Solvent-Controlled Michael Addition Reaction for Modulating Multiple Physical Properties in Polymeric Material †

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Abstract

In the past, various polymeric coatings, including hydrophobic, superhydrophobic as well as underwater superoleophobic coatings[1-3] were developed by adopting 1,4-conjugate Michael-addition reaction. Here in this study alcoholic solvents that are used as a media for environment-friendly Michael addition reaction, were tactically exploited to control the various physical properties of a polymeric material such as shrinkage, flexibility and special wettabilities: adhesive and ultra-non- adhesive superhydrophobicity. The embedded antifouling property is highly durable and capable of withstanding severe physical and chemical insults including the physical removal of the top surface of the material. Moreover, the antifouling property remained intact during and even after successive (100 times) deformation (75%) of the synthesized material. Furthermore, these materials were exploited to demonstrate (a) the controlled transfer of tiny liquid droplets and (b) the oil/water separations.

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3. S. L. Bechler, D. M. Lynn, Biomacromolecules, **2012**, 13, 1523.

Methods

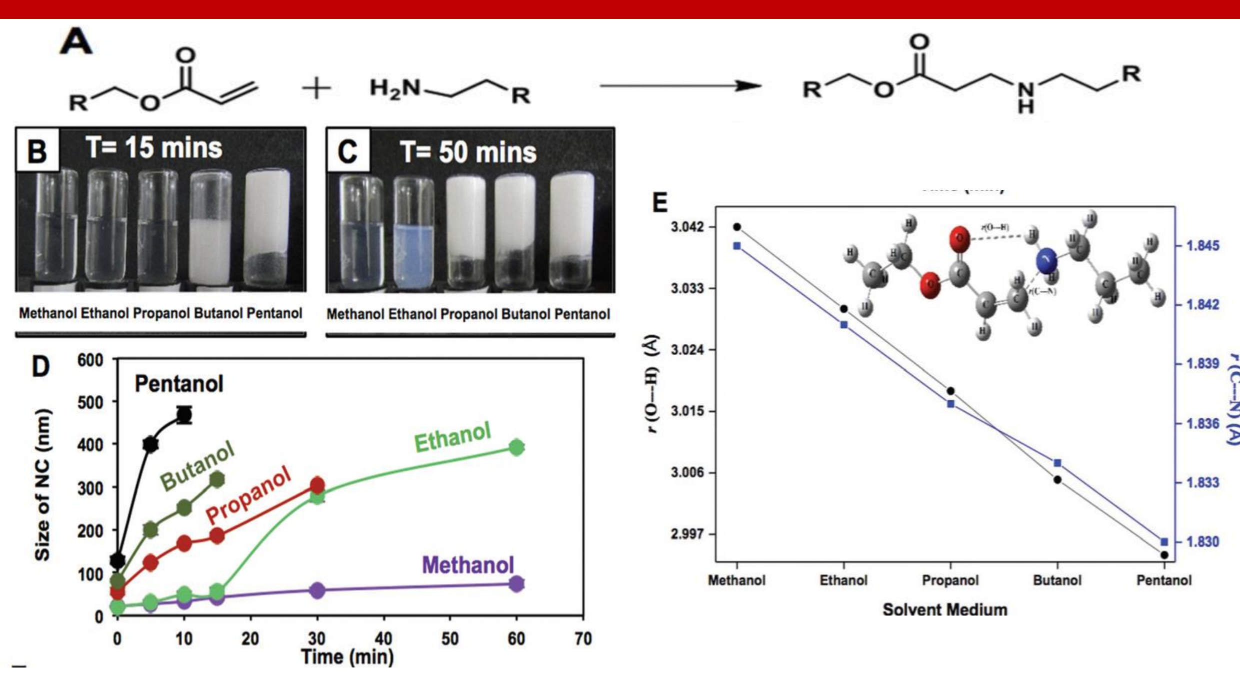

Fig. 1 (A) Schematic of 1,4 Michael addition reaction between amine and acrylate groups. (B–C) Digital images of BPEI/5Acl mixtures in methanol, ethanol, propanol, butanol and pentanol after 15 minutes (B) and after 50 minutes (C) of mixing 5-Acl and BPEI in respective alcoholic solvents. (D) DLS study on the mixture of 5-Acl/BPEI in pentanol, butanol, propanol, ethanol and methanol illustrating the gradual progression in growth of the nano-complex in different alcoholic solvents. (E) Intermolecular bond distances r (O···H, black line) and r (C···N, blue line) in the transition states of the reaction between primary amine and acrylate group in different solvent mediums.

Results and Discussion

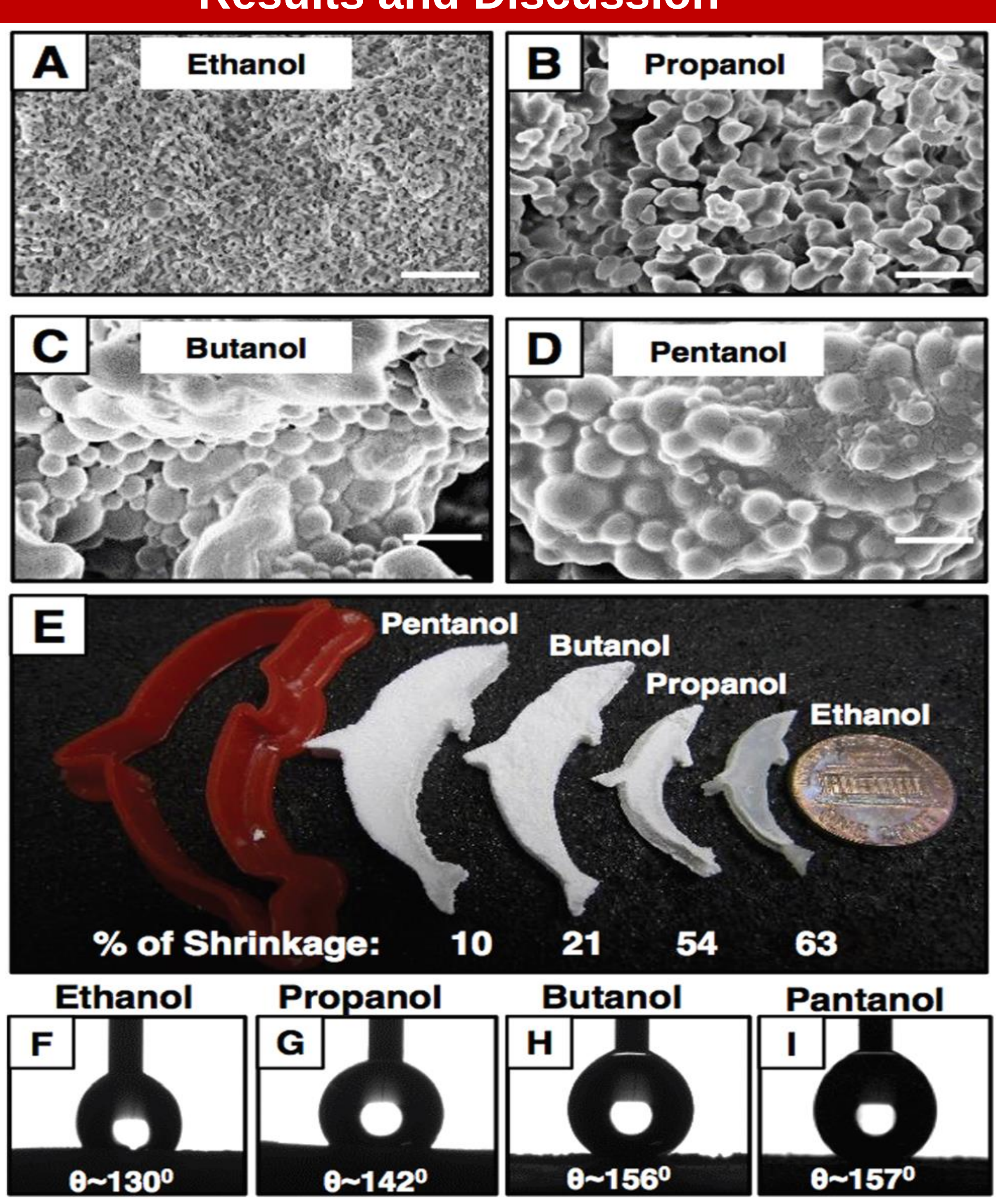

Fig. 2 (A–D) FESEM images of polymeric materials that are prepared separately in various alcoholic solvents (A) ethanol, (B) propanol, (C) butanol and (D) pentanol (scale bar: 2 μm). (E) Digital image provides the qualitative estimation of shrinkage of polymeric material prepared in pentanol, butanol, propanol, ethanol solvents after the removal of the respective solvents. Dolphin-shaped dough cutter (red) was used as a template for incurring the dolphin shape to each polymeric gel. (F–I). Water contact angle images of water droplets on the polymeric materials that are synthesized in different alcoholic solvents and post modified with octadecylamine (ODA) molecules.

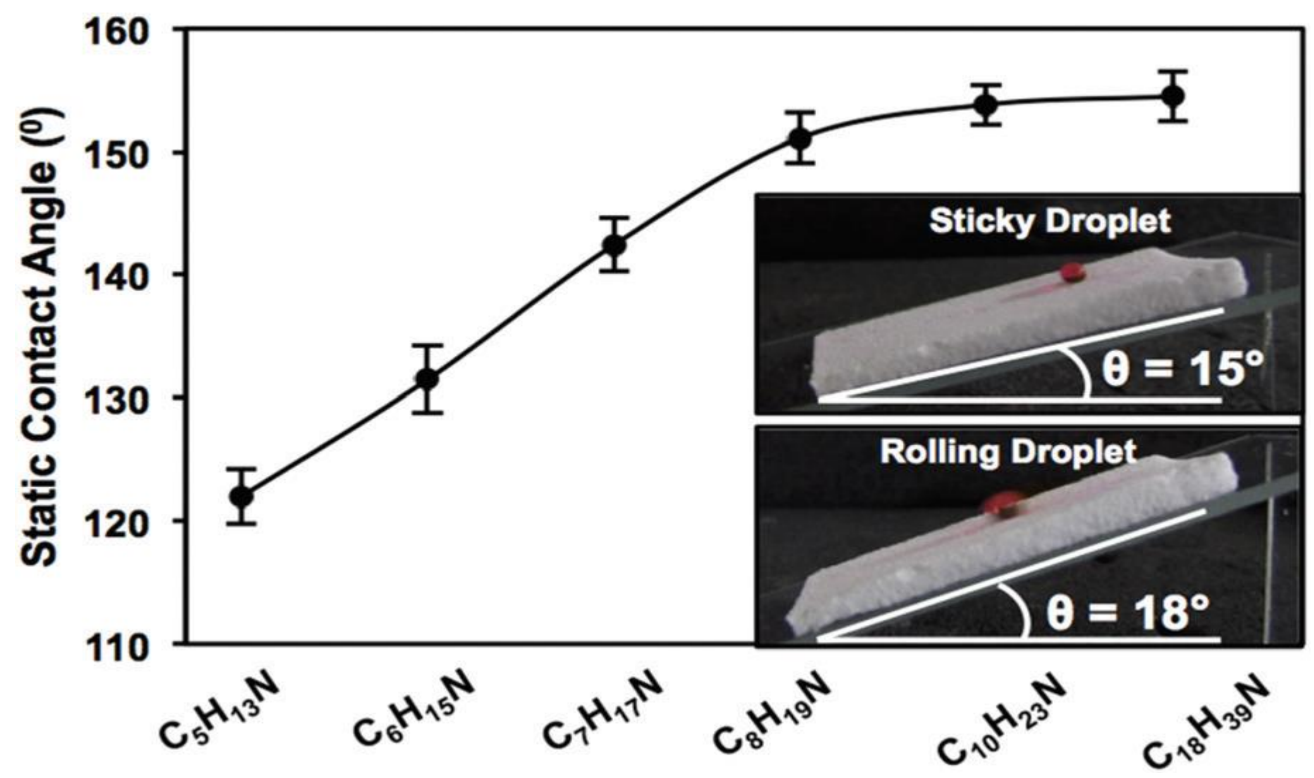

Fig. 3 The plot accounts the static contact angles of water droplet on the polymeric gel material (that is prepared in pentanol solvent) after the post modification with pentylamine, hexylamine, heptylamine, octylamine, decylamine and octadecylamine, respectively. Digital images (inset) show the behavior of water droplet (red color aids visual inspection) on octylamine post-modified material, which was tilted with angles of 15° (top) and 18° (bottom), the water droplet completely rolled off at 18° angle, while the same water droplet was adhered on inclining the interfaces at 15°.

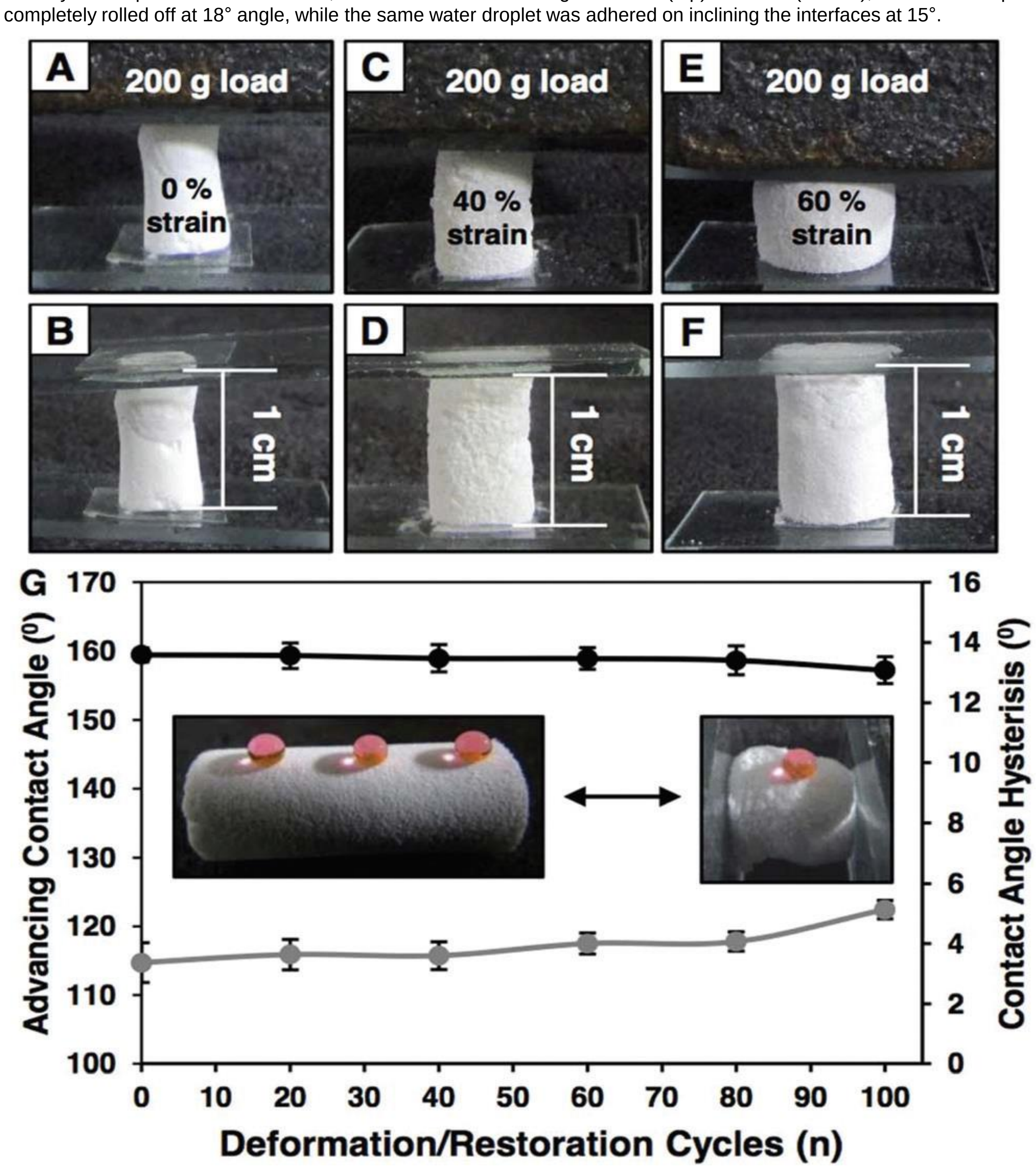

Fig. 4 (A, C, E) Digital images depict the percentage of compressive strain on the polymeric materials that were prepared in propanol, butanol, and pentanol, after the application of 200 g load. (B, D, F) Once the load was released, all polymeric materials were able to recover their original shapes and sizes; scale bar: 1 cm. (G) Plot shows the advancing contact angle (black) and contact angle hysteresis (grey) of water droplet on the polymeric material (that was synthesized in pentanol and post-modified with octadecylamine) after incurring successive deformation (75%) and followed by relaxation after the applied pressure was released. The inset displays the water droplets on the material before and after incurring deformation.

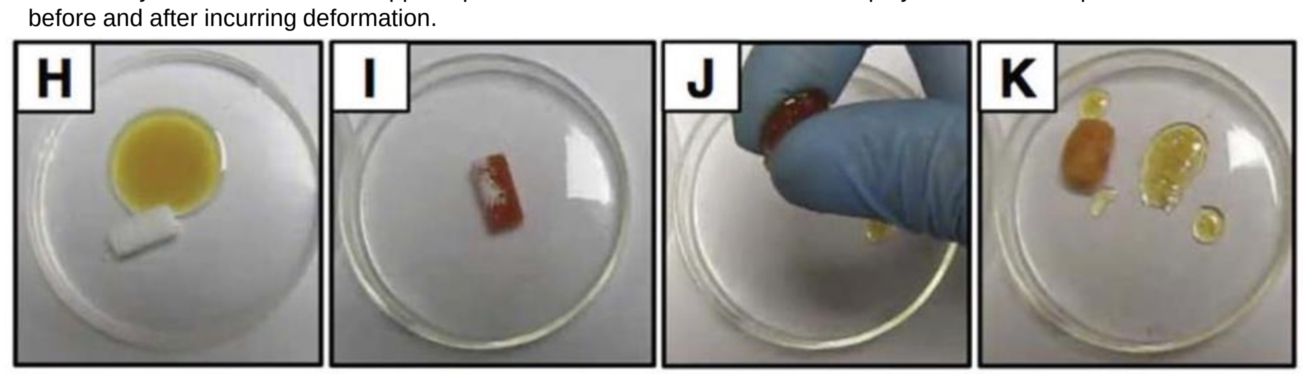

Fig. 5. (H–K) Digital images show the collection of floating motor oil droplet on the air/water interface using the polymeric material (H–I) and the absorbed oil was collected by squeezing the material (J–K).

Conclusion

In conclusion, herein, a facile and scalable approach to synthesize polymeric material through the mutual Michael addition reaction between BPEI and 5Acl with an appropriate selection of alcoholic solvents is introduced for controlling various important chemical (the material chemistry) and physical (e.g. topography, flexibility, shrinkage etc.) parameters. These special interfaces were also exploited in the no-loss tiny water droplet transfer and the separation/collection of oil from oil/water mixture. This simple and environment-friendly approach could be useful in developing functional materials for several other relevant and prospective applications of bio-inspired special wettability in practical settings.

Reference

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