Ring Polymers for Surface Modification and Enhanced Blending

Matthew Soicher, University of Florida, Gainesville, Florida, SURF 2006 Fellow
Faculty Mentor: Dr. Haskell Beckham

Introduction

When two different types of monomer are joined in the same polymer chain, the result is a copolymer. Alternating, random, and block copolymers are all examples where the monomers are arranged differently within a single polymer chain. Distinct polymer chains can also be grafted or adhered together, but this process can be difficult and expensive.

Another type of copolymer is the heterogeneous rotaxanated or pseudo-rotaxanated copolymer. In this form, a cyclic polymer is threaded onto a linear chain of another polymer. Less is known about the properties of these “topological copolymers”. The objective of this project is to synthesize cyclic poly(dimethylsiloxane) (PDMS) and then trap these cyclic molecules into the surface of linear polystyrene (PS) and poly(methylmethacrylate) (PMMA) using heat, pressure, and solvent.

Procedure

The cyclic PDMS was synthesized[1] from a linear precursor. A round-bottom, three neck flask with a stir bar was vacuum evacuated and backfilled with nitrogen. Sodium hydride (NaH) (0.08 g), tetrahydrofuran (THF) (200 mL), and linear PDMS (10.79 g) were added to the flask. An anion exchange resin was added to the flask after 10 minutes to remove the excess negatively charged linear segments from solution. The mixture was stirred overnight, the resin was vacuum filtered out, and the solvent (THF) was then removed by rotary evaporation. The material was then dissolved in toluene and washed with distilled water to remove salts. Magnesium sulfate was added to dry the sample followed by filtration and toluene removal by rotary evaporation. Finally, the material was dried under a high vacuum.

Squares of linear PS and PMMA were cast as a substrate for the cyclic PDMS. Flakes (0.5 g) of the linear polymers were added to a mold and placed into a heating press. The PS was heated to 100 ^{o}C and 1000 kg pressure for 6 minutes, while the PMMA was heated to 114 ^{o}C and 2000 kg pressure for 9 minutes. The blocks were then quenched in a cool water bath and 5 drops of a 70 wt% cyclic PDMS/THF solution were pipetted onto the surface. The mold was then placed back into the press and put under the same temperature and pressure for varying times (2, 3, 4, and 5 minute press times were tested). The blocks were quenched, removed from the mold, and stored. The process was repeated with drops of linear PDMS.

A single drop of water (2 µl) was pipetted onto the surface of both cyclic and linear PDMS coated blocks, as well as “neat” blocks of pure PS and PMMA. A high resolution camera took photos of the drops for contact angle measurements. The samples were then placed in a solvent bath (hexane for the PMMA substrate and dodecane for the PS substrate) and agitated for 4 hours. Contact angles were measured again.

Results and Discussion

It has been shown that linear polymer chains can become entangled at the surface of a linear substrate.[2] We wanted to see whether the cyclic polymer would also entangle and whether the entangled cyclic polymers would be more difficult to remove from the surface due to the possibility of threading onto the underlying linear substrate polymer. Contact angle measurements were used to probe the top 10 Å of the samples and examine the surface. If the PDMS is trapped at the surface, the contact angle should be between that of the pure substrate and that of the PDMS. After washing, we hypothesized that the cyclic PDMS samples should still exhibit midrange values between the two pure polymers, while the linear PDMS should dissolve, leaving the samples with contact angles closer to the pure substrate.

Contact angle data are presented in Tables 1 and 2:

Table 1: Average contact angles for all samples before washing

Pre-Wash			
	Substrate	Cyclic PDMS	Linear PDMS
120,000 g/mol PMMA	82	99	99
250,000 g/mol PMMA	83	97	94
50,000 g/mol PS	96	103	100
270,000 g/mol PS	90	100	104

Table 2: Average contact angles for all samples after washing

Post-Wash			
	Substrate	Cyclic PDMS	Linear PDMS
120,000 g/mol PMMA	85	93	91
250,000 g/mol PMMA	89	93	95
50,000 g/mol PS	104	103	98
270,000 g/mol PS	100	105	104

In all of the pre-wash samples, the PDMS coated substrate exhibited contact angles much higher than the “neat” samples. This indicates that the PDMS was trapped at the surface of the base polymer by the entrapment process. After washing, the average contact angles of the PDMS-coated samples were still higher than those for most of the "neat" substrates, indicating the washing procedure was not robust enough to remove either the cyclic or the linear PDMS. Thus, PDMS can be surface-entangled into both PS and PMMA to prepare modified surfaces that are stable to solvents.

The PS surfaces exhibit higher contact angles after washing. The explanation for this is unclear and cause for us to re-examine the details of our washing procedure. This is particularly true since the contact angles are not significantly different between the cyclic and linear PDMS coated samples.

Conclusion

Cyclic and linear PDMS can be stitched into the surfaces of PS and PMMA films using a combination of solvent, temperature, and pressure. The surface-entangled PDMS is stable to solvent, revealing a new method for permanent surface modification with PDMS. No differences were observed between the cyclic and linear PDMS. More robust washing studies are planned.

References

1. White, B.; Watson, W.P; Barthelme, E.; Beckham, H. *Macromolecules* **2002**, *35*, 5345-5348.
2. Desai, N. P.; Hubbell, J. A. *Macromolecules* **1992**, *25*, 266-232.