Phase Behavior of Temperature- and pH-sensitive Poly(acrylic acid-*g*-N-isopropylacrylamide) in Dilute Aqueous Solution

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ABSTRACT: Several different composition temperature- and pH-sensitive poly(acrylic acid-*g*-*N*-isopropylacrylamide) (P(AA-*g*-NIPAM)) graft copolymers were synthesized by free-radical copolymerization utilizing macromonomer technique. The phase behavior and conformation change of P(AA-*g*-NIPAM) in aqueous solutions were investigated by UV–vis transmittance measurements, fluorescence probe, and fluorescence quenching techniques. The results demonstrate that the P(AA-*g*-NIPAM) copolymers have temperature- and pH-sensitivities, and these different composition graft copolymers have different lower critical solution temperature (LCST) and critical phase transition pH values. The LCST of graft copolymer decreases with increasing PNIPAM content, and the critical phase transition pH value increases with increasing Poly(*N*-isopropylacrylamide) (PNIPAM) content. At room temperature (20°C), different composition of P(AA-*g*-NIPAM) graft copolymers in dilute aqueous solutions (0.001 wt %) have a loose conformation, and there is no hydrophobic microdomain formation within researching pH range (pH 3 ~ 10). In addition, for the P(AA-*g*-NIPAM) aqueous solutions, transition from coil to globular is an incomplete reversible process in heating and cooling cycles. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 4036–4042, 2008

Key words: graft copolymer; temperature- and pH-sensitivity; lower critical solution temperature (LCST); critical phase transition pH

INTRODUCTION

The so-called intelligent polymers undergo reversible phase transition in response to external stimuli such as temperature,[1] pH,[1,2] ion strength,[3] electric fields,[4] and chemicals.[5] There are many potential applications of intelligent polymer in medicine, biotechnology, industry, and environmental problems.[6,7] Most of the intelligent polymers studied previously are responsive to only one kind of stimulus.[8] Recently, there has been considerable interest in the use of materials that respond to two stimuli, either mutually or independently in specific environments, with particular emphasis on pH and temperature responsive polymers and even some have recently been investigated.[9,10] These temperature- and pH-sensitive polymers, which contain both temperature and pH-sensitive components undergo marked solubility changes in water in response to temperature and pH changes.[11,12] Makhaeva et al. used laser light scattering (LLS) and differential scanning calorimetry measurements to investigate the behavior of Poly(*N*-vinylcaprolactam-*co*-methacrylic acid) (PVCL-MAA) macromolecules in aqueous solution, and proved that PVCL-MAA, as well as mixtures of PMAA and PVCL form insoluble macromolecular complexes at low pH in water by cooperative H-bonding between VCL and MAA units. Macromolecular complex formation appears to be the cause of the pH-sensitive properties of PVCL-MAA copolymers.[13–15]

Poly(*N*-isopropylacrylamide) (PNIPAM) is one of the popular temperature sensitive polymers as it exhibits a sharp phase transition at around 32°C.[16] Poly(acrylic acid) (PAA) is one of the pH-sensitive polymers. It is expected that the pH sensitivity of PAA may be introduced into a temperature-sensitive polymer, such as PNIPAM, to form graft copolymers, and the copolymers could have double sensitive properties to external temperature and pH stimulus. Furthermore, studies on the properties of the graft copolymer in aqueous solution may form the basis of the preparation for new intelligent hydrogels and films. In view of this possibility, we investigated the phase behavior of P(AA-*g*-NIPAM) in dilute aqueous solution in this article.

In recent years, macromonomer technique has been a powerful and versatile method for the syn-

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thesis of well-defined graft copolymers,[17,18] because the length and the content of macromonomers, which are the branches in the graft copolymer can be easily controlled.[19] Preparation of macromonomers by free-radical polymerization has become one of the most convenient and widely employed methods.[20] For above reasons, we have synthesized P(AA-*g*-NIPAM) graft copolymers by free-radical copolymerization of AA with *N*-isopropylacrylamide (NIPAM) macromonomer utilizing macromonomer technique. These synthesized copolymers are the different ratio of NIPAM macromonomer and AA, which are temperature- and pH-sensitive monomers, respectively.

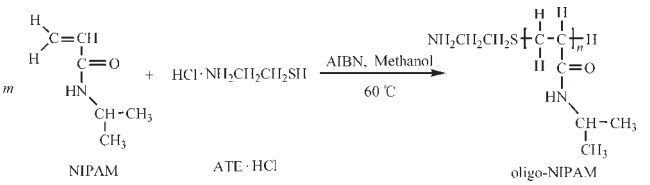
To further investigate the phase behavior of P(AA-*g*-NIPAM) in aqueous solution, UV–vis transmittance measurement and fluorescence techniques such as fluorescence probe and fluorescence quenching techniques are utilized. It is well-known that UV–vis transmittance is one of the usual method to study the phase behavior of stimuli-responsive polymers. Furthermore, the advantage of fluorescence techniques is that information about the behavior of the polymers on the molecular level can be obtained.

In this article, we have synthesized graft copolymers P(AA-*g*-NIPAM) composed of temperature-sensitive PNIPAM side chains and pH-sensitive PAA backbone chains. The phase behavior of P(AA-*g*-NIPAM) in aqueous solution is investigated by UV–vis transmittance measurements and fluorescence techniques. The UV–vis transmittance measurements and the fluorescence techniques are useful methods for investigating the phase behavior of temperature- and pH-sensitive polymers and their conformational changes in dilute aqueous solution.[21,22] This study can be regarded as the bases for the design and preparation of new stimuli-responsive materials such as hydrogels and films, and the graft copolymer unique properties may be used in design and synthesis of novel sensitive gels and nanocomposite materials.

EXPERIMENTAL

Materials

2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Pyrene (Py, Aldrich-96%) was purified by recrystallization from ethanol and then extracted with ethanol in Soxhlet's extractor. AA was distilled under vacuum before use. Acryloyl chloride was prepared according to literature procedures.[23] NIPAM (Aldrich-95%) was purified by recrystallization from hexane. Triethylamine (TEA), tetrahydrofuran (THF), methanol, diethyl ether, 2-aminoethanethiol hydrochloride ($NH_2CH_2CH_2SH$ HCl, AET HCl), and nitromethane were used as received (analytical grade). Double distilled water was used throughout. The pH of the solution was adjusted using 0.5*M*, 5*M* NaOH solution and/or 0.5*M*, 5*M* HCl solution.



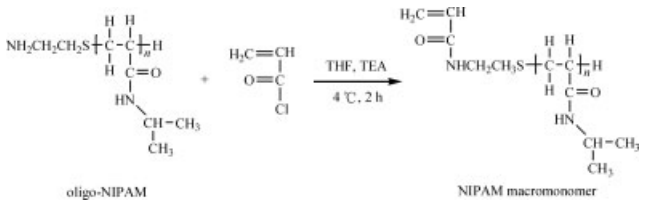
Scheme 1 Synthesis of the oligo-NIPAM.

Synthesis

Preparation of P(AA-g-*NIPAM*)[24,25]

P(AA-*g*-NIPAM) was prepared involving three steps:

1. Synthesis of oligo-NIPAM. The oligo-NIPAM with a terminal amino group was synthesized by free radical polymerization of NIPAM (11.3 g, 100 mmol) in methanol (40 mL) at 60°C for 20 h using AIBN (0.164 g, 1 mmol) and AET HCl (0.904 g, 8 mmol) as initiator and chain transfer reagents, respectively. The oligomer was obtained by precipitating the reaction solution into diethyl ether. The procedure of preparing amino terminated oligo-NIPAM is an intermediate step in the preparation of NIPAM macromonomer. The synthetic process of the oligo-NIPAM is shown in Scheme 1.
2. Synthesis of NIPAM macromonomer. The NIPAM macromonomer was prepared by reacting of amino-terminated oligo-NIPAM (5.0 g, 2.27 mmol) with acryloyl chloride (0.55 mL, 6.79 mmol) in 120 mL of dry THF and TEA (0.94 mL, 6.79 mmol) mixed solution at 4°C for 2 h, and then continued for 6 h at room temperature (20°C). The macromonomer was obtained by precipitating the filtered reaction solution into diethyl ether. The synthetic process of the NIPAM macromonomer is shown in Scheme 2.
3. Synthesis of P(AA-*g*-NIPAM). The P(AA-*g*-NIPAM) was synthesized by copolymerizing the NIPAM macromonomer with AA in methanol (10% w/v) using AIBN as initiator, at 60°C for 2 $\sim$ 3 h, and the molar ratios ($n_{AA} : n_{NIPAM}$ in monomer units) in the feed of four copolymers P(AA-*g*-NIPAM)-1, P(AA-*g*-NIPAM)-2, P(AA-*g*-NIPAM)-3, and P(AA-*g*-NIPAM)-4 were 95 : 5, 90 : 10, 80 : 20, and 70 : 30, respectively. The resultant copolymers were purified by multiple dissolution ($\times$3) in methanol, followed by precipitation into diethyl ether and then dried at room temperature under vacuum. The molar



Scheme 2 Synthesis of the NIPAM macromonomer.

ratios (n_{AA} : n_{NIPAM} in monomer units) in the resultant copolymers P(AA-*g*-NIPAM)-1, P(AA-*g*-NIPAM)-2, P(AA-*g*-NIPAM)-3, and P(AA-*g*-NIPAM)-4 determined by elemental analysis for nitrogen were 2.05 : 0.18, 1.98 : 0.37, 0.72 : 0.62, and 0.69 : 1.81, respectively. The synthetic process of the P(AA-*g*-NIPAM) is shown in Scheme 3.

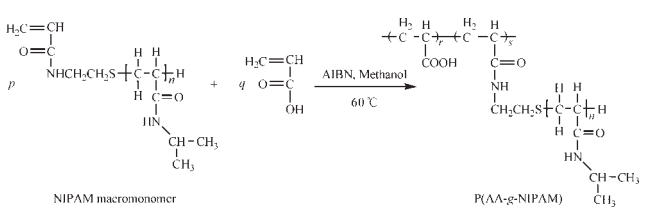
Polymer characterization

Transmittances of the solution were determined on a UV–vis spectrophotometer (TU-1901). pH measurements were measured on a PHS-1 acidimeter. All fluorescence measurements were conducted on a Perkin–Elmer LS-50B luminescence spectrometer. The number–average molecular weight (M_n) of the graft copolymers were mensurated on a Waters-breeze gel permeation chromatography. The eluent used for the GPC was *N*,*N*-dimethylformamide (DMF) and the reference polymer was polystyrene. Elemental analysis was conducted on the Elementar Vario EL (Germany).

Sample preparation

Concentration of the polymer solution used for the UV–vis measurements was 0.2 wt %, but when used for the fluorescence measurements it was 0.001 wt %.

For the fluorescence experiments involving dissolution of organic probe molecules into the water-soluble polymer solutions, the probe Py was initially dissolved in diethyl ether to obtain a stock solution of known concentration (ca. 10^{-3} mol L^{-1}). This solution was diluted to 10^{-5} mol L^{-1}, just before use. One milliliter of the probe solution (10^{-5} mol L^{-1}) was injected into a 10 mL volumetric flask. The ether was evaporated at room temperature. Subsequently, a polymer solution of known pH (10^{-3} wt %) was added to the flask. To ensure solubilization and equilibration, the polymer/probe solution was sonicated for 20 min, and laid at room temperature for more than 12 h.



Scheme 3 Synthesis of the P(AA-*g*-NIPAM).

For the fluorescence quenching experiment, nitromethane was initially dissolved in methanol to obtain a stock solution of known concentration (ca. 1.8 mol L^{-1}). To determine the influence of the quencher on polymer aqueous systems, 5 μL of nitromethane stock solution was added to 3 mL fluorescence cell of polymer and Py solutions at a given pH. The mixture solution was shaken before fluorescence quenching measurements.

RESULTS AND DISCUSSION

For convenience of discussion, we will define these copolymers P(AA-*g*-NIPAM)-1, P(AA-*g*-NIPAM)-2, P(AA-*g*-NIPAM)-3, and P(AA-*g*-NIPAM)-4 as AN1, AN2, AN3, and AN4, respectively. The number–average molecular weights (M_n) of the AN1, AN2, AN3, and AN4 graft copolymers were 0.97×10^6, 1.24×10^6, 1.97×10^6, and 2.63×10^6, respectively.

UV–vis spectrophotometric studies

Concentration of the polymer solution used for the UV–vis measurements was 0.2 wt %. Because of its sensitivity to the changes in the turbidity of the solution, 500 nm was selected as analyzing wavelength.[21] The sample solution was put in a sample holder and double distilled water was adopted as reference for the measurement.

Figure 1 depicts the transmittances for AN1, AN2, AN3, and AN4 solutions, respectively, at a polymer concentration of 0.2 wt % were measured as a func-

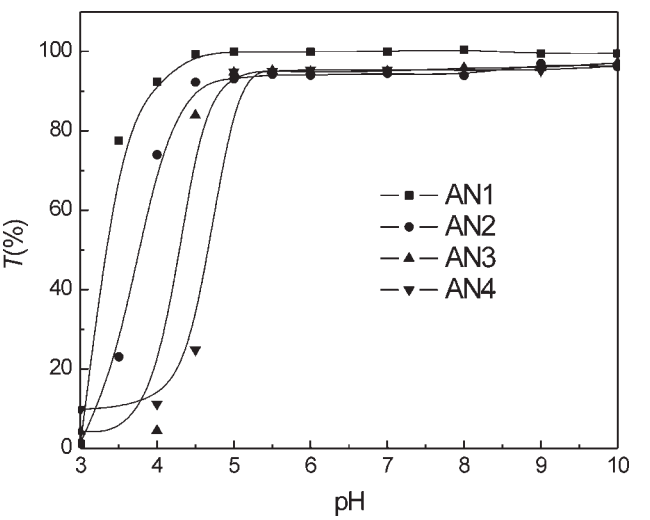


Figure 1 Curves of (0.2 wt %) graft copolymer aqueous solutions transmittance (%) versus pH at room temperature.

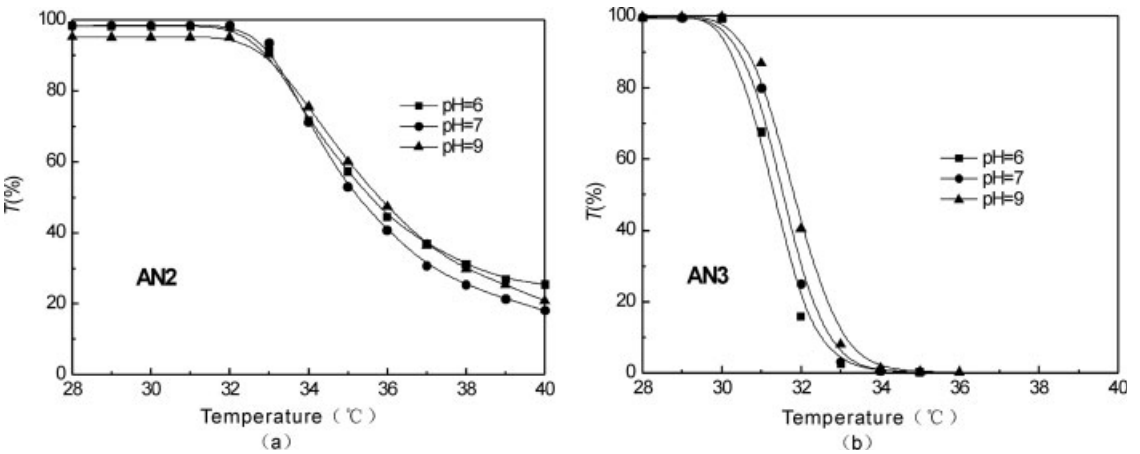


Figure 2 Curves of (0.2 wt %) graft copolymerAN2 (a) and AN3 (b) aqueous solutions transmittance (%) versus temperature at pH 6.0, 7.0, and 9.0, respectively.

tion of pH at room temperature (20°C). With reference to Figure 1, we may observe that the transmittances of AN1, AN2, AN3, and AN4 solutions decreased within a pH range of 3.0–5.0. The main reason for the results is that as pH of the solutions was lower than 5.0, the carboxylic groups on the PAA backbone chains will become less ionized, and there will be formation of inter- and intramolecular H-bonding complexes between the acid moieties of the carboxylic acid and the amide groups of PNIPAM in side chains. Consequently, the transmittances of the graft copolymer aqueous solutions decreased with decreasing pH of the solutions. This result can be compared with the behavior of Makhaeva's PVCL-MAA in aqueous solution in principle.[13–15]

In addition, according to Figure 1, we can also observe that the critical pH values of several different composition graft copolymer solutions gradually increased with increasing PNIPAM contents. For example, the critical pH values (determined from 50% of transmittance against pH curves) from AN1 to AN4 are 3.3, 3.7, 4.3, and 4.7, respectively. Because, the higher is the PNIPAM content in graft copolymers, the more is the number of inter- and intramolecular H-bonding, the higher is the degree of the graft copolymer inter- and intramacromolecular association, the higher is the critical pH value of graft copolymer.

Figure 2, the curves of the copolymer (AN2, AN3) solution transmittances versus temperature, reveals the variation of graft copolymer LCST (determined from the original transition point of transmittance against temperature curves)[21] with PNIPAM contents at pH 6.0, 7.0, and 9.0, respectively. The results shown in Figure 2 indicate that the graft copolymer LCST decreases with increasing PNIPAM contents, and the graft copolymer solution transmittance curves become increasingly sharper and the graft copolymer temperature sensitivity is strengthened with increasing PNIPAM contents. The main reasons of the above results are as the contents of PNIPAM side chains on PAA backbone chains increase, the distance between PNIPAM side chains is shorter, the intra- and interchain hydrophobic interaction of the PNIPAM side chains is stronger. Besides, according to Figure 2, we can know that the LCST values of AN2 and AN3 are less affected by aqueous solution pH. The most of the carboxyl groups are ionized into carboxyl anions at pH 6.0, 7.0, and 9.0, the H-bonding interaction between carboxyl groups and amide groups does not exist basically. After the copolymer acquire negative charges, the static electricity repulsive effect make the PAA backbone chains of the graft copolymers in aqueous solutions become loose conformation.

Figure 3, the transmittances versus temperature curves in the process of heating and cooling cycles for the AN2 and AN3 graft copolymer aqueous solutions shows that the polymer conformation transition is an incomplete reversible process in the process of heating and cooling cycles. Wu[10,26] observed through static and dynamic LLS techniques that the transition of PNIPAM-*g*-PEG conformation from coil to globular was an incomplete reversible process. For PNIPAM-*g*-PEG solution, when the temperature is higher than 32°C, the PNIPAM-*g*-PEO backbone chain undergoes the intrachain ''coil-to-globule'' transition and the interchain aggregation to form nanoparticles with a hydrophobic PNIPAM core and a soluble hydrophilic PEO shell. When $T <$ LCST, the conformation of PNIPAM backbone chain is a random loose coil, and with a rise of temperature, the inter- and intramacromolecular hydrophobic interaction of the PNIPAM backbone chain is strengthened, ultimately the random coil becomes globular gradually,

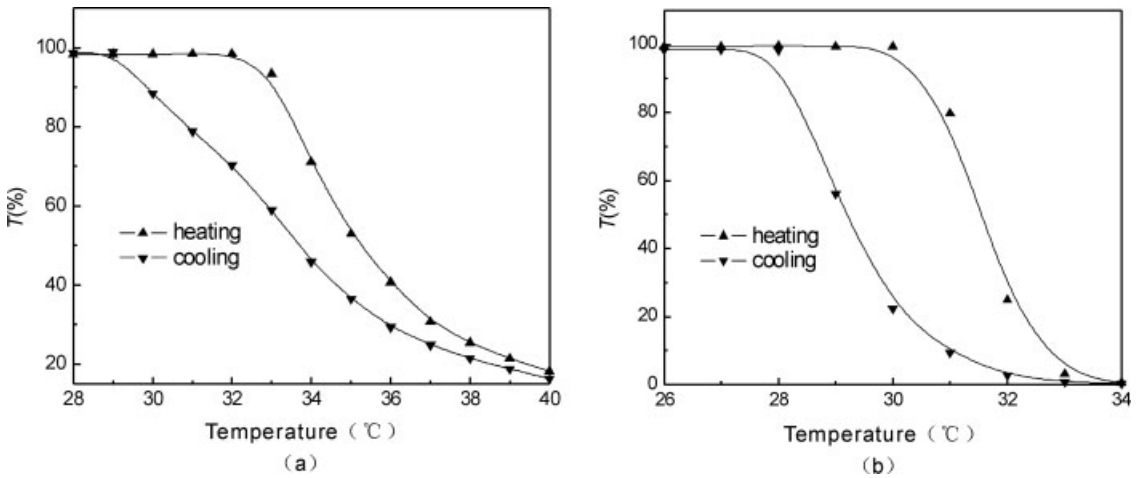


Figure 3 The curves of the AN2 (a), and AN3 (b) graft copolymer aqueous solutions (0.2 wt %) transmittance (%) versus temperature at pH 7.0 in the process heating and cooling cycles.

resulting in a core-shell nanostructure with a collapsed PNIPAM core and a swollen PEO shell. For P(AA-*g*-NIPAM) solution, the graft chain is temperature sensitive PNIPAM, when T is higher than its LCST (for gradually heating process), the inter- and intramacromolecular hydrophobic interaction of the PNIPAM side chains surpasses H-bonding interaction between PNIPAM side chain and water, thus the transition of the PNIPAM macromolecular chain conformation from coil to globular completed quickly, and macroscopically PNIPAM aqueous solution exhibits the phase behavior of temperature sensitivity, so this change is a sudden process. The PNIPAM chain conformation is tightly globular. On the contrary, when temperature gradually debases from high to low (for gradually cooling process), the strong hydrophobic interaction and intersegment H-bonding interaction because of collapse process make it difficult for water to enter into the globular. Because the process of PNIPAM globular swelling is a slow one by forming H-bonding between the amide groups of the PNIPAM side chain and water, the transition for the P(AA-*g*-NIPAM) from globular to coil is a gradual change process. Hence, the reason why the heating and cooling cycles curves do not superpose for the P(AA-*g*-NIPAM) graft copolymers aqueous solutions is similar to one of the PNIPAM-*g*-PEO graft copolymers.[10,26]

Moreover, according to Figure 3, it is found that the increase in the NIPAM contents in the graft copolymer deepens the gap between heating and cooling route. This result can be explained by the fact that the intrachain hydrophobic interaction of the thermosensitive PNIPAM side chains strengthens with increasing NIPAM contents, this stronger hydrophobic interaction makes it difficult for water to enter into the globular, and the distance between heating and cooling curves is broadened.

Probe studies

Py was used as probe in this study, because the fine structure of its fluorescence emission spectrum, especially the I_3 (383 nm)/I_1 (373 nm) value is highly sensitive to the changes in the polarity of its microenvironment. The higher I_3/I_1 value indicates a more hydrophobic environment. This property has been widely employed to monitor the conformational behavior of water soluble polymers in aqueous phase.[22,27–29]

The I_3/I_1 values for Py (10^{-5} mol L^{-1}) solubilized in AN1, AN2, AN3, and AN4 graft compolymer aqueous solutions, respectively, were measured as a function of pH at room temperature (20°C). The results shown in Figure 4 reveal that, for AN1, AN2, AN3, AN4, and Py solution systems, their I_3/I_1 value change ranges are 0.625–0.78, and are less

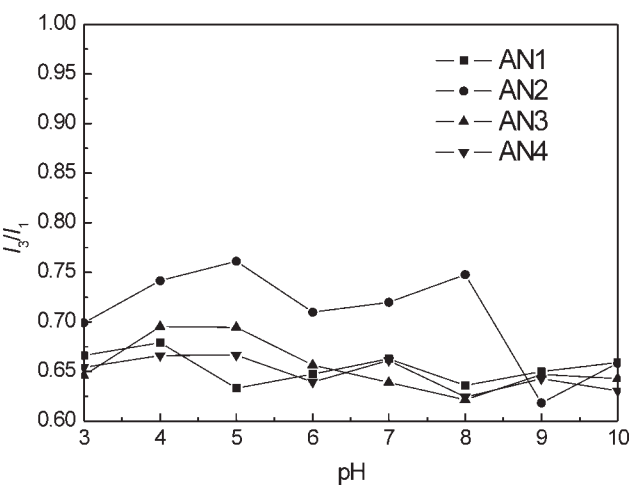


Figure 4 Plots of I_3/I_1 values for Py against pH in the graft copolymer aqueous solutions (0.001 wt %) at room temperature.

affected by graft copolymer composition and solution pH values. Their I_3/I_1 value changes are little, which demonstrates that Py in the AN1, AN2, AN3, and AN4 graft copolymer aqueous solutions are in a polar environment. It may be attributed to the cause that there is no hydrophobic microdomain forming in graft copolymer dilute solutions within research pH range at room temperature (20°C). The reason is that, at pH $<$ 5.0, the formation of H-bonding between the carboxyl groups on the PAA backbone chains and the amide groups on the PNIPAM side chains makes the PAA main chains adopt an expanded conformation. At pH $>$ 5.0, the carboxyl groups are ionized into carboxyl anions, the coulombic repulsive forces also make the PAA main chain adopt an expanded conformation. Moreover, the PNIPAM side chains also adopt an expanded conformation at room temperature (20°C) because of the H-bonding between water and the amide groups on the PNIPAM. So, the I_3/I_1 value change ranges for the AN1, AN2, AN3, and AN4 graft copolymer aqueous solutions are 0.625 $\sim$ 0.78, and are less affected by pH values.

Fluorescence quenching studies

The determination of quenching rate may obtain quenching constant, by which we can deduce probe Py microenvironment and differentiate the conformation changes of different composition graft copolymers in dilute aqueous solutions. For the AN1, AN2, AN3, and AN4 graft copolymer aqueous solutions, the modified Webber's equation[30] plots for the fluorescence quenching results at pH 4.0 and 9.0 are shown in Figures 5 and 6, respectively. The modified Webber's equation is as follows:

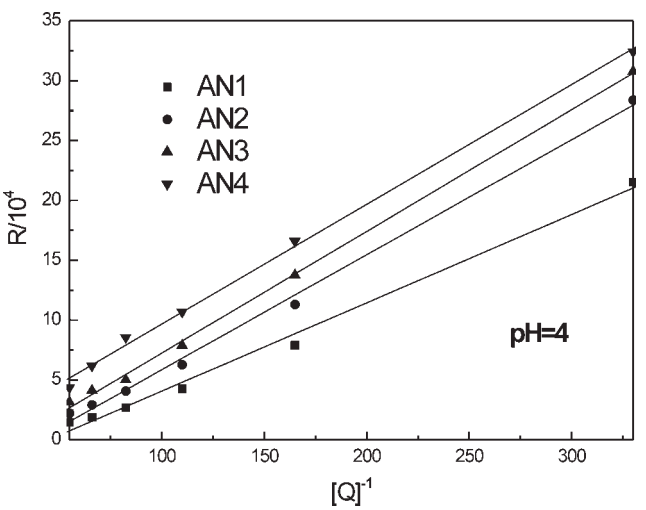


Figure 5 The modified Webber's equation plots for the fluorescence quenching results, R stands for $((I_0/I_1)-1)/[Q]^2$.

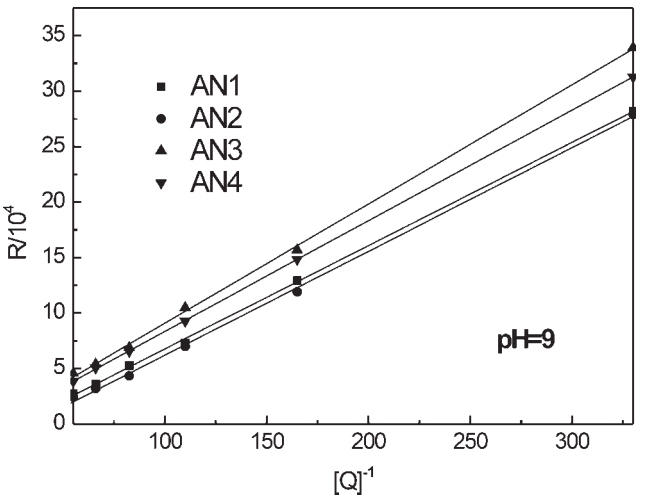


Figure 6 The modified Webber's equation plots for the fluorescence quenching results, R stands for $((I_0/I_1)-1)/[Q]^2$.

$$[(I_0/I) - 1]/[Q]^2 = A + K_D/[Q]$$

where I_0 is the fluorescence intensity without a quencher, I is the fluorescence intensity in the presence of quencher, [Q] is the concentration of quencher, K_D is the normal Stern-Volmer quenching constant, and A is the coefficient for the higher order term and reflects the deviation from the linear Stern-Volmer behavior.

From Figure 5, we acquire K_D of AN1, AN2, AN3, and AN4 graft compolymer aqueous solutions at pH 4.0 is about 0.09541×10^4 mol L^{-1}, and from Figure 6, we gain their K_D at pH 9.0 is about 0.09917×10^4 mol L^{-1}. According to this result, we can deduce that the Py microenvironments at pH 4.0 and 9.0 are

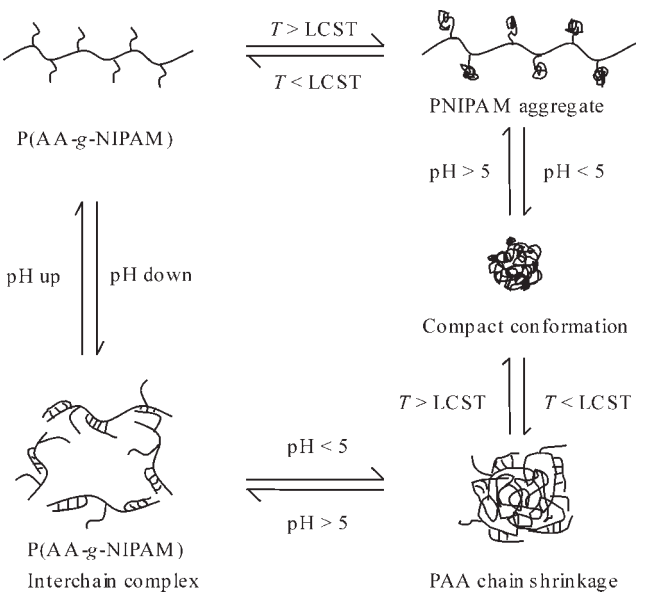


Figure 7 Schematic illustration of stimuli-responsive process of P(AA-*g*-NIPAM) graft copolymer in aqueous solution.

less different, which indicates the P(AA-*g*-NIPAM) conformation in dilute aqueous solutions does not change basically from pH 4.0 to 9.0. Therefore, the results from quenching experiment are the same as the results from probe studies above. Namely, there is no hydrophobic microdomain forming in dilute solutions within researching pH range (pH 3 $\sim$ 10) and at room temperature (20°C).

According to the experimental results described earlier, it may be reasonable to propose a model for the phase behavior of the P(AA-*g*-NIPAM) in dilute aqueous solution (refer Fig. 7). The aggregate process of the temperature- and pH-sensitive P(AA-*g*-NIPAM) is described in this model with changing temperature and pH.

CONCLUSIONS

The P(AA-*g*-NIPAM) graft copolymers possess temperature- and pH-sensibilities. The more are the PNIPAM content, the stronger the temperature sensitivity of the graft copolymers, and the higher are the critical phase transition pH. At room temperature (20°C), within researching pH range (pH 3 $\sim$ 10), the P(AA-*g*-NIPAM) may adopt a relatively expanded conformation and there is no hydrophobic microdomain forming in dilute aqueous solutions. Moreover, for the P(AA-*g*-NIPAM) aqueous solutions, the conformational transition from coil to globular of the PNIPAM side chains is incomplete reversible process in heating and cooling cycles.

References

1. Zhang, X. Z.; Yang, Y. Y.; Wang, F. J.; Chung, T. S. Langmuir 2002, 18, 2013.
2. Tanaka, T. Phys Rev Lett 1980, 45, 1636.
3. Shibayama, M.; Ikkai, F.; Inamoto, S.; Nomura, S.; Han, C. J. Chem Phys 1996, 105, 4358.
4. Osada, Y.; Gong, J. Prog Polym Sci 1993, 18, 187.
5. Hassan, C. M.; Doyle, F. J.; Peppas, N A. Macromolecules 1997, 30, 6166.
6. Brazel, C. S.; Peppas, N. A. Macromolecules 1995, 28, 8016.
7. Bergbreiter, D. E.; Zhang, L.; Mariagnanam, V. M. J Am Chem Soc 1993, 115, 9295.
8. Ricka, J.; Tanaka, T. Macromolecules 1984, 17, 2916.
9. Beltran, S.; Baker, J. P.; Hooper, H. H.; Blanch, H. W.; Prausnitz, J. M. Macromolecules 1991, 24, 549.
10. Qiu, X. P.; Wu, C. Macromolecules 1997, 30, 7921.
11. Brazel, C. S.; Peppas, N. A. J Controlled Release 1996, 39, 57.
12. Liu, S. X.; Liu, M. Z. J Appl Polym Sci 2003, 90, 3563.
13. Makhaeva, E. E.; Tenhu, H.; Khokhlov, A. R. Macromolecules 2002, 35, 1870.
14. Okhapkin, I. M.; Nasimova, I. R.; Makhaeva, E. E.; Khokhlov, A. R. Macromolecules 2003, 36, 8130.
15. Burova, T. V.; Grinberg, N. V.; Grinberg, V. Y.; Kalinina, E. V.; Lozinsky, V. I.; Aseyev, V. O.; Holappa, S.; Tenhu, H.; Khokhlov, A. R. Macromolecules 2005, 38, 1292.
16. Fujishige, S.; Kubota, K.; Ando, I. J Phys Chem 1989, 93, 3311.
17. Stejskal, J.; Kratochvil, P.; Jenkins, A. D. Macromolecules 1987, 20, 181.
18. Raj, D. J. A.; Wadgaonkar, P. P.; Sivaram, S. Macromolecules 1992, 25, 2774.
19. Ohnaga, T.; Sato, T. Polymer 1996, 37, 3729.
20. Tsukahara, Y.; Nakanishi, Y.; Yamashita, Y.; Ohtani, H.; Nakashima, Y.; Luo, Y. F.; Ando, T.; Tsuge, S. Macromolecules 1991, 24, 2493.
21. Idziak, I.; Avoce, D.; Lessard, D.; Gravel, D.; Zhu, X. X. Macromolecules 1999, 32, 1260.
22. Fang, Y.; Liu, S. X.; Hu, D. D.; Cui Y. L.; Xue, M. Polym Bull 1999, 43, 387.
23. Stempel, G. H.; Cross, J. R. P.; Mariella, R. P. J Am Chem Soc 1950, 75, 2299.
24. Chen, G. H.; Hoffman, A. S. Nature 1995, 373, 49.
25. Shibanuma, T.; Aoki, T.; Sanui, K.; Ogata, N.; Kikuchi, A.; Sakurai, Y.; Okano, Y. Macromolecules 2000, 33, 444.
26. Chen, H. W.; Li, J. F.; Ding, Y. W.; Zhang, G. Z.; Zhang, Q. J.; Wu, C. Macromolecules 2005, 38, 4403.
27. Kalyanasundaram, K.; Thomas, J. K. J Am Chem Soc 1977, 99, 2039.
28. Dong, D. C.; Winnik, M. A. Can J Chem 1984, 62, 2561.
29. Wilhelm, M.; Zhao, C. L.; Wang, Y. C.; Xu, R. L.; Winnik, M. A.; Mura, J. L.; Riess, G.; Croucher, M. D. Macromolecules 1991, 24, 1033.
30. Morrisan, M. E.; Dorfman, R. C.; Clendening, W. D.; Kiserow, D. J.; Rossky, P. J.; Webber, S. E. J Phys Chem 1994, 98, 5534.