CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2010,** *22,* 5653–5659 5653
DOI:10.1021/cm102266x

Available Plasma-Ignited Frontal Polymerization Approach toward Facile Fabrication of Functional Polymer Hydrogels

Jin Zhou, Huan Shao, Jun Tu, Yuan Fang, Xin Guo, Cai-Feng Wang, Li Chen, and Su Chen*

State Key Laboratory of Material-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Road, Nanjing 210009, People's Republic of China

Received August 9, 2010. Revised Manuscript Received August 30, 2010

We report a novel approach for quickly fabricating poly(NVP-*co*-NMA) hydrogels (NVP = 1-vinyl-2-pyrrolidone, NMA = *N*-methylolacrylamide) by using plasma-ignited frontal polymerization (PIFP). Frontal polymerization was initiated by igniting the upper side of the mixture with plasma. Once initiated, no additional energy was required for the polymerization to occur. We thoroughly investigated the influence of the molar ratios of NVP/NMA on the properties of poly(NVP-*co*-NMA) hydrogels via this PIFP approach. The swelling rate, swelling behavior, and morphology of polymer hydrogels prepared via PIFP were comparatively investigated on the basis of water contact angle, swelling measurement and scanning electron microscopy (SEM). Results show that the swelling property of poly(NVP-*co*-NMA) hydrogels depends on NVP/NMA molar ratios, and the swelling capacity of the hydrogels prepared using PIFP approach is superior to that obtained using traditional batch polymerization (BP) method. More interestingly, these hydrogels, able to absorb quantum dots (QDs), exhibit obvious switching effect via altering the process of swelling and deswelling, which can be developed as QD-based moisture sensor.

Introduction

Frontal polymerization (FP) has attracted much attention as an alternative means with additional advantages of fast and efficient way to produce a variety of polymers and polymeric networks. Typically, FP is a mode of converting monomer into polymer via a localized reaction zone that propagates through the coupling of thermal diffusion and the temperature-dependent reaction rate of an exothermic polymerization in a rapid fashion. An external energy source is used only in the first instant to create the front, and then no additional energy is required for polymerization to occur. Up to now, all the FP in available literature falls into three types: thermal frontal polymerization (TFP), isothermal frontal polymerization (IFP), and photoinitiated frontal polymerization (PFP). Since its first discovery by Chechilo et al. in 1972,[1] FP has been employed effectively to fabricate various multifunctional materials. Pojman and co-workers have extended this method to include numerous polymers at ambient pressure. They demonstrated FP for a number of acrylic monomers,[2−5] epoxy resins,[6] ionic liquid,[7] functionally gradient materials,[8] and polymer-dispersed liquid crystal materials.[9] Washington and Steinbock[10] first prepared temperature-sensitive poly(*N*-isopropylacrylamide) hydrogels by FP. Crivello et al. reported photoinduced cationic ring-opening FPs of oxetanes and oxiranes.[11] Moreover, they demonstrated hybrid free radical/cationic frontal photopolymerizations.[12] In 2005, Hoyle and co-workers investigated multifunctional (meth)acrylates by UV-induced frontal polymerization.[13] Mariani et al. successfully prepared dicyclopentadiene by frontal ring open metathesis polymerization.[14] Furthermore, they obtained polyurethane,[15] epoxy resin-montmorillonite,[16] and poly(diurethane diacrylates).[17] Recently, they prepared stimuli-responsive

---

*To whom correspondence should be addressed. Fax: 86-25-83172258. E-mail: chensu@njut.edu.cn.

(1) Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 1180.
(2) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284.
(3) Fortenberry, D. I.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1129.
(4) Nason, C.; Roper, T.; Hoyle, C.; Pojman, J. A. *Macromolecules* **2005**, *38*, 5506.
(5) Nason, C.; Pojman, J. A.; Hoyle, C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 8091.
(6) Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A. *J. Appl. Polym. Sci.* **1997**, *66*, 1209.
(7) Jiménez, Z.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2745.
(8) Chekanov, Y. A.; Pojman, J. A. *J. Appl. Polym. Sci.* **2000**, *78*, 2398.
(9) Gill, N.; Pojman, J. A.; Willis, J.; Whitehead, J. B. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 204.
(10) Washington, R. P.; Steinbock, O. *J. Am. Chem. Soc.* **2001**, *123*, 7933.
(11) Crivello, J. V.; Falk, B.; Zonca, M. R. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1630.
(12) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4331.
(13) Nason, C.; Roper, T.; Hoyle, C.; Pojman, J. A. *Macromolecules* **2005**, *38*, 5506.
(14) Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A. *Macromolecules* **2001**, *34*, 6539.
(15) Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *Macromolecules* **2003**, *36*, 2674.
(16) Mariani, A.; Bidali, S.; Caria, G.; Monticelli, O.; Russo, S.; Kenny, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2204.
(17) Mariani, A.; Fiori, S.; Bidali, S.; Alzari, V.; Malucelli, G. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3344.

hydrogels,[18] polyacrylamide,[19] poly(*N*,*N*-dimethylacrylamide) hydrogels[20] and thermoresponsive super water absorbent hydrogels.[21] In our previous work, FP was proposed as a method for obtaining segmented polyurethane,[22] polyurethane-nanosilica hybrids,[23] epoxy resin-polyurethane hybrid networks,[24] poly(*N*-methylolacrylamide)/polyhedral oligomeric silsesquioxane graft copolymer hybrids,[25] poly(*N*-vinyl pyrrolidone),[26] and poly(*N*-methylolacrylamide).[27] Very recently, we synthesized glycerol-assisted thermosensitive hydrogels,[28] and amphiphilic gels[29] which showed good swelling capacity both in water and organic solvents.

Despite tremendous effort on FP initiated by heat or UV light, there is sparse information for the utilization of other external energy source, which motivates us to explore a new available plasma external energy source to induce FP. Plasma is a unique medium for the applications in chemical reactions and materials fabrications.[30] With regard to material preparation and processing, plasma techniques have gained much popularity in thin-film deposition,[31] etching,[32] plasma-initiated polymerization,[33−36] and surface modifications.[37] Compared with other types of plasmas, air plasmas, by virtue of avoiding vacuum operation, are dramatically easy to generate and control, which offers a robust and inexpensive way for wide use in industry.[38,39] Herein, we report the first synthesis of functional hydrogels based on plasma-ignited frontal polymerization (PIFP). Different from traditional thermally induced FP reactions, this approach proposed here depends on the electron energy of the air plasma. For plasmas in laboratory scale, the electron energy is typically in the order of 1−10 eV (1 eV $\approx$ 11 600 K).[40] The high-energy plasma electrons rapidly generate a large amount of heat that can effectively ignite FP reaction. In comparison with traditional TFP, PIFP is further more time-saving and convenient.

Hydrogels have three-dimensional network structures that qualify them as high-performance water absorbent materials. To date, some versatile hydrogels have been rapidly synthesized by using FP. Considering the excellence of their swelling−deswelling properties and stimuli-responsive behaviors, hydrogels have been widely applied in soft contact lenses,[41] chemical sensors,[42] diagnostics,[43] tissue engineering,[44] wound dressing,[45] and controlled drug delivery materials.[46] In this work, we first employ PIFP approach to prepare poly(NVP-*co*-NMA) hydrogels with different molar ratios. More interestingly, these hydrogels are found to effectively absorb quantum dots (QDs), conferring the nanocomposites to have obvious switching effect via altering the process of swelling and deswelling, which can serve as ideal candidates for QD-based moisture sensor.

Experimental Section

Materials. 1-Vinyl-2-pyrrolidone (NVP), *N*-methylolacrylamide (NMA), *N*-methyl-2-pyrrolidone (NMP), and *N*,*N*′-methylenebisacrylamide (MBAA) were purchased from Aldrich and used as received. The redox couple, ammonium persulfate (APS)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), was also purchased from Aldrich and used as the redox initiator. Nanosilica with an average diameter of 20 nm was kindly supplied by Nissan Chemicals Company.

PIFP of Poly(NVP-*co*-NMA) Hydrogels. In a typical frontal polymerization process, a stable front is very essential to avoid "fingering", an phenomena observed under the descending front due to the interference of double-diffusive convection, which leads partial reacted material to sink from the reaction zone. To obtain a stable front, Pojman et al. added fillers[47] or performed the reactions in weightlessness.[48] In this case, we added an amount of nanosilica to prepare poly(NVP-*co*-NMA) hydrogels with stable front. The appropriate amount of nanosilica was dissolved in NMP in a flask, and the mixture was sonicated in an ultrasound bath for fully distributed at ambient temperature for several minutes. The fixed amounts of NVP, NMA, and MBAA were then added and mixed together at ambient temperature. After complete homogenization, APS was added to the system. The flask was shaken vigorously in order to obtain a homogeneous mixture. Finally, the homogeneous solution was mixed

---

(18) Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J. M.; Mariani, A. *Biomacromolecules* **2009**, *10*, 2672.

(19) Gavini, E.; Mariani, A.; Rassu, G.; Bidali, S.; Spada, G.; Bonferoni, M. C.; Giunchedi, P. *Eur. Polym. J.* **2009**, *45*, 690.

(20) Caria, G.; Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J. M.; Mariani, A. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1422.

(21) Scognamillo, S.; Alzari, V.; Nuvoli, D.; Mariani, A. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2486.

(22) Chen, S.; Sui, J. J.; Chen, L. *Colloid Polym. Sci.* **2005**, *283*, 932.

(23) Chen, S.; Sui, J. J.; Chen, L.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1670.

(24) Chen, S.; Tian, Y.; Chen, L.; Hu, T. *Chem. Mater.* **2006**, *18*, 2159.

(25) Fang, Y.; Chen, L.; Chen, S. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1136.

(26) Cai, X. J.; Chen, S.; Chen, L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2177.

(27) Chen, L.; Hu, T.; Yu, H.; Chen, S.; Pojman, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4322.

(28) Fang, Y.; Yu, H.; Chen, L.; Chen, S. *Chem. Mater.* **2009**, *21*, 4711.

(29) Tu, J.; Chen, L.; Fang, Y.; Wang, C. F.; Chen, S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 823.

(30) Zheng, J.; Yang, R.; Xie, L.; Qu, J. L.; Liu, Y.; Li, X. G. *Adv. Mater.* **2010**, *22*, 1451.

(31) Collins, R. W.; Ferlauto, A. S. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 425.

(32) Abe, H.; Yoneda, M.; Fujlwara, N. *Jpn. J. Appl. Phys.* **2008**, *47*, 1435.

(33) Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules* **1985**, *18*, 2312.

(34) Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules* **1985**, *18*, 2318.

(35) Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules* **1986**, *19*, 1431.

(36) Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules* **1986**, *19*, 1436.

(37) Desmet, T.; Morent, R.; De Geyter, N.; Leys, C.; Schacht, E.; Dubruel, P. *Biomacromolecules* **2009**, *10*, 2351.

(38) Cui, N. Y.; Brown, N. M. D. *Appl. Surf. Sci.* **2002**, *189*, 31.

(39) Reitz, U.; Salge, J. G. H.; Schwarz, R. *Surf. Coat. Technol.* **1993**, *59*, 144.

(40) Conrads, H.; Schmidt, M. *Plasma Sources Sci. Technol.* **2000**, *9*, 441.

(41) Kim, S. H.; Opdahl, A.; Marmo, C.; Somorjai, G. A. *Biomaterials* **2002**, *23*, 1657.

(42) Lee, Y. J.; Braun, P. V. *Adv. Mater.* **2003**, *15*, 563.

(43) van der Linden, H. J.; Herber, S.; Olthuis, W.; Bergveld, P. *Analyst* **2003**, *128*, 325.

(44) Luo, Y.; Shoichet, M. S. *Nat. Mater.* **2004**, *3*, 249.

(45) Balakrishnan, B.; Mohanty, M.; Umashankar, P. R.; Jayakrishnan, A. *Biomaterials* **2005**, *26*, 6335.

(46) Dai, H. J.; Chen, Q.; Qin, H. L.; Guan, Y.; Shen, D. Y.; Hua, Y. Q.; Tang, Y. L.; Xu, J. *Macromolecules* **2006**, *39*, 6584.

(47) Masere, J.; Stewart, F.; Meehan, T.; Pojman, J. A. *Chaos* **1999**, *9*, 315.

(48) Pojman, J. A.; Khan, A. M.; Mathias, L. J. *Microgravity Sci. Technol.* **1997**, *10*, 36.

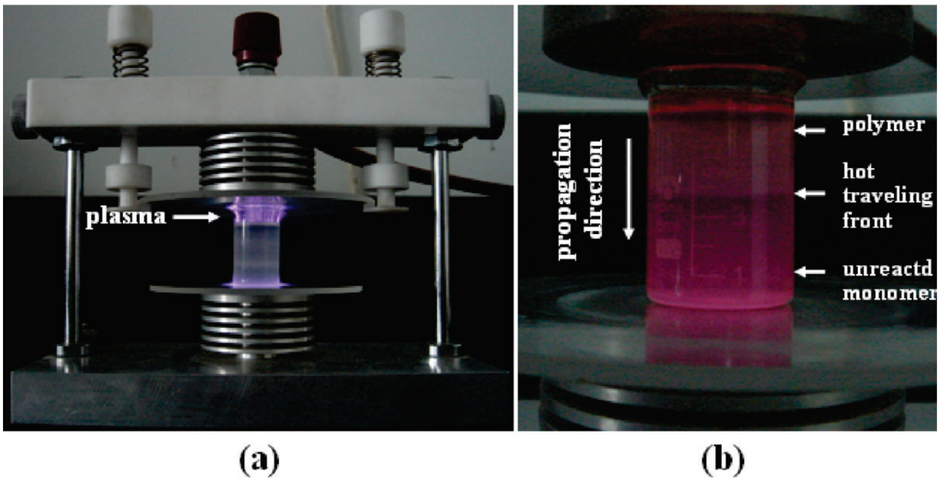

Figure 1. (a) Visual setup picture of preparing poly(NVP-*co*-NMA) hydrogel via PIFP. (b) Visual picture of propagating front of poly(NVP-*co*-NMA) hydrogel during the process of PIFP.

with the reductant TMEDA which assisted with initiator APS to effectively decrease the triggering temperature and front temperature. A typical composition was [NVP]/[NMA] = 4:6 (mol/mol), NMP = 40 wt %, MBAA = 0.5 wt %, nanosilica = 1 wt %, APS = 0.1 wt %, and TMEDA ([APS]/[TMEDA] = 1:4 mol/mol). The final reaction mixture was poured into a 5 mL flask. The filled flask was kept at ambient temperature in order to slow bulk polymerization. The upper side of the mixture was then induced by air plasma (CTP-2000K) for just ~20 s. Figure 1a presents a visual setup picture of preparing poly(NVP-*co*-NMA) hydrogel via PIFP. We add some Rhodamine B to the reaction mixture in order to obviously observe the front interface between the end-product polymer and unreacted monomer. Figure 1b shows a typical picture of propagation front of poly(NVP-*co*-NMA) hydrogel during the process of PIFP. As seen in Figure 1b, the upper layer is end-product poly(NVP-*co*-NMA) hydrogel, and the lower layer is unreacted monomer. Also, the hot traveling front between end-product polymer and unreacted monomer can be clearly seen.

Batch Polymerization (BP) of Poly(NVP-*co*-NMA) Hydrogels. Several batch runs had been performed to compare the resultant samples with the corresponding ones obtained by PIFP. In a typical run, the same amounts of each component as quoted above were mixed in a reaction vessel, immersed in a thermostatic water bath set at 60 °C for 2 h. The product was then cooled back to ambient temperature.

Velocity and Temperature Measurements. The velocities of the propagating front were determined by measuring the front position as a function of time. When the plot of the front position versus time shows a straight line, its slope is the frontal velocity. Temperature profiles were measured by using Fluke Ti30 IR thermal imager and fixed a point at a certain distance from the free surface. Subsequently, the measured temperature as a function of time was converted to a spatial profile by using the front velocity. After the complete polymerization, the samples were removed from the flask and cut into small pieces for further investigation.

Water Contact Angle Measurement. Water contact angles (WCAs) were measured by using DSA100 (KRÜSS, Germany) at ambient temperature (water drop size: 5 μL).

SEM Measurement. The structures of the samples obtained were investigated by SEM with a QUANTA 200 (Philips-FEI, Holland) at 30.0 kV. The sliced samples were immersed in deionized water at room temperature for several days to remove the residual unreacted monomer and NMP solvent. During this time, the water was changed daily. Then the samples were dried in a vacuum oven at 60 °C until the weight of the sample was constant. Dried samples were immersed again in deionized water to swell at room temperature. The samples were then freeze-dried for 12 h. Dehydrated samples used for SEM measurement were cut to expose their inner structure.

Swelling Measurement. The swelling properties of the as-prepared hydrogels were performed by gravimetric analysis. Dried samples were weighed and immersed into an excessive amount of deionized water at room temperature. At intervals, the samples were taken out, excess water was wiped off, and samples were then weighed. After that, the samples were returned to the swelling medium. The experiment was continued until a constant weight of swollen samples was achieved. The swelling ratio (SR, %) was calculated by the following equation

$$\mathrm{SR} = (W_s - W_d)/W_d \times 100\%$$

where W_s and W_d are the weights of the hydrogels in the swollen and dry state, respectively.

Fluorescence Measurement. The *N*-acetyl-L-cysteine (NAC)-capped CdTe QDs were synthesized according to a modified literature procedure.[49,50] The dry hydrogel samples ([NVP]/[NMA] = 7:3 (mol/mol)) were immersed in excess NAC-capped CdTe QDs aqueous solution (7.5 mmol/L, *d* = 3.2 nm), and the samples were then dried in a vacuum oven at 60 °C until the weight of the sample was constant. The fluorescence properties of products were measured with photoluminescence (PL) spectra. PL spectra were determined on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature operating with a 312 nm laser beam as a light source with Xe-lamp as excited source, tube voltage was 500 V, the excitation and emission slits were 5 nm. The measured samples were then immersed in deionized water at room temperature until their equilibrium swelling, and their PL spectra were determined under the same conditions as above-mentioned.

Results and Discussion

PIFP of Poly(NVP-*co*-NMA) Hydrogels. Our preliminary experiments were focused on how to prepare

---

(49) Crisp, M. T.; Kotov, N. A. *Nano Lett.* **2003**, *3*, 173.
(50) Liang, L.; Qian, H. F.; Ren, J. C. *Chem. Commun.* **2005**, 528.

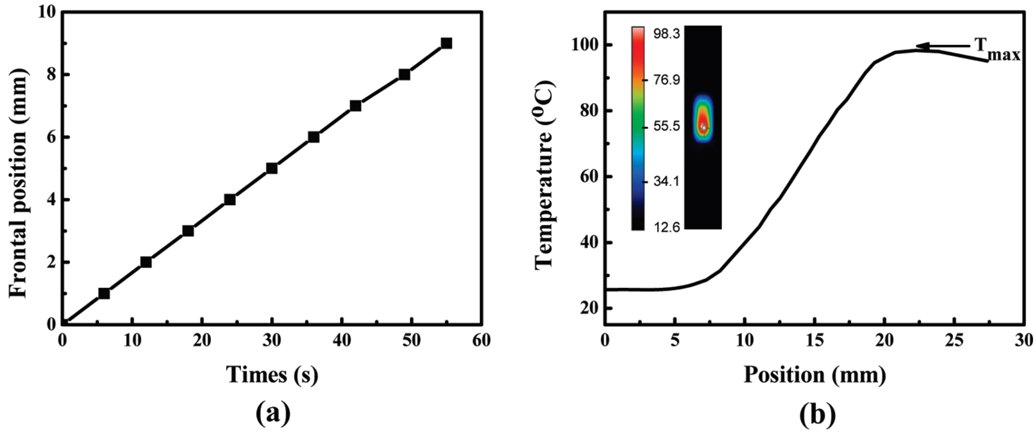

Figure 2. (a) Front position versus time for poly(NVP-*co*-NMA) hydrogel prepared by PIFP. (b) Typical temperature profile of poly(NVP-*co*-NMA) hydrogel prepared by PIFP. Initial conditions: [NVP]/[NMA] = 4:6 (mol/mol), NMP = 40 wt %, nanosilica = 1 wt %, MBAA = 0.5 wt %, APS = 0.1 wt %, and [APS]/[TMEDA] = 1:4 mol/mol.

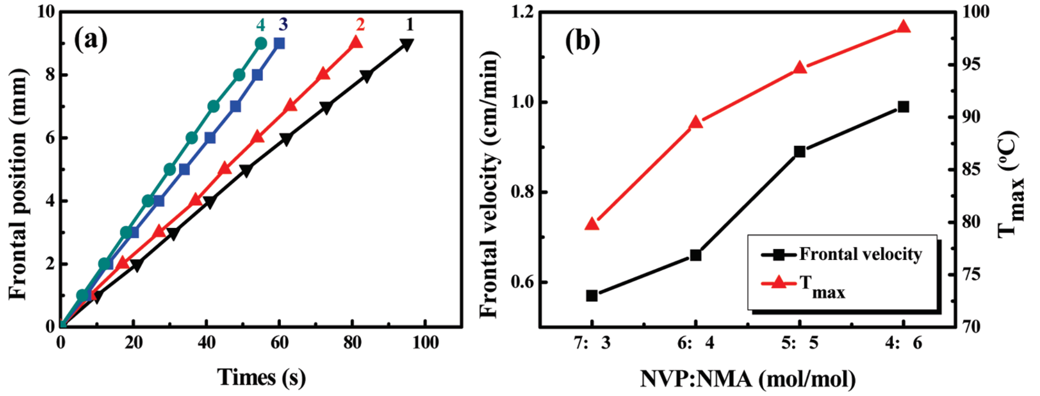

Figure 3. (a) Front position for poly(NVP-*co*-NMA) hydrogels prepared by PIFP versus different NVP/NMA molar ratios: (1) 7:3, (2) 6:4, (3) 5:5, (4) 4:6. (b) Frontal velocity and T_{max} versus the NVP/NMA molar ratios. Initial conditions: NMP = 40 wt %, nanosilica = 1 wt %, MBAA = 0.5 wt %, APS = 0.1 wt %, and [APS]/[TMEDA] = 1:4 mol/mol.

poly(NVP-*co*-NMA) hydrogel by PIFP with a stable front, while spontaneous polymerization (SP) did not occur. We assessed the pot life by mixing the reactants, leaving the homogeneous mixture at ambient temperature, and visually determining when they spontaneously polymerized. We found that the reactant mixture of [NVP]/[NMA] = 4:6 (mol/mol), NMP = 40 wt %, MBAA = 0.5 wt %, nanosilica = 1 wt %, APS = 0.1 wt %, and TMEDA ([APS]/[TMEDA] = 1:4 mol/mol) is inert and exhibits a pot life of more than 2 h at ambient temperature but very reactive after being induced by plasma for several seconds.

One of the key features in pure PIFP without SP is a constant front velocity. Figure 2a presents typical data for the position of the thermal front as a function of time. The experimental data are well-fitted by a straight line, meaning that the self-sustaining front moves at a constant velocity. This is strong evidence that pure PIFP occurs. Moreover, another convenient way to verifying the pure PIFP is a T_{max} value in a function of front temperature and front position. Conversely, SP may occur simultaneously. A typical temperature profile of PIFP is shown in Figure 2b. Because of the constant temperature value in zones far from the incoming hot front, there is a horizontal part of the curve, meaning that SP is not occurring simultaneously. A temperature increase can be observed because of the exothermic reaction, and T_{max} is 98.5 °C.

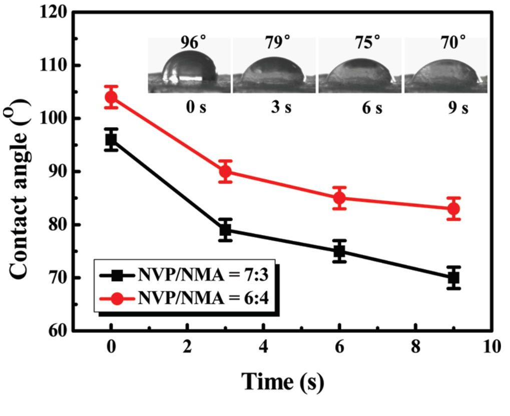

Figure 4. WCAs of of poly(NVP-*co*-NMA) hydrogels prepared by PIFP versus time with NMP = 40 wt %, nanosilica = 1 wt %, MBAA = 0.5 wt %, APS = 0.1 wt %, [APS]/[TMEDA] = 1:4 mol/mol at different NVP/NMA molar ratios of 7:3 and 6:4 (mol/mol).

Molar ratio of the monomers is an important factor in PIFP. Figure 3a presents front position as a function of time with different NVP/NMA molar ratios. The data for all sets of experiments are well fitted by straight lines, which mean that the propagation of the polymerization fronts move at constant velocities. The front velocity and

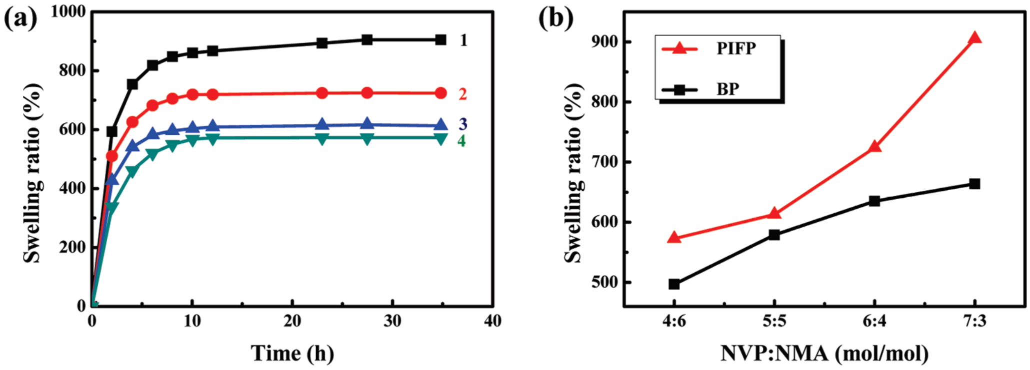

Figure 5. (a) Swelling kinetics of poly(NVP-*co*-NMA) hydrogels prepared by PIFP at different NVP/NMA molar ratios: (1) 7:3, (2) 6:4, (3) 5:5, (4) 4:6. (b) Swelling ratios of poly(NVP-*co*-NMA) hydrogels prepared by PIFP and BP versus the NVP/NMA molar ratios. Initial conditions: NMP = 40 wt %, nanosilica = 1 wt %, MBAA = 0.5 wt %, APS = 0.1 wt %, and [APS]/[TMEDA] = 1:4 mol/mol.

T_{max} as a function of NVP/NMA molar ratios are given in Figure 3b. The front velocities at [NVP]/[NMA] = 7:3, 6:4, 5:5, and 4:6 (mol/mol) are 0.57, 0.66, 0.89, and 0.99 cm/min, respectively. Corresponding to this velocity trend, the decrease in molar ratios from 7:3 to 4:6 (mol/mol) leads to an increase in T_{max} from 79.7 to 98.5 °C. We have found that the front velocity increases with the concentration of NMA in this system, and the front velocity reaches a maximum value when [NVP]/[NMA] = 4:6 (mol/mol), T_{max} enhances correspondingly with the frontal velocity. We emphasize that the whole experiments were carried out under nonadiabatic conditions, thus, the increased velocity reduced the time for heat loss.

WCA Measurement. We investigate the dynamic WCAs of poly(NVP-*co*-NMA) hydrogels with different NVP/NMA molar ratios versus residence time at room temperature to quickly judge the absorption rate of water for hydrogels. As seen in Figure 4, we can observe the dynamic WCAs of the hydrogels decrease rapidly at the initial stage, and then gradually slow down. Compared with the sample of [NVP]/[NMA] = 6:4 (mol/mol), the sample of [NVP]/[NMA] = 7:3 (mol/mol) shows a faster absorption rate of water. This result is consistent with the results of swelling behavior (Figure 5a). The inset in Figure 4 shows the WCAs with different residence time of water droplet for poly(NVP-*co*-NMA) hydrogels prepared by PIFP at [NVP]/[NMA] = 7:3 (mol/mol). With time passing, the dynamic WCAs of the hydrogel are 96° (0 s), 79° (3 s), 75° (6 s) and 70° (9 s), respectively.

Swelling Behavior of Poly(NVP-*co*-NMA) Hydrogels. We investigated the swelling behaviors of hydrogels produced with different molar ratios of NVP/NMA by using gravimetric analysis (Figure 5a). The SRs of all the as-prepared samples increase with swelling time. As seen in Figure 5a, at the initial 5 h of swelling time, the SRs of the samples with different NVP/NMA molar ratios increase sharply. However, the swelling equilibrium for all samples is nearly achieved after 10 h of swelling time, and the equilibrium SRs at [NVP]/[NMA] = 7:3, 6:4, 5:5, and 4:6 (mol/mol) are 905, 724, 613, and 573%, respectively. The water SRs of poly(NVP-*co*-NMA) hydrogels containing high NVP concentration are larger than those with low NVP concentration, correspondingly. Because this experiment is a first example for synthesis of hydrogels by plasma-ignited method on FP, we run control sample via BP for comparing swelling properties with that of samples via PIFP (Figure 5b). As shown in Figure 5b, the SRs of the hydrogels prepared by BP at [NVP]/[NMA] = 7:3, 6:4, 5:5, and 4:6 (mol/mol) are 664, 635, 579, and 497%, correspondingly, noticing that all these SRs via BP are smaller than those by using PIFP approach, especially at [NVP]/[NMA] = 7:3 (mol/mol). In fact, this PIFP approach can be categorized into the FP method, which offers great advantage of better SR over BP, as shown in the reported literatures.[10,28] Another advantage of PIFP is time-saving and facile. In this case, the reaction time for obtaining the target hydrogels via PIFP is less than 5 min, which is much less than that of BP (2 h). This approach opens up a new available strategy for fast and facilely producing hydrogels with good properties.

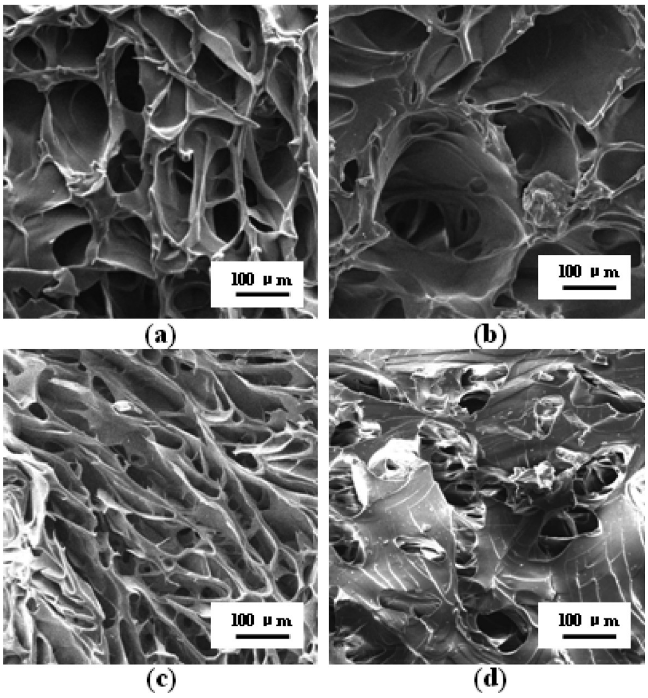

Figure 6. SEM micrographs of poly(NVP-*co*-NMA) hydrogels prepared by PIFP with NMP = 40 wt %, nanosilica = 1 wt %, MBAA = 0.5 wt %, APS = 0.1 wt %, [APS]/[TMEDA] = 1:4 mol/mol at different NVP/NMA molar ratios: (a) 7:3, (b) 6:4, (c) 5:5, (d) 4:6.

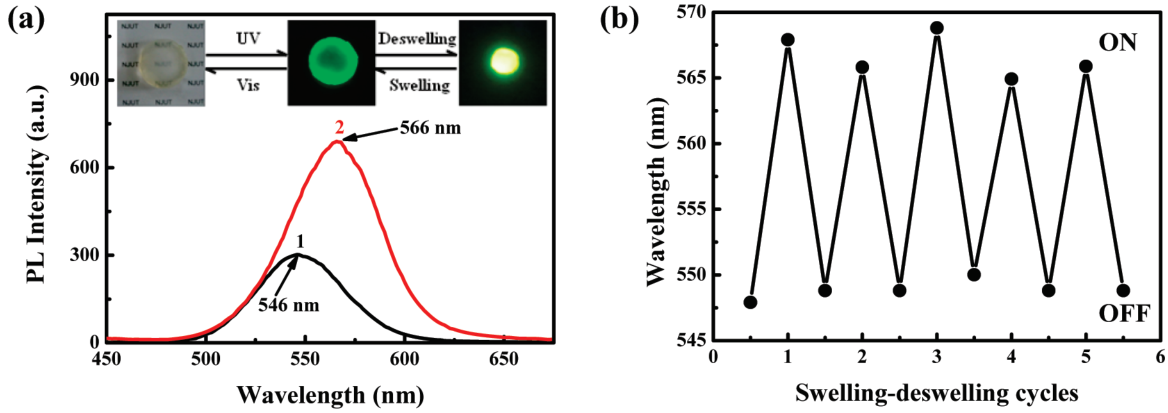

Figure 7. (a) PL spectra of poly(NVP-*co*-NMA) hydrogels prepared by PIFP (1) after swelling in NAC-capped CdTe QDs aqueous solution and (2) deswelling. Inset: images of the CdTe/poly(NVP-*co*-NMA) hydrogels under different conditions. (b) Reversible luminescence transition of CdTe/poly(NVP-*co*-NMA) hydrogels against the number of swelling−deswelling cycles.

Morphology of Poly(NVP-*co*-NMA) Hydrogels. We investigated the porous structures of hydrogels synthesized with different molar ratios of NVP/NMA by using scanning electron microscopy (SEM). As indicated in Figure 6, the morphological structure of poly(NVP-*co*-NMA) hydrogels with different NVP/NMA molar ratios is distinctly diverse at microscale. The pore diameter of the samples at [NVP]/[NMA] = 7:3, 6:4, 5:5, and 4:6 (mol/mol) are nearly 100, 200, 38, and 50 μm, respectively. As shown in Figure 6a and 6b, the morphology of the hydrogels at [NVP]/[NMA] = 7:3 (mol/mol) exhibits more compactly arranged microstructures, compared with those at [NVP]/[NMA] = 6:4 (mol/mol). The similar result can be observed at [NVP]/[NMA] = 5:5, and 4:6 (mol/mol), shown in images c and d in Figure 6.

Fluorescence of CdTe/Poly(NVP-*co*-NMA) Hydrogel Composites. The incorporation of QDs into polymer matrices has attracted impressive attention because of the appealing scientific and industrial interests. Up to now, a variety of elegant methods have been proposed for constructing QD/polymer composites, such as in situ polymerization,[51] catalytic chain transfer polymerization technique,[52] and physical entrapment.[53] In this case, we prepared QD/polymer composites via simple procedure, allowing poly(NVP-*co*-NMA) hydrogels to immerse in excess NAC-capped CdTe QDs aqueous solution (7.5 mmol/L, d = 3.2 nm). As we expected, the poly(NVP-*co*-NMA) hydrogels after immersing in CdTe QDs aqueous solution exhibit good fluorescence, indicating these hydrogels exhibit a higher adsorption capacity toward CdTe QDs than ordinary materials. It can be explained by the following two aspects: on one hand, CdTe QDs can be easily coordinated to PVP chains.[54] On the other hand, the hydrogel networks make it easier for the samples to capture the CdTe QDs. As shown in Figure 7a, the swollen samples present an emission wavelength at around 546 nm. Perhaps more interestingly, the samples after deswelling present an obvious red shift of the PL emission at about 566 nm. Analogue result can be found in literature.[52,53] As documented in the literature, this variation in PL emission is more likely due to the change in hydrogel conformation during the process of deswelling, which may cause the change of the dielectric constant of the CdTe QDs absorbed in the hydrogels. Also, the CdTe QDs in the deswollen samples could form a close-packed structure in the hydrogels. Another indication is the PL intensity of CdTe/poly(NVP-*co*-NMA) hydrogels after deswelling can cause a 2-fold increase in the relative intensity of the PL peak as compared with parent samples (Figure 7a). This discovery confirms that the CdTe/poly(NVP-*co*-NMA) hydrogels during the deswelling process is beneficial for capturing harvested fluorescent QD particles, promoting the density of nanoparticles.

More interestingly, CdTe/poly(NVP-*co*-NMA) hydrogels show luminescence switching behavior by altering the process of swelling and deswelling. As shown in the inset in Figure 7a, the fluorescent color of the transparent sample is green under irradiation with a 302 nm UV light in the swelling step, whereas it switches to yellow after deswelling. Through the process of swelling and deswelling, reversible switch between the green emission and the yellow emission is realized. The repeated cycles shown in Figure 7b reveal that luminescence switching is reproducible. We note that the emission wavelength of the hydrogels in the deswelling step are fluctuated slightly, which should be attributed to the inconstant deswelling condition in each cycle. However, the emission wavelength is nearly constant and the relative error is acceptable. The results suggest that CdTe/poly(NVP-*co*-NMA) hydrogels might show potential applications as QD-based moisture sensor. These CdTe/poly(NVP-*co*-NMA) hydrogels in yellow emission (ON state) indicate that the environment is dry, whereas in green emission (OFF state), they show that the environment is wet.

Conclusion

We have demonstrated a new facile approach for quickly fabricating poly(NVP-*co*-NMA) hydrogels via plasma-ignited

---

(51) Chen, S.; Zhu, J.; Shen, Y.; Hu, C.; Chen, L. *Langmuir* **2007**, *23*, 850.

(52) Yang, S. Y.; Li, Q.; Chen, L.; Chen, S. *J. Mater. Chem.* **2008**, *18*, 5599.

(53) Li, J.; Hong, X.; Liu, Y.; Li, D.; Wang, Y. W.; Li, J. H.; Bai, Y. B.; Li, T. *J. Adv. Mater.* **2005**, *17*, 163.

(54) Ham, S.; Paeng, K. J.; Park, J.; Myung, N.; Kim, S. K.; Rajeshwar, K. *J. Appl. Electrochem.* **2008**, *38*, 203.

frontal polymerization. We add some nanosilica in order to obtain stable front and enhance the intensity of hydrogels. A well-fitted experimental data and temperature profile reveal that only pure PIFP occurs. We found that a variety of characteristics of as-prepared samples can be tuned by varying the molar ratios of NVP/NMA. The hydrogels with [NVP]/[NMA] = 7:3 (mol/mol), exhibiting compact and regular microporous structure, have the best swelling rate and capacity. The swelling capacity of the hydrogels prepared using the PIFP approach is superior to that obtained using the traditional BP method.

Moreover, we found that the as-prepared hydrogels can effectively absorb CdTe QDs. Reproducible luminescence switching of CdTe/poly(NVP-*co*-NMA) hydrogels can be achieved via altering the process of swelling and deswelling, which may open a door toward developing QD-based moisture sensor. These results allow us to conclude that the PIFP approach can be exploited as an alternative means for synthesis of polymer hydrogels in a fast and efficient way.

Acknowledgment. This work was supported by National Natural Science Foundation of China-NSAF (Grant 10976012), the Natural Science Foundation for Jiangsu Higher Education Institutions of China (Grant 07KJA53009, 09KJB530005) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (20093221120002).