropanol−water. The number of pulling events strongly depends on the time the surfaces are kept in contact.

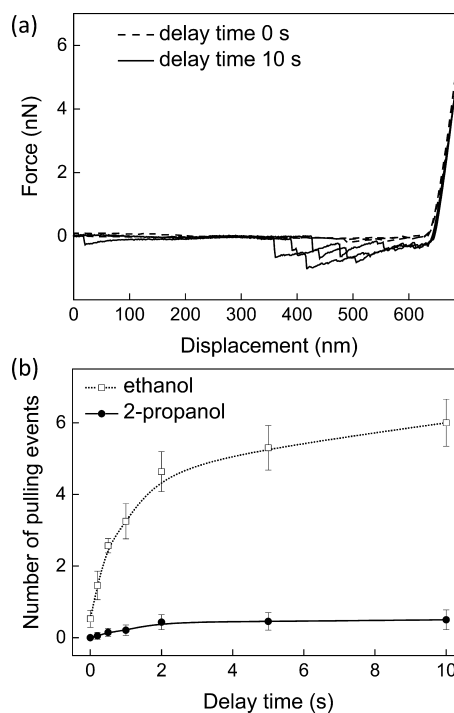Figure 4(a) shows typical force versus sample displacement curves obtained upon retract of the PMMA brushes in an 80−

Figure 4. (a) Force versus displacement curves that are obtained upon retracting the cantilever directly or after a delay time of 10 s from the surface. The PMMA brushes are solvated in an 80−20 vol % ethanol−water mixture. (b) The evolution of the number of pulling events as a function of the delay time for an 80−20 vol % ethanol−water mixture (open symbols) and for an 80−20 vol % isopropanol−water mixture (closed symbols). The error bars denote the standard error of the mean with a 95% confidence interval.

20 vol % ethanol−water mixture for no delay time (dashed lines) and 10 s delay time (full lines). The delay time is the extra time that the surfaces are kept in contact at the maximum in the normal force, on top of the time that the surfaces are already in contact (typically 0.25 s) during a default approach−retract cycle. Figure 4(a) clearly shows that the number of pulling events N increases with the delay time. Figure 4(b) shows how N evolves as the delay time is increased. For the 80−20 vol % ethanol−water mixture N increases approximately exponentially from 0.4 at 0 s to 6 at 10 s delay time. The shape of the exponential suggests that there are several relaxation

processes during contact formation, as was observed before by others via monitoring the density profile of a dry polystyrene brush that is brought into contact with a polystyrene network.[55] For the 80−20 vol % isopropanol−water mixture N increases to only 0.5 after a 10 s delay time, which is much less than for the experiments in ethanol−water mixtures. We attribute this difference to the different effective solvent qualities for PMMA that are created by the ethanol−water and the isopropanol−water mixtures. The isopropanol−water mixture is a better solvent for PMMA than the ethanol−water mixture, such that there is more solvent absorbed into the brush using the isopropanol−water mixture (see Figure 1). This makes the effective PMMA−PMMA interaction smaller. As a consequence, one would expect that the number of pulling events is higher for measurements in pure solvents, where there is even less solvent absorbed in the brush. However, a higher polymer density also implies that the relaxation time of interdigitation increases (up to 3−4 h for dry brushes[55]) such that the polymers do not have enough time to interdigitate during the experiment. For the PMMA/ethanol/water cosolvent system, there is just the right amount of solvent absorbance to induce bond-breaking pulling events that can be measured on the time scale of the experiment. These results are in agreement with the observation that strong permanent adhesives can be formed by cross-linking PMMA films that are swollen in ethanol−water mixtures.[56] Since pulling events can significantly increase the adhesion hysteresis after longer contact times and because bond-breaking events will damage the surface coating, we propose that the PMMA/isopropanol/water system is a better candidate for the development of a switchable adhesive than the PMMA/ethanol/water system.

In summary, we have shown that the adhesion between two opposing brushes can be switched from high to low and back using cosolvency of PMMA in isopropanol−water and ethanol−water mixtures. The adhesive force between PMMA brushes in pure isopropanol or ethanol was found to be a factor of 5 higher than in an 80−20 vol % alcohol−water mixture. The system in pure solvent will show high adhesion, while low adhesion can be triggered by addition of the cosolvent. Therefore, our technique is very suitable for "pick-up and place"-type of applications. Moreover, we showed that switchable adhesion can best be obtained in isopropanol−water mixtures instead of ethanol−water mixtures, due to bond-breaking pulling events that can occur in the latter system.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods employed for the experiments and the FTIR spectra of the PMMA brushes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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