Supporting Information

Exceptional Control on Physical Properties of Polymeric Material Through Alcoholic-Solvent Mediated Environment Friendly Michael Addition Reaction

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Experimental section

Materials: Branched poly (ethylenimine) (PEI, MW ~25000), dipentaerythritol penta-/Hexa-acrylate (5Acl, MW ~524.21), were obtained from Sigma Aldrich (Bangalore India). Propanol, butanol, pentanol, were purchased from Thermo Fischer Scientific (Mumbai India). Primary amine containing small molecules: propylamine, pentylamine, hexylamine, heptylamine, octylamine and decylamine were purchased from Sigma Aldrich (Bangalore India) and cctadecylamine (ODA) was purchased from Alfa-Aesar (Hyderabad India). Absolute ethyl alcohol (CAS 64-17-5, Lot 1005150) was purchased from TEDIA Company (United States of America). Microscopic glass slides were acquired from JSGW (Jain Scientific Glass Works) India. Methanol was obtained from Merck Life Science Pvt. Ltd (Bengaluru India). Reagent grade THF was purchased from RANKEM (Maharashtra). HCl was purchased from Fischer Scientific Mumbai India. NaOH was obtained from Emparta (Merck Specialties Private Limited). Rhodamine 6G (Rh6G) was purchased from Labo Chemie (Laboratory Reagents and Fine Chemicals Mumbai India). Play dough cutter dolphin was purchased from fabric castell India. Motor oil was obtained from Castrol India Limited. Sand paper was obtained from the local hardware shop in Guwahati city (Assam India). Adhesive tape was obtained from Jonson Tapes India. Sand was collected from a construction site at Indian Institute of Technology Guwahati Assam India and was rinsed thoroughly prior to use. All materials were used as obtained without any further purification unless otherwise mentioned.

General considerations: Glass Vials used for preparation of polymer solutions were thoroughly washed with acetone and ethanol prior to use. The contact angles were acquired using Kruss Drop Shape Analyser-DSA25 instrument at ambient conditions. Advancing and receding water contact angles were measured using 4µL deionized water droplet at four different positions for each sample. Field emission scanning electron microscope (FESEM) images were acquired using Sigma Carl Zeiss Scanning electron microscope, and a thin layer of gold was deposited on top of each sample prior to imaging. FTIR spectra was recorded using PerkinElmer instrument at ambient condition by grinding the sample with KBr to prepare pellet for analysis. Dynamic light scattering (DLS) study was performed by using Zeta Sizer Nano ZS90 (modelno.ZEN3690) instrument. Digital images were obtained using a canon power shot SX420 IS digital camera.

Computational Methodology: The geometries of the reactants of primary amine, acrylate group and their corresponding transition states were fully optimized in the gas and also in different solvent mediums (methanol,

ethanol, propanol, butanol and pentanol) using quantum chemical methods of B3LYP/6-311++G(2d,2p). The effect of the solvent in the reaction process were considered using the polarizable continuum model (PCM) with the integral equation formalism variant (IEFPCM). Vibrational frequencies were performed at the same level of theory to characterize all the optimized structures as true minima or transition states on the potential energy surface. Intrinsic reaction coordinate (IRC)[1,2] analyses with mass weighted coordinates were performed at the same level of theory in gas phase and also in solvents to confirm the reactant structures. Gaussian 09 program package was used to perform all the calculations.[3] The topological properties of different transition states were analyzed in terms of electronic charge density at B3LYP/6-311++G(2d,2p) level using atoms in molecules (AIM) approach as implemented in AIMALL suite of program.[4] The input wave functions for AIM calculations were generated from Gaussian 09 program.

Preparation of Polymeric Gels in Various Alcoholic Solvents

Afore gelation of BPEI polymer in various alcoholic solvents individually, the BPEI and the 5-Acl solutions were prepared in methanol, ethanol, propanol, butanol and pentanol separately by dissolving 0.5 g of BPEI and 1.325 g of 5-Acl in 10 mL of each alcoholic solvents. Afterwards solutions of BPEI and 5Acl in same alcoholic solvent were mixed with appropriate concentrations (1 mL of 5-Acl and 0.3 mL of BPEI, where the molar ratio (5Acl:BPEI) is 7.966) and kept with continuous agitation. Over the time, the colorless mixtures of BPEI/5Acl in alcoholic solvents were appeared as the milky turbid solution, and eventually transformed into gel material, except the mixture of BPEI/5Acl in methanol. The gelation process was faster with increasing the hydrocarbon tail length in the alcoholic solvents, and polymeric gel materials were appeared after 210 min, 50 min, 20 min and 15 min of mixing BPEI/5Acl in ethanol, propanol, butanol and pentanol respectively. The rate of gelation was noticed to be different with the change in the composition of BPEI and 5Acl in the reaction mixtures as shown in Table S1.

Post-Chemical Modification of the Synthesized Polymeric Gels:

Then all the synthesized gels were rinsed thoroughly with THF for one hour to remove the traces of solvent before immediate post-modification with amine containing small molecules. So the polymeric gels that are prepared in various alcoholic solvents, were individually exposed to solutions of propylamine (30.0 mg/mL), pentylamine 30.0 mg/mL), hexylamine (30.0 mg/mL), heptylamine (30.0mg/mL), octylamine (30.0 mg/mL), decylamine (30.0 mg/mL) and octadecylamine (30 mg/mL) respectively in THF for overnight. After treatment of these gel materials with selected amine containing small molecules, each of those polymeric materials were further washed with THF for one hour to remove the loosely adhered molecules from the polymeric materials and let them dry at ambient conditions. Then, the water wettability on each of the synthesized materials, were investigated by beading the red colored aqueous droplet (for visual inspections) and measuring the water contact angle.

Physical and chemical stability tests

Standard physical and chemical durability tests were applied on the polymeric materials (which were synthesized from pentanol and post modified with ODA) to examine the robustness of the embedded antifouling property in the material. Detailed procedures are explained described in following sections:

1. Sand paper abrasion test: In this particular test, the abrasive sand paper was immobilized on the microscopic glass slide using double sided adhesive tape. Then, the superhydrophobic material was rubbed on abrasive surface of the sand paper with 200 g applied load, and the polymeric material was moved back and forth multiple times (5 times). Top surface of the material was abraded during this abrasion process. Some portion of the eroded material was even adhered on the sand paper. Next, the antifouling property in the material was examined with visual inspection and measuring contact angle of the beaded water droplet.

2. Sand drop test: The superhydrophobic material was immobilized on a microscopic glass slide using adhesives tape. Then, 150 g of sand grains were dropped on the polymeric material (which was tilted with 45° angle) from the height of 20 cm with continuous flow. Afterwards, the anti-wetting property of the material was investigated by visual inspection and by contact angle measurements.

3. Adhesive tape test: This experiment was performed using a double side adhesive tape, where the superhydrophobic material was brought in contact with adhesive surface of the tape and a 500 g of load was applied on top of material to facilitate the better contact between the material and the surface of the adhesive tape. Then, the material was manually peeled off from the adhesive tape, and some portion of the material was arbitrarily raptured and transferred on the adhesive tape during this peeling process. Next, the water wettability was examined on those freshly exposed interior of the material by measuring the contact angle of beaded water droplets.

Chemical stability test: Chemical durability of the polymeric material (post modified with octadecylamine) was investigated by exposing the materials to various chemically harsh aqueous phases including highly acidic (pH 1.0), and alkaline (pH, 12.0) water, artificial sea water and river water (Brahmaputra Assam India). The artificial sea water was prepared by dissolving $Mgcl_2$ (0.226 g), $MgSO_4$ (0.325 g), NaCl (2.673 g) and $CaCl_2$ (0.112 g) in 100 mL of deionized water in volumetric flask.

Oil/water separation: The polymeric material (0.135g, post treated with ODA) was placed on the air /water interface where the oil droplet (motor oil, 1000 µL) was floating. The floated oil is soaked immediately and selectively by superhydrophobic material after getting contact with polymeric material. Later the collected oil was collected in a separate container by manually squeezing the oil soaked material.

References.

1. C. Gonzalez and H. B. Schlegel, J. Chem. Phys., 1989, 90, 2154–2161.

2. C. Gonzalez and H. B. Schlegel, J. Phys. Chem., 1990, 94, 5523–5527.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09* (Gaussian, Inc., Wallingford CT, 2009).

4. T. A. Keith, AIMALL, version 13.11.04, TK Gristmill Software, Overland Park, KS, USA, 2013, http://aim.tkgristmill.com.

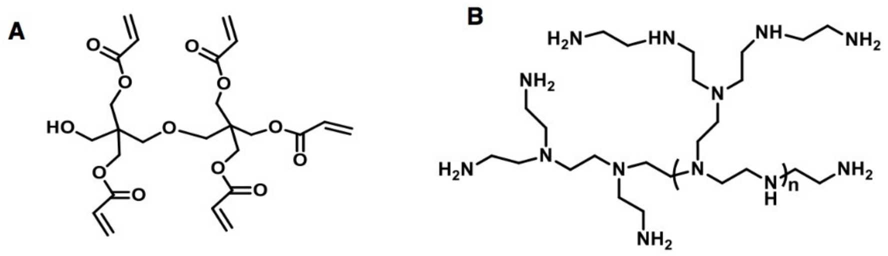


Figure S1. A-B) Chemical structures of dipentaerythritol penta-/Hexa-acrylate (5-Acl; A) and branched poly (ethylenimine) (BPEI; B).

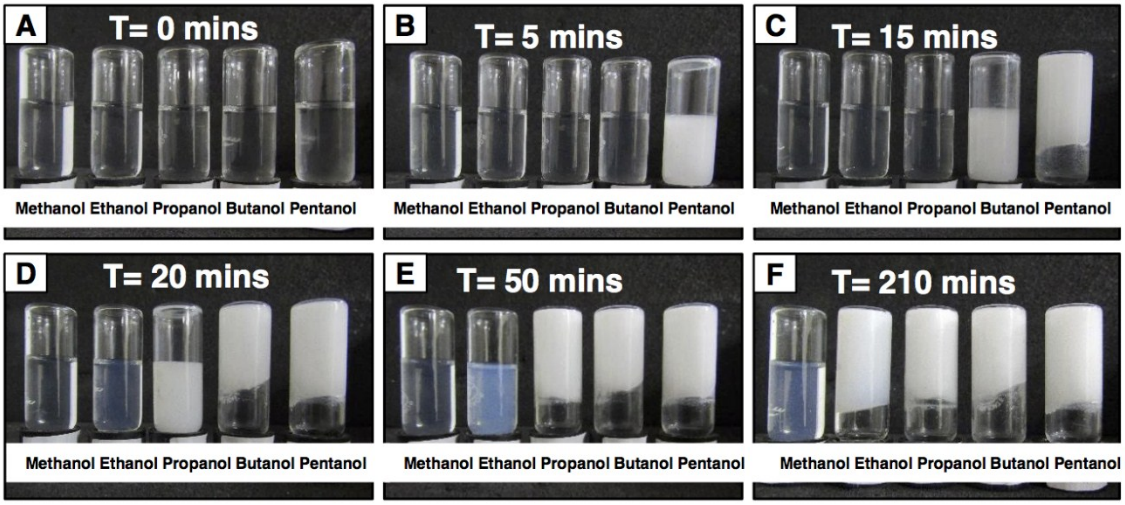
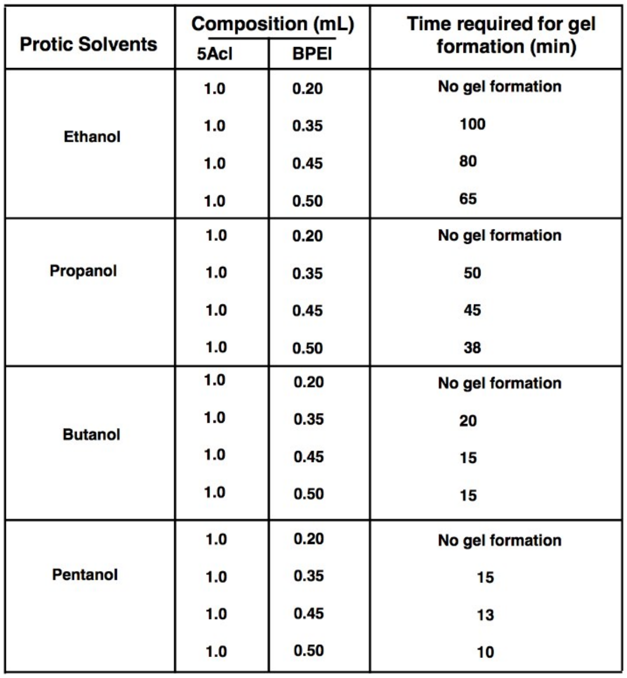


Figure S2 A-F) Digital images illustrating the gelation process of BPEI/5Acl mixtures separately in different alcoholic solvents including methanol, ethanol, propanol, butanol and pentanol after 15 minutes (pentanol; C), 20 minutes (propanol; D), 50 minutes (butanol; E) and 210 minutes (ethanol; F). The BPEI/5Acl mixture in methanol was appeared as faint turbid after 210 minutes (F).



Protic Solvents	Composition (mL)		Time required for gel formation (min)
	5Acl	BPEI	
Ethanol	1.0	0.20	No gel formation
	1.0	0.35	100
	1.0	0.45	80
	1.0	0.50	65
Propanol	1.0	0.20	No gel formation
	1.0	0.35	50
	1.0	0.45	45
	1.0	0.50	38
Butanol	1.0	0.20	No gel formation
	1.0	0.35	20
	1.0	0.45	15
	1.0	0.50	15
Pentanol	1.0	0.20	No gel formation
	1.0	0.35	15
	1.0	0.45	13
	1.0	0.50	10

Table S1. Examining the rate gelation of BPEI/5Acl mixtures in different protic solvents (including ethanol, propanol, butanol and pentanol) with the change in the composition of BPEI and 5Acl in the reaction mixtures. The concentration of BPEI and 5Acl were 50mg/ml and 132.5mg/ml respectively.

Aprotic Solvents	Compositions(mL)		Physical appearance
	5Acl	BPEI	
THF	1.0	0.30	Turns turbid in colour
Chloroform	1.0	0.30	No gelation
Acetone	1.0	0.30	No gelation
Ethyl acetate	NA	NA	BPEI not dissolved

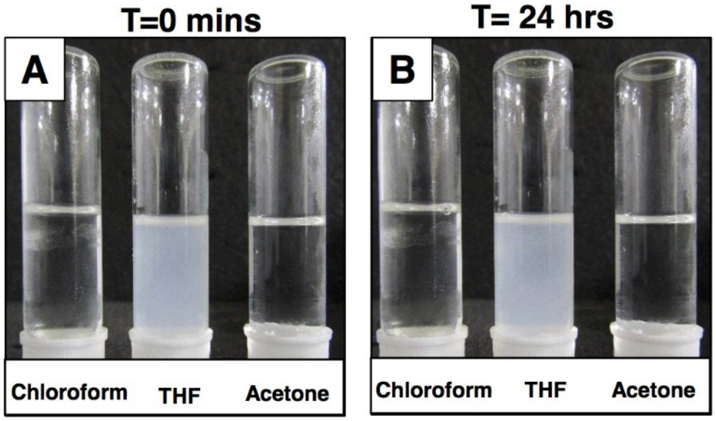


Figure S3. The table accounts the effect of aprotic solvents in the reaction mixtures of BPEI and 5Acl. A-B) Digital images revealed that the reaction mixture were incapable of forming gel in aprotic solvents (THF, chloroform and acetone) even after 24 h.

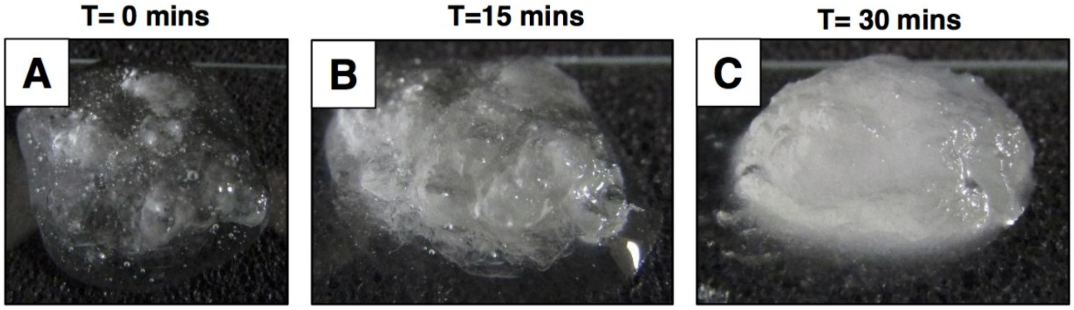


Figure S4 A-C) Digital images are illustrating the gelation of BPEI/5Acl mixture in absence solvent.

Table S2: IE and SE of the reactants in different solvent mediums along with electron density values (ρ) at bond critical points (BCP) for the intermolecular bond C---N in the transition states.

Solvent medium	**IE (kJ/mol)**	**SE (kJ/mol)**	**ρ (C---N)**
Methanol	0.89	-21.06	0.108
Ethanol	0.99	-20.71	0.109
Propanol	1.09	-20.40	0.110
Butanol	1.18	-20.08	0.111
Pentanol	1.27	-19.78	0.112

‘IE’ is ‘interaction energy’; ‘SE’ is ‘energy of solvation’. All computations are at B3LYP/6-311++G(2d,2p) level of theory. Electron density (ρ) is calculated using AIM program; IE is calculated using the equation ‘IE = $(E_{AB}) - (E_A+E_B)$’ where ‘E_{AB}’ is the ‘total energy of the whole system’, ‘E_A’ is the ‘total energy of part-1’ and ‘E_B’ is the ‘total energy of the part-2’.

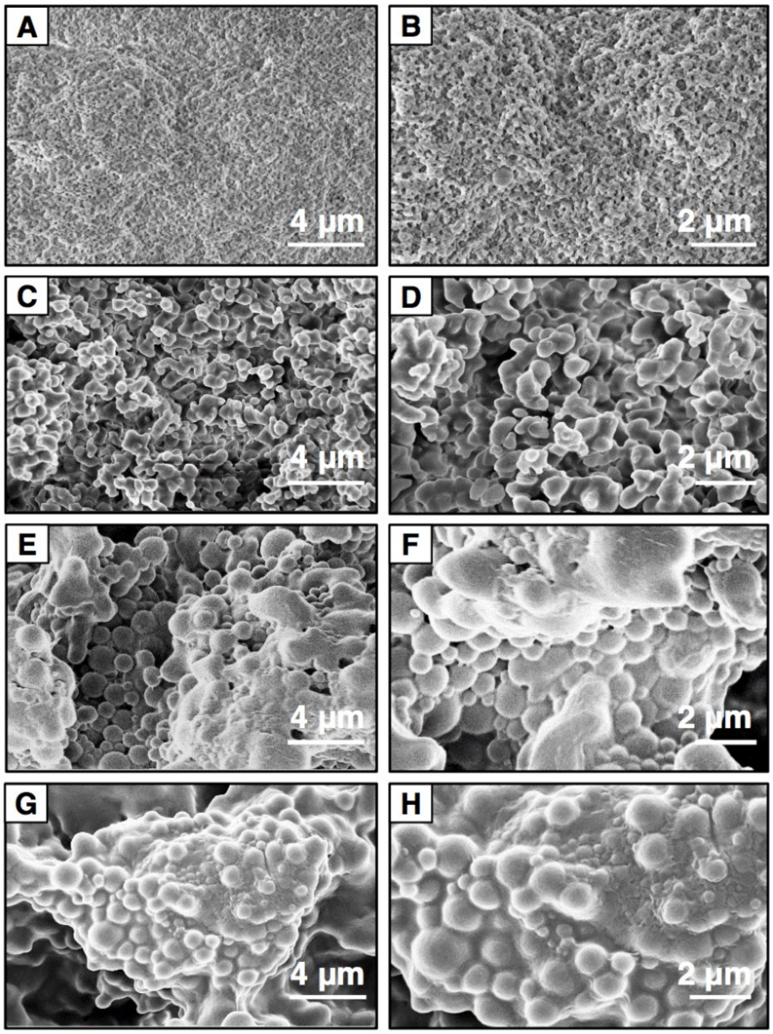


Figure S5. A-H) FESEM images of the polymeric gel materials that were prepared in ethanol (A, B), propanol (C, D), butanol (E, F) and pentanol (G, H) respectively in low (A, C, E, G; scale bar: 4µm) and high (B, D, F, H; scale bar: 2µm) magnifications.

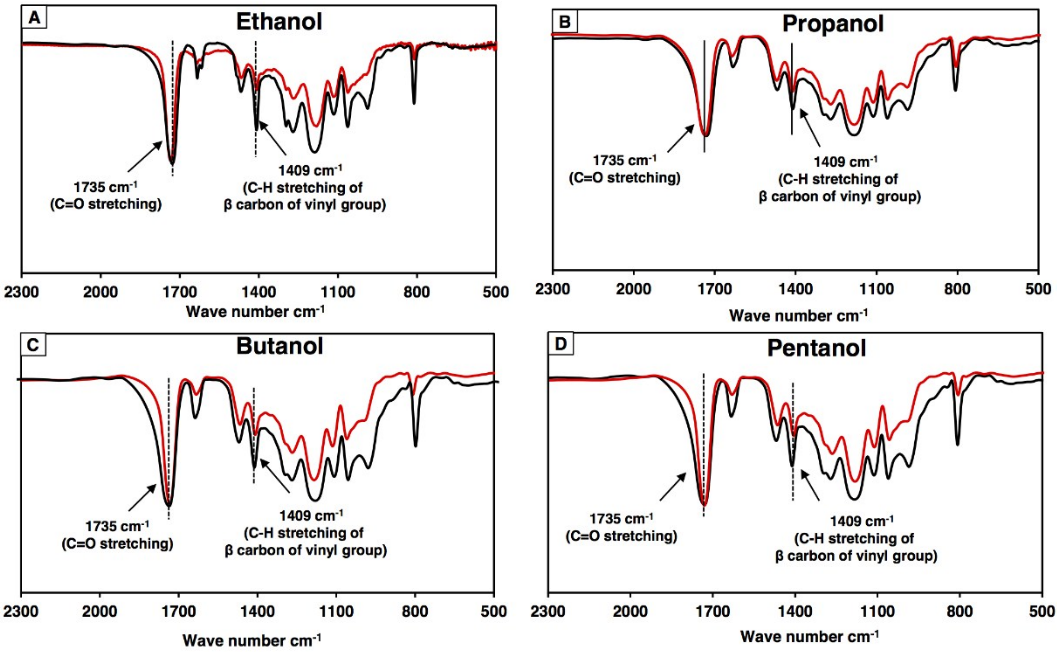


Figure S6. A-D) FTIR spectra of polymeric gel material that are synthesized in ethanol (A), propanol (B), butanol (C) and pentanol (D) solvent, before (black) and after post chemical modification with octadecylamine (red). The peaks at 1735 cm^{-1} 1410 cm^{-1} corresponds to carbonyl streching and symmetric deformation of C-H bond for the β carbon of the vinyl group.

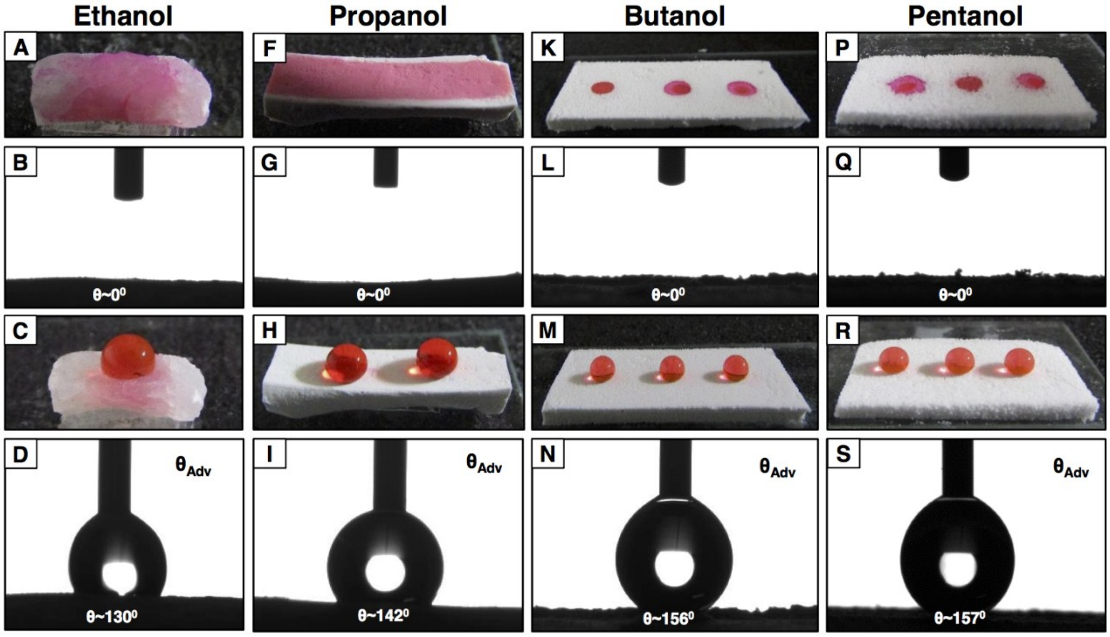


Figure S7. A-T) Digital images (A, C, F, H, K, M, P, R) and water contact angle (advancing) images (B, D, G, I, L, N, Q, S) of beaded water droplet on the polymeric material that are prepared using ethanol (A-D), propanol (F-I), butanol (K-N), pentanol (P-S) separately as reaction medium for 1, 4 conjugate addition reaction, before (A-B, F-G, K-L, P-Q) and after (C-D, H-I, M-N, R-S) post modification with octadecylamine.

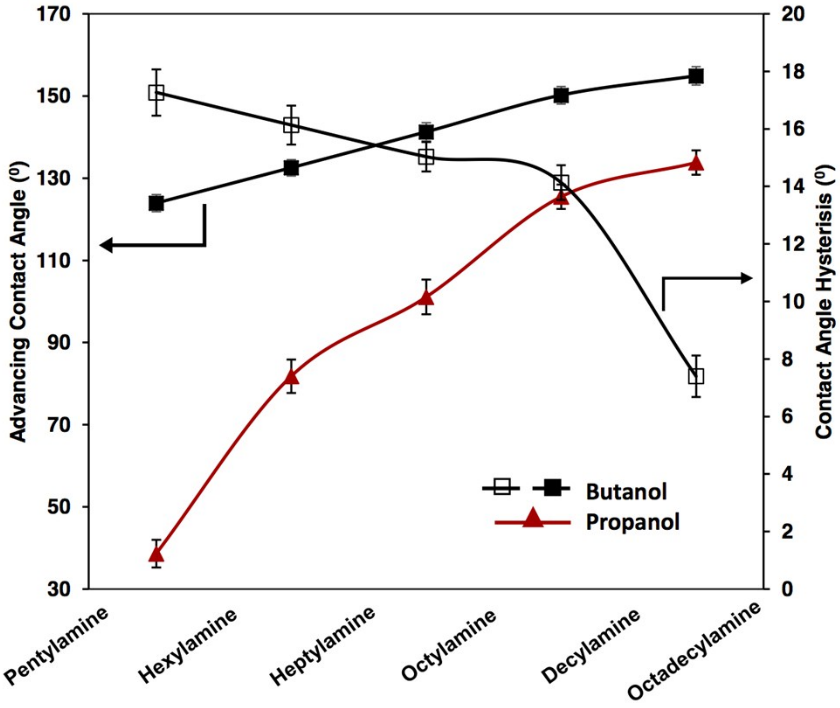


Figure S8. The plot showing the advancing contact angle and contact angle hysterisis of polymeric material prepared in butanol (black; ,) and propanol (red, ▲) after post functionalization with pentylamine, hexylamine, heptylamine, octylamine, decylamine and octadecylamine respectively.

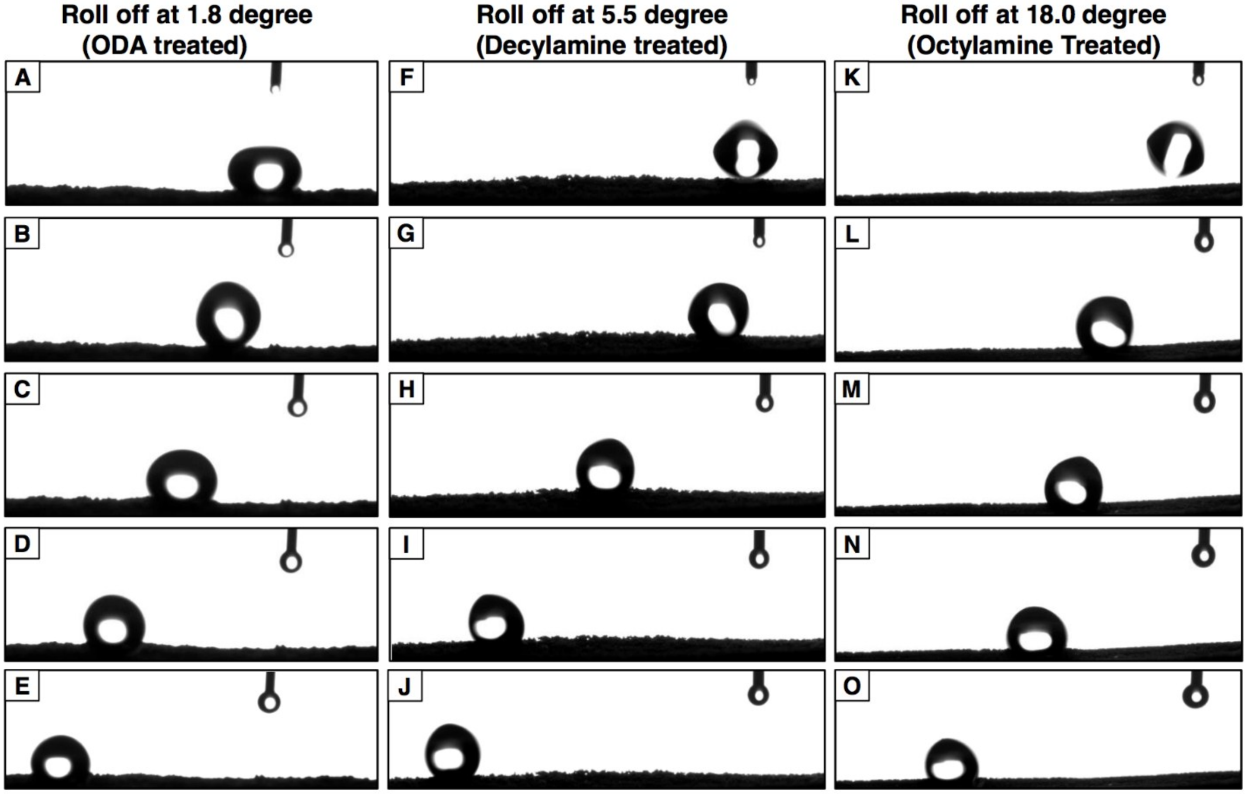


Figure S9. A-O) Contact angle images showing the rolling of water droplet on the surface of polymeric material which was prepared in pentanol and post functionalization with octadecylamine (A-E, tilt angle: 1.8 degree), decylamine (F-J, tilt angle: 5.5 degree) and octylamine (K-O, tilt angle: 18.0 degree). The water droplet (4μL) was dispensed from the 5 cm height on the surface of polymeric material.

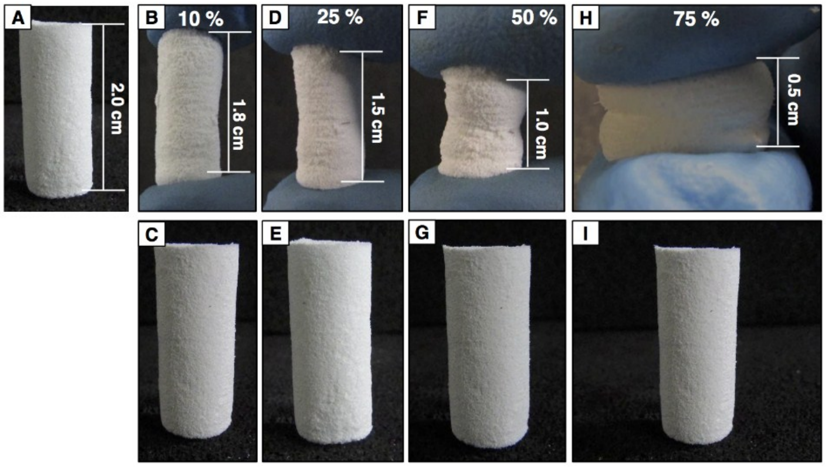


Figure S10. A-I) Digital images of the polymeric material before (A) and after (B, D, F, H) manual incurring of compressive strains (from 10 % to 75 %). The polymeric material (synthesized in pentanol) recovered its native shapes (C, E, G, I) after releasing the manual pressure.

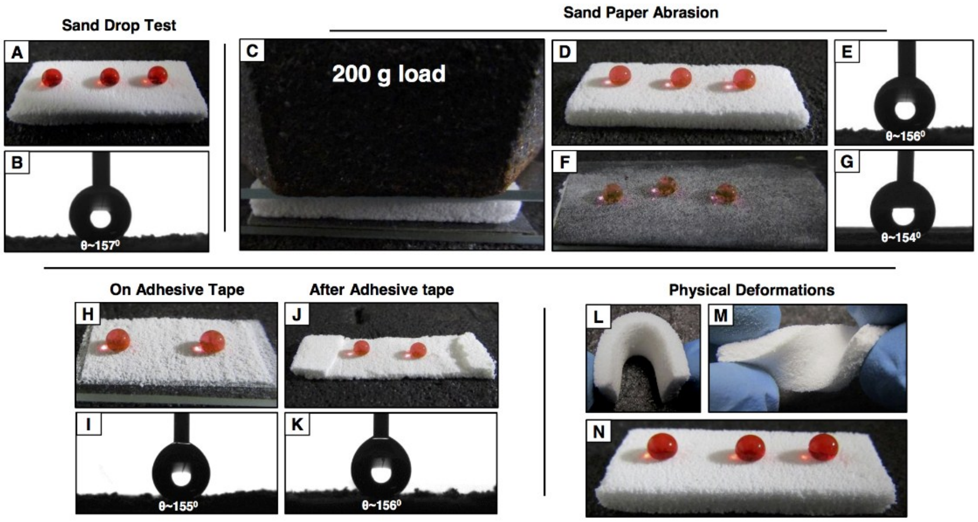


Figure S11. (A-J) Digital images accounting separation of oil from complex aqueous phase/oil mixtures, where the aqueous phases are deionized water (A,B), acidic water, pH,1.0) (C,D), alkaline water, pH, 12.0) (E,F), artificial sea water (G,H) and river (Brahmaputra, Assam, India) water (I,J).

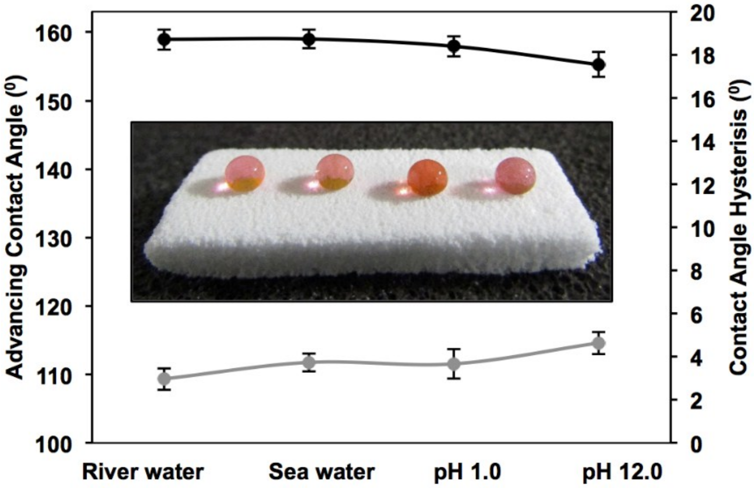


Figure S12. The plot showing the advancing contact angle (black) and contact angle hysterisis (grey) of the beaded water droplet on the polymeric material after exposure to various harsh chemically harsh environments and the digital image illustrating the ability of the material to repel chemically harsh aqueous droplets.

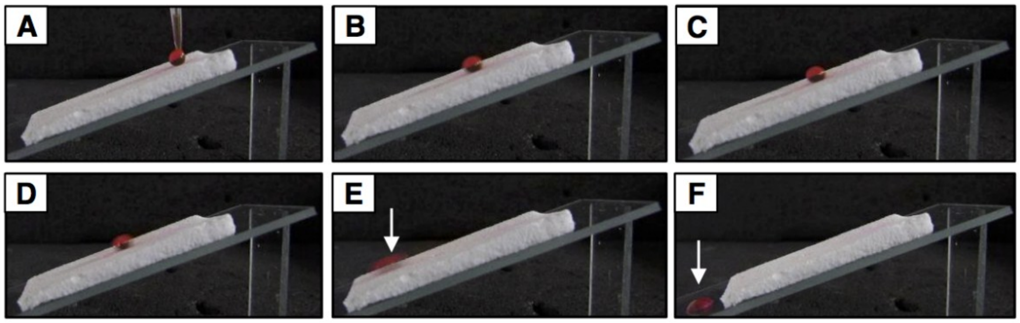


Figure S13. A-F) Digital images are depicting the pinning (A-C) and rolling (D-F) of beaded water droplet (red color aids visual inspection) on the surface of the polymeric material (which was prepared in pentanol and post functionalization with octylamine) after tilting the material at 15° and 18° respectively.

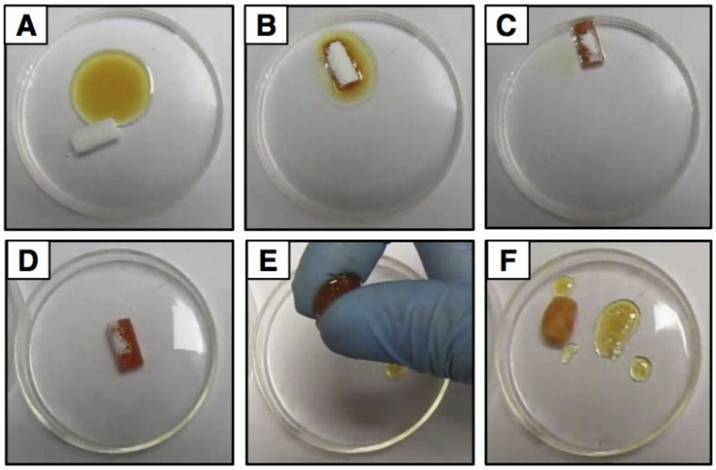


Figure S14. A-F) Digital images showing the separation (A-D) of floating oil (motor oil) from air/water interface selectively using the polymeric material (post functionalized with ODA) and the oil was collected (E-F) from the material by manual compression.