Electronic Supplementary Material (ESI) for Polymer Chemistry.

Vat Photopolymerization of Charged Monomers: 3D Printing with Supramolecular Interactions

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Supplemental

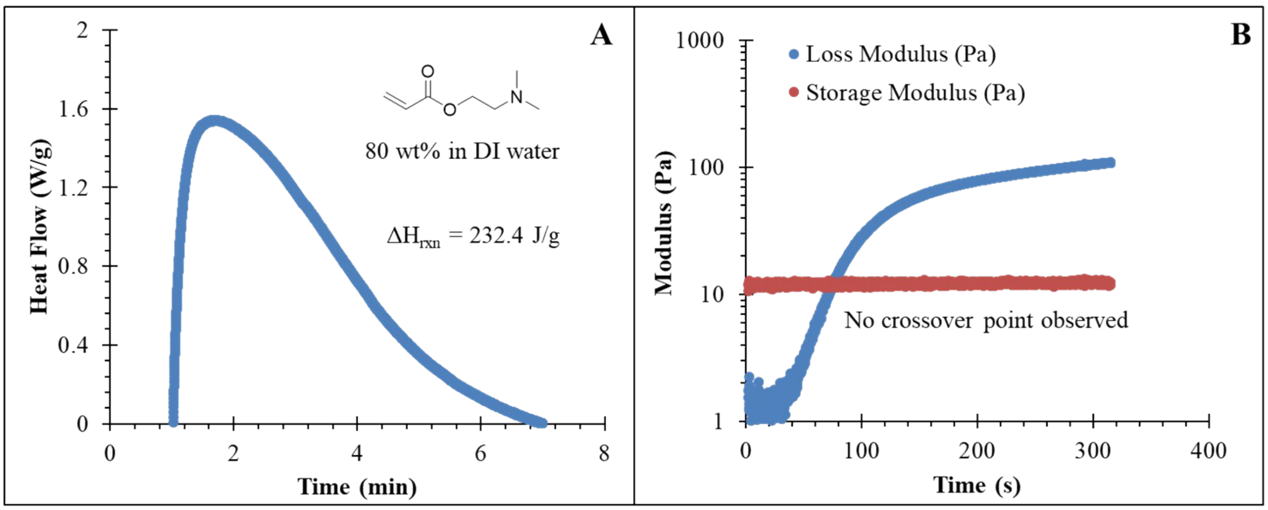

Figure S1. (A) Photo-DSC of 2-(dimethylamino)ethyl acrylate in 80 wt% DI water as a non-charged control compared to TMAEA. **(B)** Photo-rheology of the same system where no crossover point is observed, which suggested a solid was not formed.

Table S1. Photo-DSC results and subsequent percent conversion calculations of every homopolymer and TMAEA/NVP copolymer system.

Sample	Theoretical $\Delta H_{polymerization}$ (J/g)	Measured $\Delta H_{polymerization}$ (J/g)	Percent Conversion (%)
TMAEA	387	290	75
AAS	360	126	35
AASNa	325	130	40
SPAK	322	145	45
TMAEA/NVP2.5	354	290	82
TMAEA/NVP5	365	317	87
TMAEA/NVP10	342	307	90
TMAEA/NVP20	346	305	88
TMAEA/NVP30	325	292	90

Table S2. Tensile results of photopolymerized films of homopolymers.

Sample	Stress at 100 % elongation (MPa)	Elongation (%)
TMAEA	$9.2\ 10^{-2} \pm 0.53$	1250 ± 100
AAS	$6.7\ 10^{-3} \pm 0.21$	250 ± 55
AASNa	$9.7\ 10^{-3} \pm 0.34$	550 ± 130
SPAK	$3.7\ 10^{-3} \pm 0.2$	1130 ± 80
PEGMEA480	$5.1\ 10^{-3} \pm 0.43$	830 ± 240

Sample	Stress at 100 % elongation (MPa)	Elongation (%)	Hysteresis (%) Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
TMAEA	0.092 ± 0.0053	1250 ± 100	14 ± 2.1	10 ± 3.5	9 ± 1.5	9 ± 2.2	9 ± 2.9
TMAEA/VP2.5	0.11 ± 0.0073	1170 ± 88	20 ± 4	16 ± 3	15 ± 1	13 ± 4	13 ± 4
TMAEA/VP5	0.13 ± 0.0053	1030 ± 69	35 ± 6	28 ± 7	28 ± 5	25 ± 7	24 ± 5
TMAEA/VP10	0.21 ± 0.0081	900 ± 17	41 ± 3.4	35 ± 8.7	33 ± 10	33 ± 3.4	31 ± 6.7
TMAEA/VP20	0.29 ± 0.15	640 ± 49	68 ± 12	54 ± 13	50 ± 9.8	48 ± 10	48 ± 5.3
TMAEA/VP30	2.6 ± 0.47	160 ± 35	87 ± 15	65 ± 17	61 ± 12	55 ± 12	52 ± 13

Table S3. Tensile and hysteresis results of photopolymerized films TMAEA/NVP copolymers.

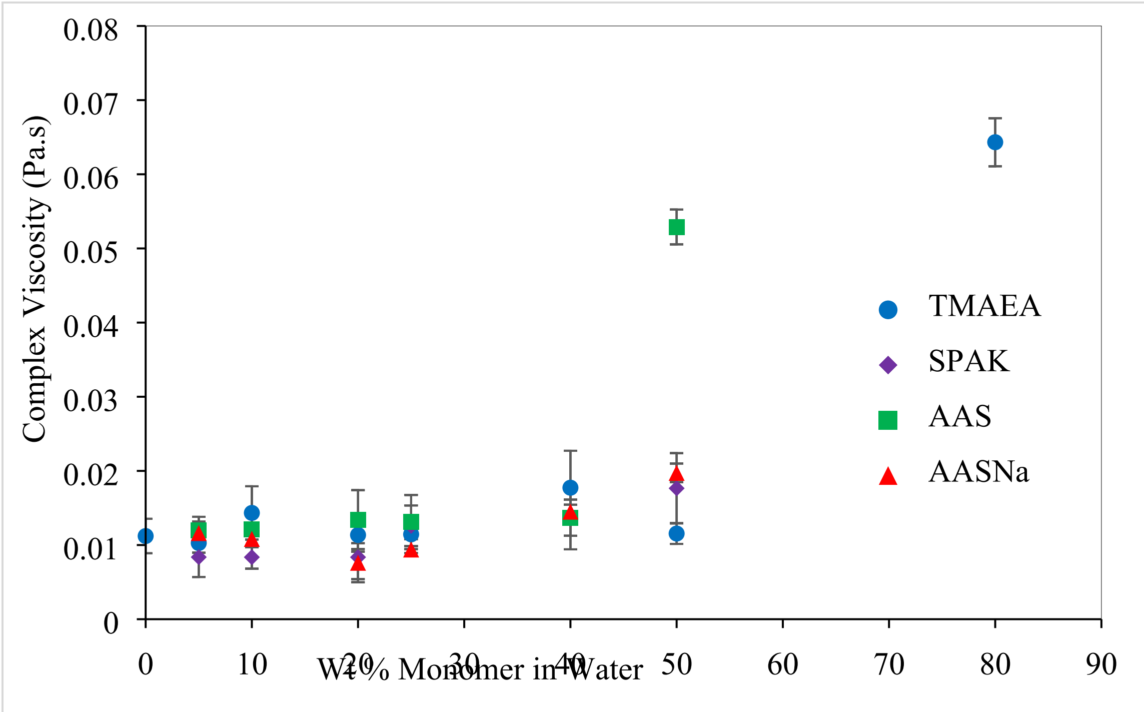

Figure S2. Concentric cylinder rheology provides complex viscosity of monomer solutions as a function of monomer concentration ($n = 3$, $p < 0.05$). TMAEA and AAS exhibit increased viscosity at photopolymerization concentration compared to AASNa and SPAK.

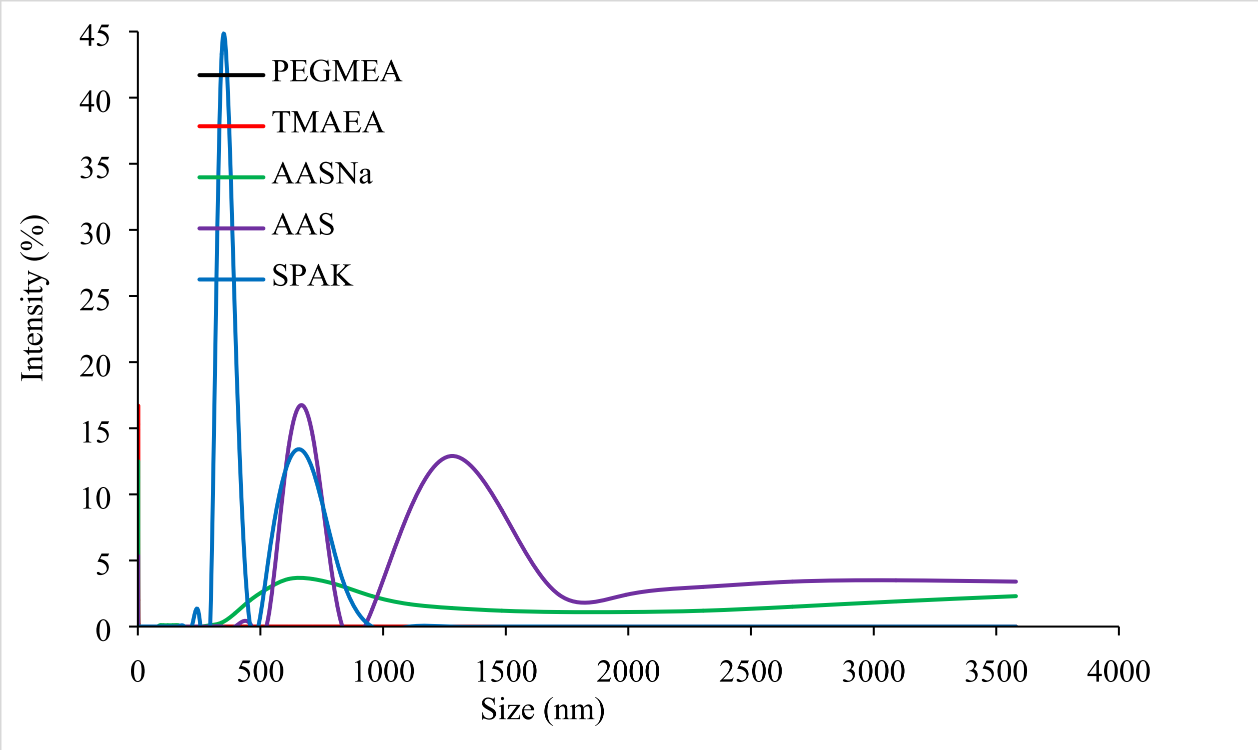

Figure S3. Dynamic light scattering reveals ionic aggregation in monomer.

Rheology of monomer solutions revealed complex viscosity as a function of monomer concentration (**Figure S2**). The increased viscosity of TMAEA and AAS at monomer concentrations relevant to photopolymerization (80 wt% and 50 wt%, respectively) suggests a role of monomer viscosity on final film modulus. This viscosity decreased significantly upon the addition of water to monomer solutions, confirming aggregate presence in monomer solutions. Interestingly, AASNa and SPAK, which both contain large counterions, failed to exhibit this increase in viscosity at 50 wt% in water. This decreased viscosity corresponded to a decrease in final film modulus, suggesting the potential for solution viscosity to aid in monomer selection for vat photopolymerization.

The discrepancies between monomers based on photo-DSC potentially arises from varied ionic aggregation in the monomer solution prior to polymerization (**Figure S3**). As seen in dynamic light scattering, each of the ionic monomers exhibited larger aggregates as compared to $PEGMEA_{480}$, suggesting a role in monomer aggregation for the successful formation of free-standing films. The size of each of these aggregates and their shape potentially direct both the kinetics of polymerization and the properties of the free-standing film.[34-35] Further studies as to the particular mechanism and the potential extension of these monomers is currently underway.

34. Noor, S. A. M.; Sun, J.; MacFarlane, D. R.; Armand, M.; Gunzelmann, D.; Forsyth, M., Decoupled ion conduction in poly (2-acrylamido-2-methyl-1-propane-sulfonic acid) homopolymers. *Journal of materials chemistry a* **2014,** *2* (42), 17934-17943.

35. Abdullah, M. M.; AlQuraishi, A. A.; Allohedan, H. A.; AlMansour, A. O.; Atta, A. M., Synthesis of novel water soluble poly (ionic liquids) based on quaternary ammonium acrylamidomethyl propane sulfonate for enhanced oil recovery. *Journal of Molecular Liquids* **2017,** *233*, 508-516.