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Remarkable Swelling Capability of Amino Acid Based Cross-Linked Polymer Networks in Organic and Aqueous Medium

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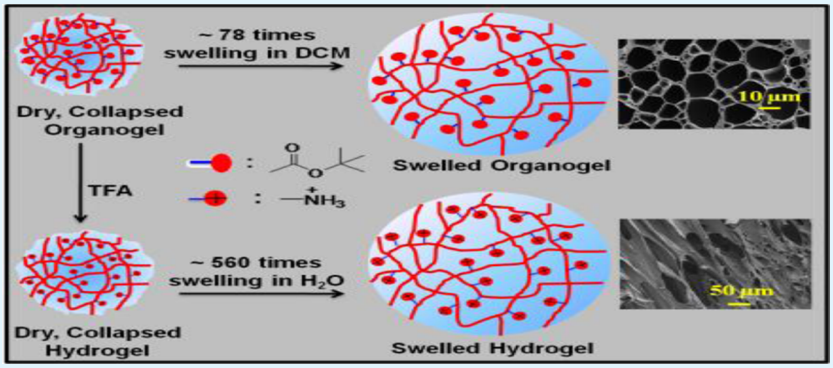
Supporting Information



ABSTRACT: This work reports design and synthesis of side chain amino acid based cross-linked polymeric gels, able to switch over from organogel to hydrogel by a simple deprotection reaction and showing superabsorbancy in water. Amino acid based methacrylate monomers, *tert*-butoxycarbonyl (Boc)-L/D-alanine methacryloyloxyethyl ester (Boc-L/D-Ala-HEMA), have been polymerized in the presence of a cross-linker via conventional free radical polymerization (FRP) and the reversible addition−fragmentation chain transfer (RAFT) technique for the synthesis of cross-linked polymer gels. The swelling behaviors of these organogels are investigated in organic solvents, and they behave as superabsorbent materials for organic solvents such as dichloromethane, acetone, tetrahydrofuran, etc. Swollen cross-linked polymer gels release the absorbed organic solvent rapidly. After Boc group deprotection from the pendant alanine moiety, the organogels transform to the hydrogels due to the formation of side chain ammonium ($-NH_3^+$) groups, and these hydrogels showed a significantly high swelling ratio (~560 times than their dry volumes) in water. The morphology of organogels and hydrogels is studied by field emission scanning electron microscopy (FE-SEM). Amino acid based cross-linked gels could find applications as absorbents for oil spilled on water as well as superabsorbent hydrogels.

KEYWORDS: *amino acids, cross-linking, hydrogel, organogel, swelling*

1. INTRODUCTION

Based on the liquid media that can be adsorbed on to the network, cross-linked polymer gels can be of two types: hydrophilic gels (hydrogels) and organic gels (organogels). Hydrogels are 3-dimensional water-insoluble high molecular weight networks that can absorb water molecules and swell to more than several folds compared to its dry state.[1,2] High water content in the network enhances their softness and biocompatibility,[3] and hydrogels find many applications in controlled drug delivery, enzyme recycling, protein chromatography, tissue engineering, etc.[4−6] Hydrophilic superabsorbent polymers (SAPs) and hydrogels usually collapsed in most of the organic solvents due to the unfavorable interactions inside the network.[7] On the other hand, organogels are gaining increasing interest due to their ability to absorb organic solvent or oil spilled on water.[8−13] For example, superabsorbent materials for conventional volatile organic compounds (VOCs) with lipophilic polyelectrolyte polymer gel containing *tetra*-alkylammonium tetraphenylborate showed swelling in a variety of nonpolar organic solvents up to 500 times their dry size, and a high degree of swelling was attributed to the dissociation of ionic groups in low polar media.[8]

Naturally occurring amino acid based polymers have generated considerable interest over recent years, because incorporation of amino acid functionality may create highly ordered hierarchical structures through intra- and interchain associations via noncovalent forces, such as hydrogen bonding.[14−18] Amino acid moiety can be introduced into the polymers either in the main chain or in the side chain, and much attention has recently been devoted to the amino acid based vinyl monomers (amino acid moiety in the side chain).[19−22] These vinyl monomers can be prepared by modifying amino acids either

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at the amine site or at the carboxylic acid site to generate *N*-terminus[23] or *C*-terminus[24] vinyl monomers, respectively. Several amino acid based polymers have been synthesized by free radical polymerization of *N*-terminus modified vinyl monomers.[25−28] Using atom transfer radical polymerization (ATRP), Sun and Gao recently prepared amino-acid based polymers from *C*-terminus vinyl monomers (amine site was protected with Boc-group), which showed low cytotoxicity, electropositive character, and strong binding effect with DNA.[29] Our group reported reversible addition−fragmentation chain transfer (RAFT) polymerization of *C*-terminus modified amino acid based methacrylate monomers from alanine, phenylalanine, tryptophan, leucine, and isoleucine.[30−34] Amino acid containing thermosensitive hydrogels have been synthesized by radiation-induced polymerization, and their use as matrices for the controlled release of drugs has been described.[35−39] Acryloyl-L-proline methyl ester based copolymer hydrogels have also been reported.[40] There is no report on polymeric gels with *C*-terminus modified protected or unprotected amino acid based vinyl monomers, although their reported polymers showed positive surface charge in aqueous media and ideal to show superabsorbancy in water.

In this study, we investigated both conventional free radical polymerization (FRP) and controlled radical polymerization (CRP) technique such as RAFT for the synthesis of cross-linked polymer gels (organogels) from *C*-terminus modified amino acid based methacrylate monomers, in which primary amine functionality was protected with the Boc-group. These amino acid based organogels show fast and excellent organic solvent uptake ability, and Boc-groups can be easily deprotected to hydrogels under acidic conditions. Transformation of a polymeric cross-linked organogel to hydrogel by a simple method would facilitate the use of these soft materials for various industrial and domestic applications. Due to the presence of amino acid pendants, these hydrogels are expected to show enhanced biocompatibility for tissue engineering and other biological applications.

2. EXPERIMENTAL SECTION

Materials. Boc-L-alanine (Boc-L-Ala-OH, 99%), Boc-D-alanine (Boc-D-Ala-OH, 99%), and TFA (99.5%) were purchased from Sisco Research Laboratories Pvt. Ltd., India and used as received. 4-Dimethylaminopyridine (DMAP, 99%), anhydrous *N*, *N*′-dimethylformamide (DMF, 99.9%), dicyclohexylcarbodiimide (DCC, 99%), and 2-hydroxyethyl methacrylate (HEMA, 97%) were obtained from Sigma and used without any further purification. DEGDMA (99%) was purchased from Sigma and passed through activated basic alumina before use. 2,2′-Azobisisobutyronitrile (AIBN, Sigma, 98%) was recrystallized twice from methanol. $CDCl_3$ (99.8% D) was purchased from Cambridge Isotope Laboratories Inc., USA for NMR study. The solvents such as hexanes, acetone, ethyl acetate, MeOH, DCM, THF, etc. were purified by standard procedures. The chain transfer agent (CTA) 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDP) was synthesized as reported elsewhere (Figure S1 for the ^{1}H NMR spectrum of CDP).[41]

Monomers Synthesis. Amino acid based vinyl monomers were synthesized by the coupling reaction of Boc protected L- and D-alanine with HEMA in the presence of DCC and DMAP following the previously reported procedure.[24] In a typical example, Boc-L-Ala-OH (52.85 mmol, 10.00 g) was dissolved in 100 mL of dry DCM in a 500 mL double necked round bottom flask containing a magnetic stir bar. Under nitrogen atmosphere, DCC (52.85 mmol, 10.90 g) in 50 mL of DCM was added dropwise under vigorous stirring followed by the addition of DMAP (5.28 mmol, 0.64 g). Then, the reaction vessel was kept on ice-water bath, and HEMA (52.85 mmol, 6.88 g) was added dropwise for 15 min. After 30 min, ice-water bath was removed, and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was filtered to remove insoluble *N*,*N*′-dicyclohexylurea (DCU), and the filtrate was washed successively with 0.1 N HCl (200 mL × 4), saturated $NaHCO_3$ (200 mL × 4), and brine solution and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, and the resulting solid was further purified by column chromatography using ethyl acetate/hexane (R_f = 0.5; 1:9) as eluent. The final product (Boc-L-Ala-HEMA, 13.5 g, yield = 85%) is pure white solid. ^{1}H NMR (Figure S2, 500 MHz, $CDCl_3$, 20 °C): δ = 6.12 and 5.59 (s, 2H, C═CH_2), 5.02 (s, 1H, N*H*COO), 4.49−4.29 (m, 5H, OCH_2CH_2O and CH_3C*H*COO), 1.94 (s, 3H, C═CCH_3), 1.44 (s, 9H, C(CH_3)$_3$), 1.38 ppm (m, 3H, CH_3CHCOO,). ESI-MS (Figure S3): [M + Na^+] = 324.22 *m*/*z*.

Similarly, Boc-D-Ala-HEMA was synthesized from Boc-D-Ala-OH and HEMA (yield: 81%). ^{1}H NMR (Figure S4, 500 MHz, $CDCl_3$, 20 °C): δ = 6.12 and 5.59 (s, 2H, C═CH_2,), 5.03 (s, 1H, N*H*COO), 4.49−4.29 (m, 5H, OCH_2CH_2O and CH_3C*H*COO), 1.94 (s, 3H, C═CCH_3), 1.44 (s, 9H, C(CH_3)$_3$), 1.38 ppm (m, 3H, CH_3CHCOO). ESI-MS (Figure S5): [M + Na^+] = 324.24 *m*/*z*.

General Procedure of Gel Synthesis. All cross-linked RAFT gels were synthesized in the presence of AIBN as radical source, CDP as CTA, and DEGDMA as cross-linker in a septa sealed 20 mL glass vial. A typical example of RAFT gel synthesis is as follows: Boc-L-Ala-HEMA (1.00 g, 3.32 mmol), DEGDMA (16.08 mg, 0.0664 mmol), CDP (6.69 mg, 0.0166 mmol), AIBN (0.54 mg, 3.32 × 10^{-4} mmol; 0.1 mL solution of 5.4 mg AIBN in 1.0 mL DMF), and 0.4 mL of anhydrous DMF were taken in a 20 mL septa sealed vial equipped with a magnetic stir bar. Then the reaction vial was purged with nitrogen for 20 min, and gelation reaction was carried out in a preheated reaction block at 70 °C for 24 h. Finally, the reaction was quenched by rapid cooling in an ice-water bath and exposure to air. The FRP gels were synthesized following the same procedure as RAFT gels but in the absence of CTA, and the reactions were carried out for 6 h.

Purification of Crude Gels. All gels were collected from the reaction vial by breaking the glass vial very carefully and unreacted monomers, cross-linkers, CTA, and DMF were removed by soaking the gel in hexanes/acetone mixture (250 mL, 1:1, v/v) for two days. The hexanes/acetone mixture was replaced 8−10 times a day. Finally, all gels were dried in air for 1 day followed by drying under high vacuum at 40 °C for three days.

Solvent Uptake Kinetics by Gravimetric Method. Solvent uptakes kinetics of synthesized cross-linked gels was studied gravimetrically at room temperature, and tea bags were employed for this purpose.[42] The tea bag was absorbed in the solvent, and the surface was blotted quickly with a tissue paper. A measured amount of dry gel was added into the tea bag and weighed. Then, the tea bag containing the dry gel was immersed in solvent, taken out in a certain interval of time, blotted the surface quickly, and weighed. Solvent uptakes of swelled gels were determined[43] using the following formula (eq 1)

$$\text{Swelling Ratio} = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_d and W_s are the mass of the dried and swollen cross-linked polymer samples, respectively.

Solvent Retention Kinetic. Solvent retention kinetics studies in air at room temperature were performed by weighing the fully swelled gels as a function of time.

Deprotection of Boc Protected Cross-Linked Gels. The Boc-protecting groups from the side chains of the cross-linked gels were removed using TFA to obtain hydrogels with ammonium ($-NH_3^+$) groups. In a typical example, 35.5 mg of RL100 (Table 1) was soaked in 5 mL of TFA for 48 h. Then, the swelled gel was washed six times with diethyl ether, and in this process the gel collapsed to its original volumes. The modified gel was dried in air for one day followed by drying under high vacuum at 40 °C for two days.

Effect of pH on Swelling Ratio. The swelling ratio of hydrogels was determined at various pHs ranging from 2.0 to 10.0. Since swelling properties are strongly affected by ionic strength and buffer composition,[44] we adjusted the pH of the medium using 0.1 N NaOH or 0.1 N HCl stock solutions.

Table 1. Synthesis of Amino Acid Based Cross-Linked Polymer Gels in DMF at 70 °C[a]

gels	monomer	[monomer]/[DEGDMA] /[CDP]/[AIBN]	gelation time (min)	conv. (%)[d]
FL100[b]	Boc-L-Ala-HEMA	100/2/-/0.1	30	95
FL200[b]	Boc-L-Ala-HEMA	200/2/-/0.1	40	96
FL300[b]	Boc-L-Ala-HEMA	300/2/-/0.1	60	95
RL100[c]	Boc-L-Ala-HEMA	100/2/0.5/0.1	45	76
RL200[c]	Boc-L-Ala-HEMA	200/2/0.5/0.1	60	75
RL300[c]	Boc-L-Ala-HEMA	300/2/0.5/0.1	90	75
RL600[c]	Boc-L-Ala-HEMA	600/2/0.5/0.1	140	69
RD100[c]	Boc-D-Ala-HEMA	100/2/0.5/0.1	45	76
RD200[c]	Boc-D-Ala-HEMA	200/2/0.5/0.1	60	75
RD300[c]	Boc-D-Ala-HEMA	300/2/0.5/0.1	90	77

[a]RAFT gels were synthesized for 24 h and FRP gels were synthesized for 6 h. [b]Synthesized by FRP. [c]Synthesized by RAFT mechanism. [d]Determined gravimetrically by comparing the weight of the dry gels with respect to the monomer.

Instrumentation. The ^{1}H NMR spectra were measured on a Bruker Avance^{III} 500 spectrometer using $CDCl_3$ solvent at 25 °C. Solid-state ^{13}C CP/MAS NMR was conducted in the same Bruker Avance^{III} 500 spectrometer. A broad band channel was tuned to 125 MHz, the resonance frequency of ^{13}C, and a 4 mm MAS probe was used for the experiment. A typical ^{13}C value of pulse length was used for 4 μs, and a relaxation delay of 20 s was used. The spinning speed for the sample was regulated to 10 kHz. Positive mode electrospray ionization mass spectrometry (ESI-MS) was carried out on a Q-Tof Micro YA263 high resolution (Waters Corporation) mass spectrometer. The FT-IR spectrum was recorded on KBr pellets using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Thermal studies were carried out using a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min^{-1} with a sample weight of approximately 4−7 mg in nitrogen atmosphere.

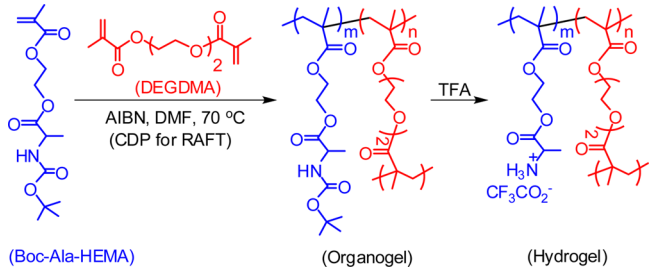
FE-SEM Analysis. The interior morphology and porous structures of synthesized cross-linked organo- and hydrogel matrix were examined by FE-SEM. A small piece of dried gel samples was immersed in DCM (for organogels) or DI-water (for hydrogels) overnight to reach its maximum swelling state. The swelled organogels were cross sectioned and dried over silicon wafer, whereas hydrogels were frozen in liquid nitrogen and freeze dried using a lyophilizer (Orleon instrument) under high vacuum at −50 °C for 32 h. The dry gel sample was coated with a very thin layer of gold−palladium alloy for 1 min under high vacuum and examined by FE-SEM (Carl Zeiss Supra SEM instrument).

Rheology Study. The rheological measurements were carried out on a TA-ARG2 rheometer using a steel parallel plate with 40 mm diameter at 25 °C. Gap spacings of 1.0 mm for organogels and 1.5 mm for hydrogels were used. The dynamic shear moduli (G' and G'') were recorded in the linear viscoelastic regime at a strain of γ = 0.5% as a function of angular frequency (0.1−100 rad/s). For rheological measurements, organogels were swelled in MeOH, and hydrogels were swelled in DI water overnight. The organogel surface was wiped with tissue paper and allowed to evaporate for 5 min to reduce the effect of solvent evaporation during experiment. For hydrogels, surface water was wiped and measurements were carried out.

3. RESULTS AND DISCUSSION

Synthesis and Characterization Gels. Amino acid based cross-linked poly(Boc-L/D-Ala-HEMA) gels were synthesized by conventional FRP of Boc-L/D-Ala-HEMA monomers in the presence of diethylene glycol dimethacrylate (DEGDMA) as a cross-linker at different monomer/cross-linker ratios using AIBN as initiator and DMF as solvent at 70 °C. Since the RAFT polymerization of Boc-L-Ala-HEMA in the presence of CDP in DMF at 70 °C produced linear poly(Boc-L-Ala-HEMA) polymers with controlled molecular weight and narrow polydispersity,[24] cross-linked gels with different amounts of cross-linker were prepared using the RAFT mechanism in the presence of CDP as CTA (Scheme 1). Ten sets of gels were synthesized, and variables for the gelation reactions are summarized in Table 1. The cross-linked polymers were named according to the following rules (Table 1): the first letter R or F signifies the polymerization mechanism, RAFT or FRP, respectively; the second letter L or D represents the L-alanine or D-alanine monomers; the number 100, 200, or 300 stands for the monomer/cross-linker ratios, respectively. Hence, for example, gel RL100 was synthesized by RAFT polymerization of Boc-L-Ala-HEMA monomer with Boc-L-Ala-HEMA/DEGDMA = 100/2.

Scheme 1. Synthesis of Amino Acid Based SAP for VOCs and Hydrogel



A lower concentration of initiator was used to satisfy gel formation condition, [DEGDMA]/[AIBN] > 1.[45] Also, we maintained [CDP]/[DEGDMA] ≤ 0.5 for the favorable occurrence of gelation,[46] which was observed after 30, 40, and 60 min for the FL100, FL200, and FL300 gels, respectively (Table 1). However, gelation time for the RAFT gels was 45 min for RL100 and RD100, 60 min for RL200 and RD200, 90 min for RL300 and RD300, and 140 min for RL600, respectively. It is observed that gelation time for the RL and RD gels is the same due to their same chemical reactivity, and gelation time increases as cross-linker density decreases in the reaction media. Longer gelation time for RL600 could be explained by the retardation effect offered by a higher concentration of the RAFT agent compared to cross-linker ensuring more and more intermolecular cross-linking, by slowing down the reaction rate.[47] Gelation time for the RAFT gels are higher compared to FRP gels due to fast initiation followed by slow propagation in the RAFT mechanism. Therefore, to attain maximum monomer conversion the RAFT gels were synthesized for 24 h, whereas FRP gels were synthesized for 6 h. The conversion of the gels was calculated by a gravimetrical method by comparing the weight of the dry gels with respect to the monomer, and the results are shown in Table 1.

Structural evidence for the gels was obtained from solid state ^{13}C CP/MAS NMR, FT-IR spectroscopy, and thermogravimetric analysis (TGA) study. The ^{13}C NMR (Figure 1a) of the RL300 gel shows characteristic resonance signals from different carbon atoms in the gel. Note that we did not observe carbon peaks from cross-linker (DEGDMA) and CDP, because they are present in very small amounts in the gel network. Note that we did not observe resonance signals from the vinyl group, indicating complete removal of unreacted vinyl monomer from the gel network. In the FT-IR spectrum of RL300 gel (Figure 2), the characteristic absorption peaks of amide groups are observed at 3388 and 1514 cm^{-1}. The stretching vibrations of C−O and

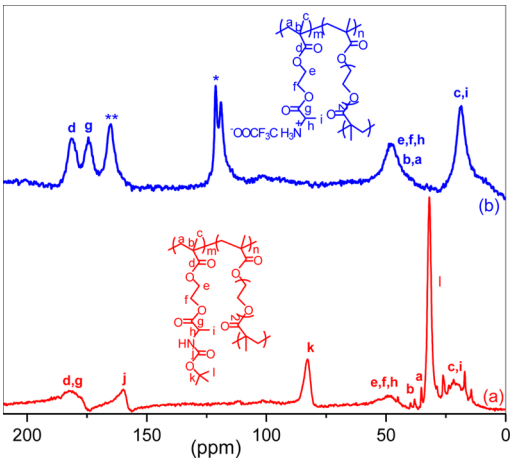


Figure 1. ^{13}C solid state NMR spectra of RL300 gel before (a) and after (b) Boc deprotection. * peak appeared due to the CF_3 group and ** peak comes from COO- group.

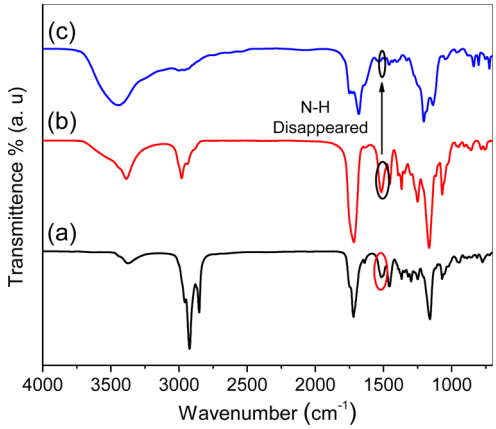


Figure 2. FT-IR spectra of Boc-L-Ala-HEMA (a), RL300 gel before (b) and after (c) Boc deprotection.

carbonyl (C═O) groups appeared at 1166 and 1650−1830 cm^{-1}, respectively. The signals in the region 2837−3067 cm^{-1} due to the symmetric and asymmetric C−H stretching vibrations of CH_2 and CH_3 groups are also observed. The TGA study under N_2 confirmed thermal stability of cross-linked polymer gels up to ca. 200 °C (Figure S6).

Swelling Properties of Cross-Linked Gels. The solvent uptake behavior of all synthesized gels was investigated in organic solvents with various solvent polarity, such as hexane (nonpolar, dielectric constant (ε) = 1.88), tetrahydrofuran (THF, polar aprotic, ε = 7.5), dichloromethane (DCM, polar aprotic, ε = 9.1), acetone (polar aprotic, ε = 20.7), methanol (MeOH, polar protic, ε = 33), and also in H_2O (polar protic, ε = 80). Swelling ratios (SR) were calculated (using eq 1) at room temperature by taking a measured amount of gel in the tea bag, and it was immersed in the particular solvent for 24 h. Then, the tea bag was taken out from the solvent, quickly blotted with tissue paper, and weighed. The results of the solvent uptake ratio of gels are summarized in Table 2. It has been observed that all the gels showed maximum solvent uptake in DCM and minimum in methanol, whereas swelling ratios of polymer gels in hexane and H_2O are negligible. The solvent uptake ratio gradually decreases from DCM to methanol as the ε of the solvent gradually increases. These results indicate that the swelling decreased with increasing solvent polarity, and the gels collapsed in the more polar protic solvents (like water).[8] The swelling degree of the polymer gel mostly depends on the compatibility between the polymer chain and polarity of the absorbing solvent media. The pendent group in the polymer backbone is composed of two C═O bonds, and partially polar nature of the side chain would be the most favorable for the dipole−dipole interaction with the polar aprotic solvent (e.g., DCM, THF, acetone) compared to polar protic solvent (MeOH) with high ε and *H*-bonding capability. The swelling ratio in MeOH (ε = 33) is comparatively low, whereas solvent uptake capacity in water (ε = 80) is negligible for all RAFT and FRP gels, confirming that the dipolar attraction force is dominant rather than *H*-bonding. The swelling degree for all the gels in hexane (ε = 1.9) is almost zero because the gels collapsed in nonpolar solvents. It has also been observed that the swelling degree of all synthesized gels is reduced to its half value in the hexane/DCM mixture (50/50, v/v) compared to DCM. We further studied swelling ratios of all gels in 75/25 and 25/75 hexane/DCM mixed solvent systems. We obtained swelling ratios of 1.5, 1.7, 1.6, 1.7, 1.6, and 1.9 for FL100, FL200, FL300, RL100, RL200, and RL300, respectively, in the 75/25 hexane/DCM mixture. Similarly, swelling ratios of 15.2, 30.4, 38.7, 20.4, 37.3, and 39.2 were calculated, respectively, for FL100, FL200, FL300, RL100, RL200, and RL300 in the 25/75 hexane/DCM solvent mixture. Gels showed poor swelling in the 75/25 hexane/DCM solvent mixture may be attributed to the incompatibility of polarity between polymer chain and solvent system, whereas the 25/75 hexane/DCM solvent system showed high swelling due to close polarity to DCM itself. Therefore, incompatibility between polarities of the polymer chain in gel network and absorbing media restrict the penetration of solvent inside the gel domain. Table 2 demonstrates that the swelling ratio for the RAFT made gels are high compared to FRP gels. This is because FRP gels are formed by the tying up of microgel domains at a critical monomer conversion, whereas CRP gels are created by linking of branched and hyperbranched preformed polymers resulting in more structured and homogeneous CRP gels compared to FRP gels,[48,49] which increases the solvent absorbency of RAFT made gels. Also, Table 2 shows that the swelling ratio of RAFT and FRP gels gradually increased as [monomer]/[cross-linker] is varied from 100/2 to 200/2 to 300/2. This indicates that the swelling degree is related to the cross-linker (DEGDMA) density of the gels, which is directly proportional to cross-linker concentration during the gelation reactions. Heterogeneity inside the gel network structure increases with the increasing cross-linking density, which limits the swelling ratio of highly cross-linked gels.[50] In contrast, low cross-linking density produces a more homogeneous gel arrangement which can uptake a higher percentage of solvent. However, a stable network would be formed up to a certain limit of the low cross-linking density. Therefore, we have not studied the gel materials with [monomer]/[cross-linker] beyond 300/2 except RL600, where we observed brittleness in the gel with SR = 77.8.

Swelling kinetics was studied in different solvents to estimate the saturation time of the various amino acid based gels in different solvents. All gels reached 90% swelling in DCM (Figure 3a), THF (Figure 3b), and acetone (Figure 3c) within 2 h, 3 h, and 3.5 h, respectively. Gels swelled up slowly in MeOH (Figure 3d) compared to DCM and reached its maximum swelling degree after 7 h. This observation indicates that the rate of penetration of the solvent molecules into the gels depends on dipole−dipole interaction between the solvents and polymer networks of the gels, which is higher in

Table 2. Solvent Uptake Ratios of Gels

gels	DCM	THF	acetone	MeOH	DCM:Hexane (50/50, v/v)	hexane	water	water[a]
FL100	24.5	13.4	11.6	6.7	9.2	0.07	0.08	87
FL200	32.7	28.4	20.9	12.4	14.2	0.09	0.11	103
FL300	49.5	38	28.9	17.7	22.4	0.12	0.10	430
RL100	30.3	26.8	25.0	12.7	13.4	0.09	0.15	189
RL200	43.2	37.5	34.0	13.3	17.1	0.10	0.24	326
RL300	60.7	43.9	41.0	22.4	25.0	0.10	0.11	528
RL600	77.8	46.4	38.1	22.7	22.2	0.09	0.77	560
RD100	30.9	27.4	24.7	12.4	8.3	0.08	0.08	192
RD200	42.8	37.4	33.4	13.0	13.1	0.11	0.22	319

[a]Swelling ratio of deprotected gels in water.

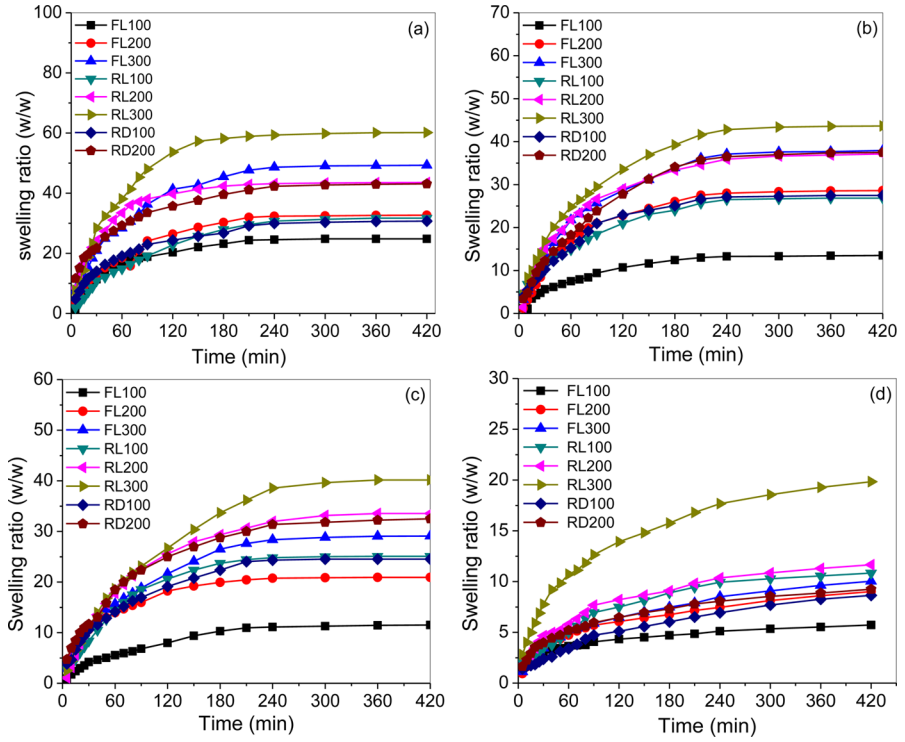


Figure 3. Swelling ratio of gels in (a) DCM, (b) THF, (c) acetone, and (d) methanol. Duplicate experiments with RL200 and FL200 in DCM suggests that there is a maximum of ±4% error from each data point.

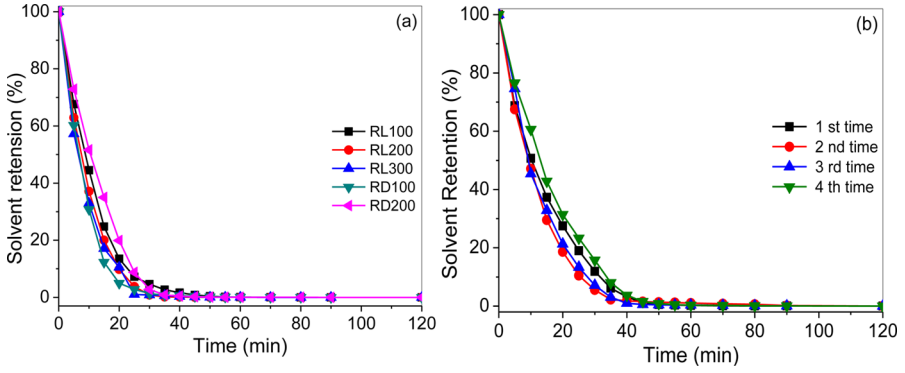


Figure 4. (a) Solvent retention (DCM) in air at 25 °C for RAFT gels. (b) Solvent (DCM) retention kinetics measurements for RL300 in air at room temperature. The RL300 was swelled for 24 h and solvent retention kinetics was studied (1st time). The same RL300 gel was again swelled in DCM for 24 h followed by solvent retention kinetics analysis (2nd time). This process was repeated two more times (3rd time and 4th time).

DCM than in methanol. Figure 3 also shows that RAFT gels swelled up at a faster rate than FRP gels due to the more structured and homogeneous network in RAFT gels compared to FRP gels.

Solvent Retention Studies of Cross-Linked Gels. The solvent retention kinetics for the cross-linked gels was studied by investigating the evaporation of DCM swollen gels in air at room temperature as a function of time (Figure 4a). All the

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RAFT and FRP gels released the absorbed DCM very fast. The RAFT gels released more than 95% absorbed DCM within 20 min, whereas in the case of FRP gels the amount is 90% (Figure S7). The remaining DCM was released in 40 min for RAFT gels and 60 min for FRP gels. Molecular mobility of the grafted chain inside the gel domain would increase in RAFT gels due to the presence of dangling chains[46] and as a result accelerate the deswelling property of RAFT gels.[51] These results suggest that amino acid based polymer gels can be used as a new class of excellent SAP material for the VOCs recovery, and they are recyclable as demonstrated below. In DCM, RL300 was swelled for 24 h, SR was measured, and solvent retention kinetics was studied. The same RL300 gel was again swelled in DCM for 24 h, and SR was measured and followed by solvent retention kinetics analysis. This process was repeated three more times, and we observed similar SR values (60 ± 5) and similar retention kinetics data were obtained within 5% error range (Figure 4b).

Transformation of Organogels to Hydrogels. Deprotection of the Boc groups from the pendant chains in the polymer gels was achieved by trifluoroacetic acid (TFA) at room temperature (Scheme 1).[52] Disappearance of signals at 82.8 and 31.8 ppm respectively for the Boc group $-OC(CH_3)_3$ and $-OC(CH_3)_3$ carbons in the ^{13}C CPMAS NMR spectrum of RL300 after TFA treatment (Figure 1b) confirmed the complete removal of the Boc group. Successful deprotection was further demonstrated by the FT-IR study of Boc protected and deprotected gels (Figure 2). It is observed that the transmittance peak at 1514 cm^{-1} due to secondary N−H bending disappeared in a deprotected gel, and a small broad peak appeared at 1537 cm^{-1} due to the $-NH_3^+$ group. After deprotection, cross-linked gels did not show swelling in common organic solvents (e.g., DCM, diethyl ether, etc.); however, they possessed swelling abilities in water indicating the transformation of organogels to hydrogels, and the very high swelling ratios determined indicate superabsorbency. Swelling experiments with deprotected RL100 was conducted in water for 6 h, and SR was calculated as 189. The swelling ratio of deprotected RAFT and FRP gels gradually increased as [monomer]/[cross-linker] varied from 100/2 to 200/2 to 300/2 (Table 2). Lower cross-linker concentration causes lower cross-linking density in the gel and increases the space between the chains and can be expanded and hold a larger amount of water.[53] However, low density cross-linked SAPs are softer (e. g., RL600) and brittle. Note that we did not observe significant differences among FL, RL, and RD series, and these amino acid side-chain based SAPs show swelling in water, which are comparable with the acrylic acid based SAPs.[53] Higher swelling abilities of amino acid based hydrogels could be due to the electrostatic repulsion between the charges on the polymer side chains and the osmotic imbalance between the interior and exterior of the gels.[54]

Cross-linked polymer hydrogels containing primary ammonium groups should be sensitive to the pH of the medium as a result of protonation and deprotonation of side chain primary amine groups.[55] The SR of Boc deprotected RL300 and RD300 hydrogels at different pH after immersion for 6 h are plotted in Figure 5, which show maxima at pH 4.0. Below this pH, swelling is restricted by a screening effect of the counter ion, which shields the charge of the ammonium cation.[44] With the increase of pH value, deprotonation of ammonium groups starts, and Boc deprotected homopolymers from Boc-L-Ala-HEMA showed hydrophilic to hydrophobic phase transition at

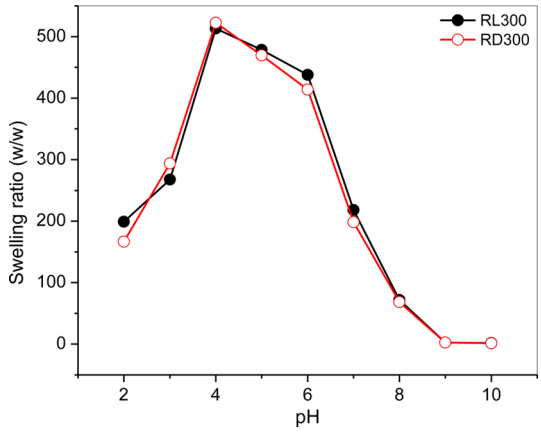

Figure 5. Variation of swelling ratio with pH for deprotected gels.

pH 6.4.[24] Since amino groups collapsed above this responsive pH, water molecules cannot penetrate into the gel matrix and SR values sharply decreased.

The SEM is one of the important diagnostic tools to investigate the surface topology and interior morphology of gel matrix. The FE-SEM micrographs of organogels and hydrogels are depicted in Figure 6 and Figure S8, which clearly demonstrate

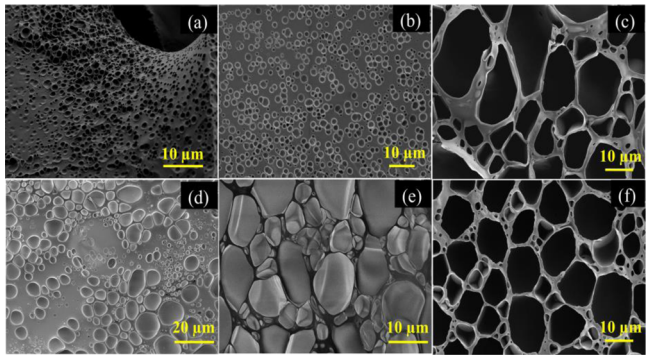

Figure 6. SEM micrographs of (a) FL100, (b) FL200, (c) FL300, (d) RL100, (e) RL200, and (f) RL300 organogels.

that morphology of both organo- and hydrogels depend on the cross-linker density in the network. For organogels, pore diameters increase as the [monomer]/[cross-linker] ratio changes from 100 to 300. Also, pore structure transforms from round to oval shape and finally to well-defined honeycomb-like structures[56] with a distinctive 4-6 member ring. Average pore diameters in the FL series increase from 3.4 ± 1 (FL100) to 10 ± 2 (FL200) to 22 ± 5 μm (FL300) and in RL gels change from 5 ± 1 (RL100) to 16 ± 3 (RL200) to 25 ± 4 μm (RL300). These results indicate that pore diameters of RL gels are a little higher compared to the corresponding FL gels of the same ratio. Therefore, the synthetic mechanism has great influence on the internal morphology of gel networks. It is also interesting to note that the morphology of hydrogels follows the same trend like organogels. However, the pores generated by diffused out DCM/water during deswelling of the RL gels are in a more ordered fashion than in a FL gel due to their more homogeneous network structures.[57,49] Since pore size increases as the [monomer]/[cross-linker] ratio changes from 100 to 300, we observed the highest solvent uptake at 300 ratio for both organogels and hydrogels.

In the next stage, we have studied rheology of gel materials to understand their mechanical strength. Measurements of storage

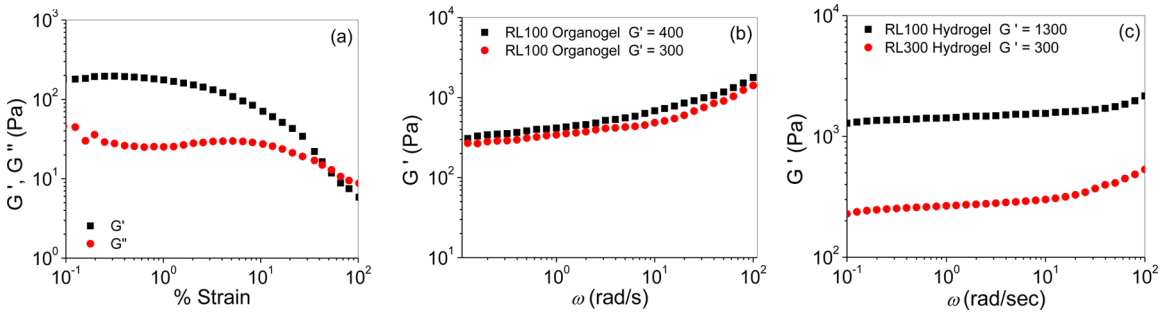

Figure 7. Storage modulus G' and loss modulus G'' on strain sweep with RL300 hydrogel (a). Storage modulus G' versus frequency (ω) (strain: 0.5%) of organogels (b) and Boc deprotected hydrogels of different cross-linking ratios (c).

modulus (G') and loss modulus (G'') versus % strain were first performed in order to establish the linear viscoelatic regime (Figure 7a), and a linear viscoelatic range up to 2.0% has been observed for swelled RL300 hydrogel. Therefore, a frequency sweep of swelled cross-linked organogels and corresponding hydrogels was carried out at a constant strain of 0.5%, which is well below the deformation limit (2%) of RL300 hydrogels. The G' of RL100 organogel and corresponding hydrogel are higher compared to the RL300 organogel and its hydrogel demonstrating that the mechanical property of a 3D cross-linked polymeric network depends on cross-linking density (Figure 7b and 7c). The low values of G' for all swelled gels (a plateau of G' has been observed up to the frequency of 10 rad/s) demonstrate the very soft cross-linked solid characteristics which are very much expected for SAP materials. The higher value of G' than G'' over the measured frequency range for all organo- and hydrogels demonstrates the desired mechanical behavior that is expected for a cross-linked 3D network.

4. CONCLUSIONS

In conclusion, the *C*-terminus modified amino acid side chain containing cross-linked polymer gels can be viewed as both superabsorbent organogels and hydrogels. Organogels possess fast and excellent solvent uptake abilities, and the absorbed solvent can be easily removed from the gel network and, thus, can be reused without any loss of absorption capacity. The swelling behavior of the organogels is controlled primarily by the compatibility of the polymer chains with the organic media, and low cross-linking density produces more homogeneous gel arrangements with a higher percentage of solvent uptake. RAFT gels showed a higher swelling ratio than FRP gels because of a lesser amount of densely cross-linked nanogel domains in the CRP mechanism. A simple Boc deprotection reaction transformed the organogels to the hydrogels, which are capable of absorbing large quantities of water, with some samples absorbing up to 560 times their dry volumes and the swelling ratio can be tuned by changing cross-linking degree in the gel network. The experimental observation of the solvent uptake ratio of synthesized organogels and hydrogels is clearly substantiated from their highly porous FE-SEM micrographs, which changes with the [monomer]/[cross-linker] ratio and synthetic mechanism. Rheological measurement of organo- and hydrogels showed the typical characteristic of cross-linked polymer gels.The simple synthetic strategy of both organogel and hydrogel architectures presented here circumvent the difficulties of their individual synthesis. Investigations are in progress to provide further insight about the effect of different amino acids on the swelling properties of the gels.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ESI-MS spectra of monomers, TGA thermogram of cross-linked gels, deswelling kinetics of FRP gels, and SEM micrograph of deprotected hydrogels. 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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