Carbonated Water Mediated Preparation of Poly(*N*-isopropylacrylamide) Thermoresponsive Gels and Liquids

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Carbonic acid solution was used a medium for the free radical polymerization synthesis of poly(*N*-isopropylacrylamide) (p-nipam) thermoresponsive polymer as an alternative to conventional inert gas purging. It was found that p-nipam cross-linked gels or linear liquids and p-nipam/dextran magnetite composite gels could be very rapidly prepared and large gels recovered intact from open air vessels. A porogen was necessary for high thermoresponse, and dextran use resulted in microporous composite gels that gave optimal thermal response at weight ratio of p-nipam:dextran of 4:1. Up to 82% weight loss was rapidly obtained upon warming above the lower critical solution temperature. Analysis of products was made by transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), and superconducting quantum interference device (SQUID). A simplified and efficient overall method for preparation of biomedical polymers is shown. A wider application of H_2CO_3 solution as a viable alternative media and to allow open air aqueous polymerizations of water soluble or hydrophilic monomers is indicated.

1. Introduction

Thermoresponsive poly(*N*-isopropylacrylamide (p-nipam) gels have received much attention due to their potential applications that include drug-release agents, immunoassay procedures, and three-dimensional cell scaffolds.[1,2] Linear (i.e., uncross-linked) p-nipam liquid has applications for enzyme immobilization and release.[3] Recently, incorporation of colloidal particles has been used to develop color-changing p-nipam gels.[4,5] These applications depend on the abrupt entropically favored conformational change of the hydrated polymer at its lower critical solution temperature (LCST) around 33 °C.[6] Uncross-linked linear p-nipam solutions above this temperature release the hydrogen-bonded water from the amide side chains of the extended polymer coil structure to form an insoluble white solid, whereas cross-linked p-nipam gels collapse into a shrunken firm gel. The LCST can be altered to a higher or lower level by grafting of copolymers with the nipam.[7–9] A recent review has discussed p-nipam applications.[10]

The many reports on the aqueous preparation of p-nipam have involved extensive nitrogen degassing of the monomer solutions and polymerization under flowing inert gas or in inert gas filled containers. It would normally be necessary to remove the polymerized product from the flask by break-up of the gel.

At room temperature and atmospheric pressure, O_2 is twice as soluble in water as N_2 by weight. Displacement of O_2 by increasing the surface partial pressure of N_2 through bubbling the gas through the solution requires a flow rate of 25 mL s^{-1} of gas per liter of solution for at least 30 min to obtain near complete O_2 removal.[11] Under the same conditions, CO_2 is approximately 80 times more soluble than N_2 and similar displacement of O_2 is very rapidly achieved by a few short CO_2 injections.

In this report, a novel preparation method was employed wherein water carbonation was used to displace dissolved oxygen. The carbonic acid (H_2CO_3) was then used to prepare monomer solutions and permitted a free radical polymerization to occur rapidly in an open vessel in open air. The effectiveness of this new approach and thermal response of p-nipam gel blocks prepared by it were then evaluated.

The H_2CO_3 solution-based polymerization was extended to the preparation of p-nipam and dextran/magnetite (DM) composites in air. These materials have an important potential application in drug delivery because the magnetite component can be inductively warmed above the LCST of the gel by an applied alternating magnetic field.[12,13] The induced deswelling provides a controlled means of delivering the aqueous component.

A number of inert diluents have been used for the preparation of porous p-nipam, which allows increased loading and faster thermal response.[14] These additives include 1,4-dioxane, silica, salts, acetone, or polyethleneglycol. In this study, dextran was incorporated in various proportions as a novel nontoxic biocompatible sacrificial porogen. The best performance in terms of deswelling property and gel strength was determined. Dextran is a water-soluble branched glucose polysaccharide comprised of straight chain α-1,6-glycosidic linkages with α-1,3 branches. Dextran has previously been grafted to p-nipam as a means of increasing its rate of enzymatic degradation or hydrophilicity[15,16] or is commonly used as a marker for release or permeability; in this study, it was introduced as a sacrificial porogen during preparation.

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Overall, this combined preparation methodology pioneers a straightforward, cost-effective, and rapid method for open air preparation of p-nipam as shaped blocks, linear liquids, or composites.

2. Experimental Section

2.1. Materials. The monomer *N*-isopropylacrylamide (nipam), cross-linker *N*,*N*′-methylenebisacrylamide (MBA), accelerator *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) and initiator potassium persulphate were obtained from Aldrich Chemical Co. Dextran (M_r 70000 and M_r 6000) was obtained from Fluka. All chemicals were used as supplied.

2.2. Preparation of Carbonated Water. Deinonized water was carbonated by using a simple pressurized “soda water”carbonation device to pCO_2 of ~2.5 atm, whereby a few short injections of CO_2 into 1 L of deionized water produced a gassed carbonic acid (H_2CO_3) solution of pH 3.8 at room temperature. At this pH, the solution essentially contains a high [CO_2] in equilibrium with [H_2CO_3] and [HCO_3^-]. In accordance with the qualitative principles of Dalton’s Law, other dissolved gases including oxygen are very largely displaced from the solution. Dissolved O_2 was reduced from 9 mg/L to 0.9 mg/L for a freshly prepared H_2CO_3 solution as measured by a DO meter. The 1 L H_2CO_3 solution was stored in a sealed bottle and used as required.

2.3. Preparation of Cross-linked p-nipam Using H_2CO_3 Solution. A one-step procedure in air was used to prepare p-nipam; typically, 4 g of nipam, 0.1 g of MBA cross-linker, and 0.3 mL of TEMED accelerator were rapidly dissolved in 50 mL of H_2CO_3 solution in a beaker with stirring. Then 0.03 g of potassium persulphate initiator dissolved in a small quantity of H_2CO_3 solution was added with stirring. Effervescence occurred for a few seconds on reagent addition due to neutralization of the H_2CO_3 by the basic components; the final pH of the reagent mixture was 8.7. The onset of polymerization was marked by solidification into a gel within approximately 5 min. This and all gels prepared subsequently were transferred as complete cylindrical blocks into deionized water 1 h after onset of polymerization. Gel blocks were washed by soaking in deionized water for 7 days with frequent water changes.

2.4. Preparation of Microporous Cross-linked p-nipam. Microporous blocks of cross-linked p-nipam were prepared as with cross-linked p-nipam using H_2CO_3, with dextran (M_r ~ 70000) added at weight ratios of nipam:dextran of 1:0, 16:1, 8:1, 4:1, 2:1, and 1:1. Unreacted monomer and dextran were removed by washing as described above.

2.5. Preparation of Linear p-nipam. Linear p-nipam liquid was prepared as with cross-linked p-nipam using H_2CO_3, except that no MBA cross-linker was added in this case. After 1 h, the liquid p-nipam solution was poured into 500 mL of deionized water held at 45 °C and stirred for 5 min. This washing process was repeated a further three times to remove unreacted monomer. The final product was stored in sealed container as a liquid solution at RT.

2.6. Preparation of Dextran/Magnetite. Dextran/magnetite (DM) was prepared by a combined dextran carboxylation and magnetite precipitation reaction by modification of a published method:[17,18] 3.8 g of $FeCl_3 \cdot 6H_2O$, 1.4 g of $FeCl_2 \cdot 4H_2O$, and 8 g of dextran ($M_r = 6000$) were dissolved in 75 mL of deionized water with stirring. Then 80 mL of NaOH 1 M was added rapidly with vigorous stirring. The mixture was stirred for 20 min, followed by heating in a microwave to 80 °C.

The mixture was then cooled in an ice bath and HCl (6 N) was added to reach pH 7. After cooling for 1 h, the mixture was centrifuged at 5300 rpm for 30 min. The supernatant was then dried under vacuum and then dispersed into water for the purification step. A sepharose G-50 column was used with deionized water as an eluant. The initial brown/black colored fractions were collected and air-dried to form a black/brown shiny solid. A solution of suspended DM product was pH 6.72.

2.7. Preparation of Microporous Dextran/Magnetite p-nipam. Dextran/magnetite p-nipam gel blocks were prepared as with the microporous cross-linked p-nipam described above (Section 2.4) but with two changes. First, 0.5 g of the premade dextran/magnetite was dissolved in the carbonic acid solution prior to addition of the other reagents, and second, TEMED accelerator was not added. A further gel was prepared in which 1 g of dextran (M_r ~ 70k) was added in addition to 0.5 g of the DM material. Absence of TEMED and presence of slightly acidic DM meant that the H_2CO_3 solution was not fully neutralized and pH of the reactant mixture solution was ~5.9.

2.8. Conventional and Control Preparations. For comparison, the counterparts to all the linear and cross-linked p-nipam materials prepared above were made with the same reagent composition but using conventional means whereby deionized water was purged by N_2 bubbling for 30 min prior to addition of reagents. DO meter measurements showed dissolved O_2 was reduced to 0.4 mg/L. For these conventional preparations, it was necessary to magnetically stir the mixture for 15 min to fully dissolve all reagents. Polymerizations were then attempted in an open beaker in open air and also conducted under N_2 in a glovebox. Cylindrical polymer blocks were removed after 1 h and washed as described above.

2.9. Thermal Response Measurement. Thermal response of prepared p-nipam in the form of ~6 cm × 6 cm cylindrical blocks that had been washed with soaking for 7 days was conducted by immersion of the weighed block into water held at 40 °C with subsequent reweighing of the block at time intervals up to 30 min The deswelling of gel blocks was recorded as the percentage ratio of the weight of gel after time (min) of immersion in water at 40 °C (W^a) to the weight of gel at maximum swelling at RT (W^b).

2.10. Characterization. Dissolved oxygen was measured to ±0.1 mg/L with a calibrated VWR DO200 meter. Fourier transform infrared (FT-IR) samples were analyzed as KBr discs on a Perkin-Elmer Spectrum One spectrometer. Scanning electron microscopy (SEM) of samples mounted on aluminum stubs and sputter coated with Pt/Pd was conducted using a Jeol 6330 field emission SEM operating at 10 keV and 12 μA and a Jeol 5600 SEM operating at 15 keV. Magnetic hysteresis loops were measured at 300 and 10 K in a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The curves were desheared under the assumption of a continuous paramagnetic background.

3. Results and Discussion

3.1. Polymerization and Transition Temperature. Degassing of water by N_2 for 30 min or by brief CO_2 injection reduced dissolved oxygen to below 1 mg/L in both cases. nipam and MBA underwent rapid dissolution upon mixing with the H_2CO_3, which was partially decomposed by the basic reagents to form a weakly acidic solution; addition of TEMED raises the pH to 8.7. Remaining carbonate as HCO_3^- is at low concentration, and residual CO_2 released may have further protected the free radical polymerization reaction in open air vessels. p-nipam gels with near-perfect optical clarity were readily obtained with polymerization of gels, as marked by complete solidification into a gel occurring within 3 min in open 50 mL beakers of 40 mm diameter. p-nipam prepared using conventional N_2 purged solutions and air-free conditions ranged between being optically clear to dense white in color, with polymerization occurring in less than 5 min in a N_2 atmosphere. White gels were obtained when a more vigorous onset of polymerization occurred that warmed the mixture beyond the LCST point of the nipam. Polymerization in open air using deionized water media that had been extensively degassed by purging with N_2 either did not take place or occurred slowly and softer low-molecular-weight polymers were obtained after 20–40 min. Dry weight of the washed polymer was 85% of the initial monomer weight; in comparison, dry weights of all other p-nipam preparations were very close to starting monomer weights .The LCST of all gels prepared was found by experiment to be unchanged at 33 ± 1 °C.

Polymerization to form linear p-nipam without MBA cross-linker using H_2CO_3 media in an open-air system successfully produced a clear liquid that rapidly solidified as a white gel on warming above the LCST.

Thermal response of cross-linked gels and comparison to gels prepared using N_2 degassed water and in air-free conditions was determined by placing washed gels into deionized water held at 40 °C. Weight loss of the gel at increasing time intervals was then assessed. In both cases, large blocks of gel (100–50 g) underwent shrinkage of only up to 5% by weight due to the formation of a dense hydrophobic crust of dehydrated p-nipam at the gel block surface[19] that significantly inhibited water outjetting from the block bulk. It is generally necessary to form the gel into granules a few millimeters in size to give rise to a high degree of deswelling at the LCST.

3.2. High Thermal Response Blocks. Use of H_2CO_3 solution allowed large or shaped blocks to be prepared easily in air, and high thermal response was achieved by the incorporation of dextran at increasing proportions from p-nipam:dextran (w/w) of 1:0 to 1:1. Thermal response of these prepared gels was again measured by weight loss from cylindrical blocks of gels prepared from 50 mL of H_2CO_3 solution with consistent reagent concentrations. Disruption of the p-nipam network by dextran polymer chains initially dispersed within the gel and subsequently washed away resulted in opacity of the washed gels. This increased greatly with increasing levels of dextran such that gels at nipam:dextran of 16:1 (w/w) were cloudy and at 8:1 (w/w) were dense white in color. Gravimetric analysis of water in which blocks were soaked and final dried weight of the polymer block indicated that the dextran was largely removed by the soaking process.

Gel swelling (from between 1.5× and 2.3× of the original weights) and softness was observed to increase with increasing dextran content. On reaching p-nipam:dextran (w/w) 1:1, the gel was mechanically weak and easily split.

Gels prepared under conventional inert gas conditions and by the H_2CO_3 solution method showed similar deswelling behavior with dextran used as a porogen. Initially, all gels reached 50% of original swollen weight after 7.5 min of warming to 40 °C, they then reached less than 40% after 15 min. The highest response gel with p-nipam:dextran of 4:1 (w/w) lost up to 82% of its original weight after 15 min. At this ratio, the maximum swelling at equilibrium on soaking was around optimum; at higher swelling, the integrity of the gel was less and its ability to expel water was reduced. At lower dextran and hence lower swelling levels, formation of a much less permeable outer skin dominated. A graph of weight loss with time for various gels warmed above the LCST is given in Figure 1. Of the conventional inert gas preparations, only weight loss curves for p-nipam and with p-nipam:dextran at 4:1 (w/w) are shown for clarity.

3.3. SEM Observation of Microporous p-nipam. Significantly, SEM observation of dried and washed deswelled gels samples taken near to the outer surface of the blocks prepared with dextran added at a nipam:dextran (w/w) of 1:1 showed the presence of approximately 0.1–0.5 μm channels throughout the gel at a density of 1–3 pores per μm^2 (Figure 2). Lower dextran levels gave a decreased pore density, and no microchannels or other features were visible in gels prepared without dextran or in gels observed prior to deswelling. This suggests ejected water from nanopores due to removed dextran accumulated into microchannels that permeated the gel to reach the outer surface.

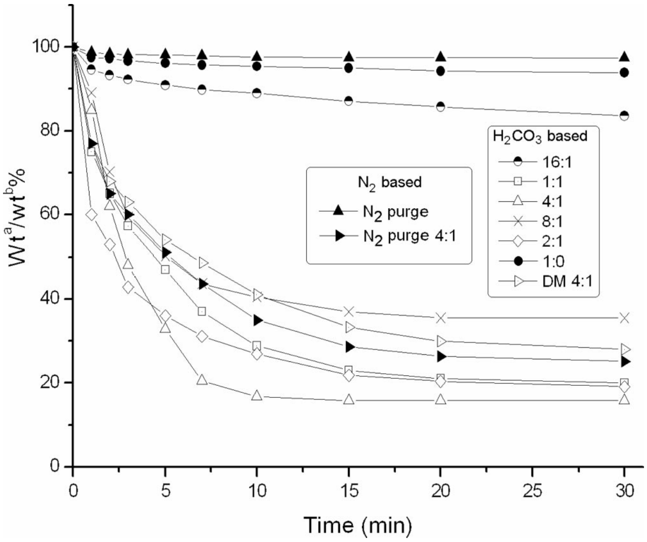

Figure 1. Percentage weight loss with time of p-nipam gels below (Wt^b) and above (Wt^a) the LCST after warming to 40 °C. P-nipam/dextran prepared using H_2CO_3 solutions together with dextran at between 1:0 and 1:1 (w/w) and a p-nipam/DM with dextran (4:1 w/w) (open triangle pointing right) are shown. Weight loss for air free control preparation (solid triangle pointing up) and control preparation at p-nipam/dextran weight ratio of 4:1 (solid triangle pointing right) are given for comparison.

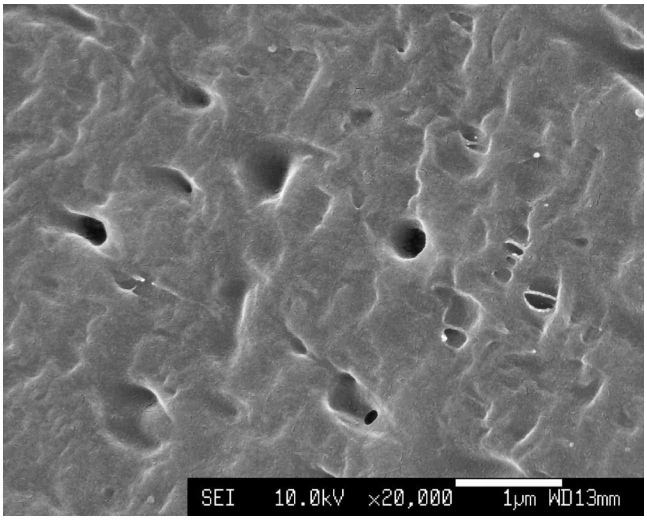

Figure 2. SEM micrograph of p-nipam with nipam:dextran (w/w) of 1:1 showing channels caused by outflowing water due to rapid deswelling. Scale bar = 1 μm.

3.4. p-nipam/Dextran Magnetite Gels Prepared in H_2CO_3 Solution. It was observed that p-nipam/DM gels prepared by polymerization involving H_2CO_3 solution (or conventional N_2 purged solution) underwent very rapid polymerization to form orange/brown gels without the requirement of the TEMED accelerator. In this case, the colloidal particles acted as seeds for polymer nucleation such that polymerization occurred almost immediately throughout the gel. pH of reaction solutions was slightly acidic at pH 5.9, and the protective effect of residual released CO_2 was likely to significantly further exclude oxygen. In comparison, gels prepared with TEMED were basic and the protective effect of releasing CO_2 of shorter duration. This may partly account for the slower polymerization of these mixtures. Both gels prepared with DM and DM together with free dextran swelled to ∼1.6 times their original weights upon washing.

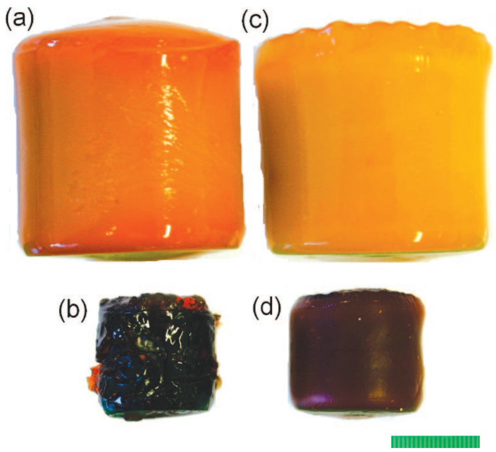

Figure 3. Optical micrographs of (a) p-nipam/DM gel at maximum swelling; (b) corresponding gel at maximum deswelling showing multiple splits; (c) Microporous p-nipam gel at maximum swelling; (d) corresponding gel at maximum deswelling. Scale bar = 2 cm.

Upon warming to 40 °C, both gels underwent a similar considerable deswelling and lost ~80% of their original weight after 30 min. Optical micrographs of fully swelled and the corresponding deswelled gel blocks of p-nipam/DM and microporous p-nipam:DM are shown in Figure 3. Graphs of weight loss on warming above the LCST are included in Figure 1. The microporous composite gels differed in that upon an initial deswelling, it was observed that unbound yellow/orange DM was expelled into surrounding water. For subsequent reswelling and deswelling cycles, no further DM was released however. It is likely that DM adjacent to macropores was washed free of the p-nipam matrix. For purely p-nipam:DM gels, no DM was observed to be released on washing or deswelling, the colloidal particles being firmly trapped within the polymer gel. Thus the final concentration of bound DM was higher in these gels, as further indicated by their darker color. This was confirmed by SQUID magnetometry measurements, and the hysteresis curves for DM, p-nipam/DM, and microporous p-nipam/DM prepared using H_2CO_3 solution are shown as Supporting Information. The DM sample shows the highest saturation (mass) magnetization $\sigma_s = 0.28$ emu/g at 300 K, dropping to 0.017 emu/g for the p-nipam/DM sample and 0.013 emu/g for the microporous p-nipam/DM sample. At 10 K, the values are 1.5 emu/g for DM, dropping to 0.17 emu/g and 0.14 emu/g for DM and microporous p-nipam/DM, respectively. The form of the curves is what would be expected for a superparamagnetic assembly, with low coercivity values H_c around 10 Oe (within the noise level) in the samples containing p-nipam at room temperature, increasing slightly to around 30 Oe at 10 K. The DM sample has a somewhat higher coercivity at 10 K of around 75 Oe, suggesting the possible presence of some larger, multidomain particles causing increased hysteresis. These results were consistent with TEM observation of the DM prepared by the modified method used here, which showed the presence of 6 ± 2 nm discrete particles of dextran-coated magnetite, with occasional aggregations of particles. Thus composite preparation with H_2CO_3 solution had not adversely affected the DM structure or properties and hypothermic warming is possible.

Microporous composite gels deswelled smoothly with retention of shape and structural integrity; in contrast, p-nipam/DM (without dextran porogen) underwent only very minor deswelling until build up of expelled water within the gels caused many small splits in the structure to allow water release. For these gels, dextran was not used to form macroporosity and aid water removal; however, bound DM present within the p-nipam matrix provided separation, some flexibility, and reduced the hydrophobic surface property. This material thus demonstrated a behavior between that of pure p-nipam gels and microporous gels in that a point was reached where the pressure of released water was sufficient to split this moderately more flexible gel at many points. As conventional inert gas preparation normally limits the size of recovered polymer product; to our knowledge, the multiple splitting behavior of large blocks has not been previously reported.

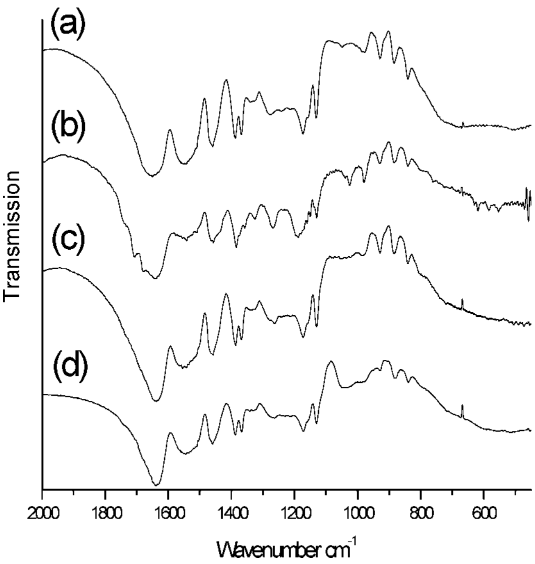

Figure 4. FT-IR spectra of p-nipam samples prepared in (a) H_2CO_3 solution; (b) H_2CO_3 without cross-linker; (c) N_2 degassed deionized water in air free conditions; (d) H_2CO_3 solution with dextran added at nipam:dextran of 1:1 (w/w).

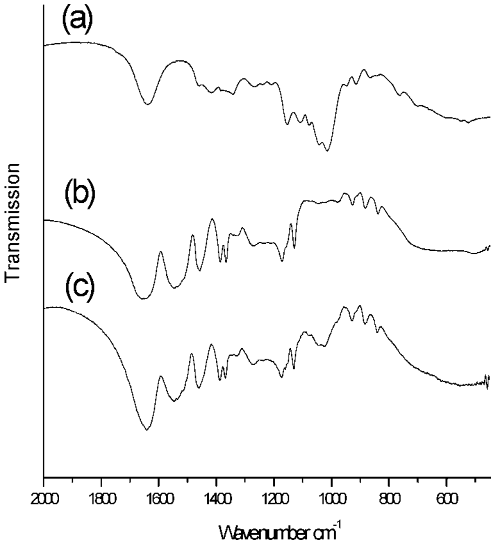

Figure 5. FT-IR spectra of (a) dextran/magnetite (DM); (b) p-nipam/DM prepared in H_2CO_3 solution; (c) microporous p-nipam/ DM with residual dextran prepared in H_2CO_3 solution.

3.5. FT-IR Analysis. FT-IR spectra over the region 450–2000 cm^{-1} of cross-linked p-nipams prepared using H_2CO_3 solution (Figure 4a) showed a shift to higher frequency from 1639 to 1650 cm^{-1} for the amide I C=O maxima compared to linear p-nipam (Figure 4b) or polymer prepared using conventional N_2 purged water and polymerization under inert gas (Figure 4c). This position of the carbonyl peak is believed to give an indication of the nature of hydrogen bonding to the carbonyl

Table 1. Table of Polymerization Conditions, Porogen, Gelling Time, And Deswelling Response for p-Nipam Preparations

media and polymerization conditions	accelerant	porogen (nipam:dextran)	gelling time	appearance	max wt change above LCST %
N_2 degassed H_2O and under N_2	TEMED		<5 min	transparent	−2
N_2 degassed H_2O in open air	TEMED		partial, >30 min	transparent	−2
	TEMED	4:1	>20 min	opaque	−72
	DM		5–10 min	Transparent, dark orange/brown	splits
	DM	4:1	5–10 min	Opaque, dark orange/brown	−78
H_2CO_3 solution in open air	TEMED		<3 min	transparent	−5
	TEMED	4:1	<3 min	opaque	−83
	DM		<6 s	Transparent, dark orange/brown	splits
	DM	4:1	<6 s	Opaque, dark orange/brown	−70

group with the maxima at higher frequency due to increased intramolecular hydrogen bonds compared to a majority of intermolecular hydrogen bonding when a lower frequency is measured.[19–21] In general, the amide I and II peaks for the linear p-nipam were relatively smaller, the C═O being broader with higher frequency shoulders suggesting a mixture of free, intramolecular, and intermolecular bonding. The amide I maxima at 1639 cm^{-1} suggests that intermolecular hydrogen bonding was still dominant, however.

No significant differences in positions of remaining peaks were found with amide II NH deformations at 1555 cm^{-1}, CH_2 and CH bends at 1461 cm^{-1}, $CH(CH_3)_2$ deformation bands at 1387 and 1368 cm^{-1}, and C─N and $CH(CH_3)_2$ vibrations at 1173 and 1131 cm^{-1} together with CH deformations at 1037 cm^{-1} and lower frequencies. Hydrocarbon deformations were generally sharper for the linear p-nipam.

Microporous p-nipam gels wherein dextran was used as a porogen and subsequently removed with washing showed some minor differences to the pure polymer. The amide I carbonyl peak maximum was at 1630 cm^{-1} and was relatively stronger compared to the NH stretch and a peak centered around 1030 cm^{-1} due to the presence of dextran C─O was also present. This suggests that hydrogen bonding occurs between the p-nipam C═O and secondary alcohol groups of a small level of residual bound dextran (Figure 4d).

FT-IR data for dextran, the prepared DM, a p-nipam/ DM composite and p-nipam/DM, and free dextran composite are shown in Figure 5. The spectrum of DM itself has a stronger C═O stretch at lower frequency than dextran at 1638 cm^{-1} plus a band at 1417 cm^{-1}. These are due to the asymmetric and symmetric stretches of the additional carboxylate groups of DM. Also additional peaks in the region around 400–600 cm^{-1} due to Fe─O produce a broadband in this region (Figure 5a). For the p-nipam/DM composites, p-nipam is the major component and dominates the spectra relative to dextran. The highest amide I frequency for all p-nipam materials made was at 1658 cm^{-1} for p-nipam/DM prepared without dextran porogen, indicating a higher level of intramolecular hydrogen bonding (Figure 5b). For microporous p-nipam, the p-nipam C═O stretch maximum shows a shift to lower frequency to 1641 cm^{-1}, again indicating hydrogen bonding to residual dextran (Figure 5c).

Summary

The results established that use of H_2CO_3 as a medium for polymerization had a number of advantages. Most importantly, the method was highly expedient: polymerizations occurred rapidly and could be conducted in open air. All reagents dissolved very quickly in the acidic medium which itself was neutralized. Polymerized gels could be recovered intact from open reaction vessels. The use of H_2CO_3 solution was found to have no detrimental effect on the formation of the polymer products or thermal response, and the LCST was unchanged. For N_2-based preparations, long solution purging and stirring to dissolve reagents was required followed by product break-up upon extraction of gels from necked vessels. Open-air polymerizations either did not occur or took place partially and slowly.

To obtain high thermal response of large blocks, a porogen was essential. Nontoxic and highly soluble dextran was found to be an excellent material for this purpose. A ratio of p-nipam: dextran of 4:1 (w/w) gave highest response while retaining good gel strength. Initial deswelling of gels produced microporous channels throughout the gel such that rapid deswelling and gel integrity were maintained. Residual dextran hydrogen bonded to the p-nipam was indicated by FT-IR. P-nipam/DM gels deswelled with splitting or deswelled smoothly when free dextran was added. Thus large and shaped blocks of high response gel can be readily prepared in open air. A summary of reaction conditions, polymerization times, and deswelling behavior of prepared materials is shown in Table 1.

Recent experiments have shown that H_2CO_3 solution can also be applied to the aqueous free radical polymerizations in air of *n*-vinyl-caprolactam to form a thermoresponsive polymer gel. Some hydrophilic acrylamides and methacrylates have also been found to be amenable to open-air polymerization by this method. Potentially, open-air free radical polymerization of a range of water-soluble or water-miscible monomers is possible by the extra protection afforded by H_2CO_3 solution, and further studies are being undertaken in this area.

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Supporting Information. SQUID magnetic hysteresis loops of (a) DM measured at 300 K; (b) at 10 K; (c) p-nipam/DM measured at 300 K; (d) at 10 K; (e) microporous p-nipam/DM with residual dextran at 300 K; (f) at 10 K. Hysteresis loops are consistent with a superparamagnetic magnetite component. P-nipam/DM composites were prepared in H_2CO_3 solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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