

Abnormal pH Sensitivity of Polyacrylate-Polyurethane Hydrogels

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ABSTRACT: A series of polyacrylate-polyurethane networks (PUA) were synthesized and their pH-sensitive behaviors were studied. An unexpected swelling-deswelling behavior was observed as the composition changed. Dynamic mechanical thermal analysis and differential scanning calorimetry were used to initially explain this phenomenon. By applying small-angle X-ray scattering and wide-angle X-ray diffraction simultaneously, a specific multiphase-transition process could be clearly detected, which made the mechanism of the observed abnormal pH sensitivity more explicit. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1047-1052, 1998

Key words: polyacrylate-polyurethane networks; abnormal pH sensitivity; multiphase-transition process

INTRODUCTION

In recent years considerable attention has been drawn to polymeric hydrogels that usually undergo a volume change in response to external stimuli, such as temperature,¹⁻³ pressure,⁴ pH,⁵⁻¹⁰ and so forth. A wide variety of hydrogels have been explored for biomedical applications in the areas of wound dressings, implant materials, chemical valves, controlled drug delivery,^{8,11-15} and so forth. The swelling-deswelling behaviors of pH-sensitive polymeric hydrogels might be summarized as follows.^{3,9,10,16-18} Generally speaking, hydrogels grafted with acid groups,^{9,10,16,17} such as carboxylic groups or sulfonic groups, swell as the pH value increases and deswell as the pH value decreases. However, hydrogels attached with basic groups,^{3,6,8,17,18} such as tertiary amine groups, expand as the pH value decreases and contract as the pH value increases. In general, as far as polyacid gels and polybasic gels are concerned, the changes

of electrostatic repulsion and osmotic pressure contribute to their specific swelling-deswelling behaviors. The difference is that ionization and the ionic dissociation process dominates the polyacid gels' pH responses, but the pH-sensitive behaviors of polybasic gels should be ascribed to the protonation-deprotonation mechanism.^{3,8-10,18}

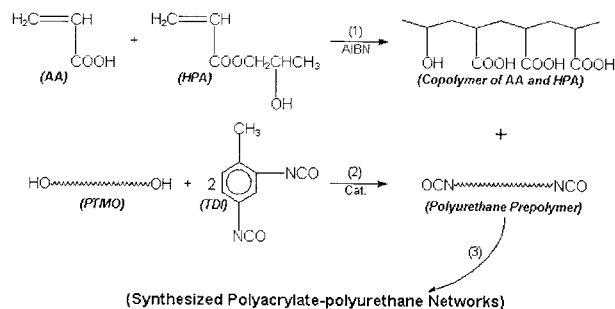
Because it is well known that polyacrylates (PAs) are pH sensitive, polyacrylate-polyurethane (PUA) networks were often treated as simple copolymerized polyacid gels and the polyurethane (PU) fraction was often treated as a mere supporting material and its effect on pH sensitivity was always neglected.¹⁰ However, we observed that with the composition of PUA changed, a more complicated situation could be encountered and an abnormal pH sensitivity could be detected, which was not reported in previous studies.¹⁰ The morphology was investigated by means of dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) in order to initially explain the phenomenon. When applying small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) simultaneously, a "multiphase-transition" process could

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Scheme 1 Synthetic route to polyacrylate-polyurethane networks.

be clearly detected, thus making the abnormal swelling-deswelling mechanism more explicit.

EXPERIMENTAL

Materials

Acrylic acid (AA), and 2-hydroxypropyl acrylate (HPA) were vacuum distilled in the presence of cuprous chloride (CuCl) as a polymerization inhibitor. The initiator 2,2'-azo-isobutyronitrile (AIBN) was recrystallized from a water-ethanol solution before use. Toluene diisocyanate (TDI) was purified by vacuum distillation. Poly(tetramethylene oxide) (PTMO, number average molecular weight of 1000, Du Pont) was degassed at 70°C under a vacuum for 5 h. *N,N*-Dimethyl acetamide (DMAc) was refluxed in the presence of calcium hydride and distilled under a vacuum. Stannous octoate catalyst was used as received. Electrolyte buffers with a total ionic strength of 0.1M were obtained from trihydrate of sodium acetate, acetic acid, ammonia water, and ammonium chloride. All buffer reagents were used as received.

Sample Preparation

PUA networks were synthesized by a three-step method. Scheme 1 shows a typical synthetic route. First, a copolymer of AA and HPA was prepared. The reaction was initiated by AIBN and continued at 80°C for 3 h in a DMAc solution. Second, a PU prepolymer was synthesized as follows. After catalyzing with stannous octoate, PTMO was added dropwise to a DMAc solution of TDI at 60°C. The mixture was stirred for 2 h. Third, the synthesized PU prepolymer was added to the copolymer of AA and HPA and the mixture was stirred for 1 h at 80°C.

Films of the produced PUA networks were formed by solution casting on Teflon plates at 60°C for about 48 h. Then the polymers were shifted to a vacuum oven and dried at 60°C. Before testing, all films were extracted with toluene in a Soxhlet apparatus for 72 h and dried in a vacuum oven again.

Characterization

pH-Sensitive Swelling-Deswelling Experiments

The pH-sensitive behaviors were studied. Pre-weighed dry slabs (6 × 6 × 0.3 mm) were initially placed in a pH 10.0 buffer at 40°C and periodically removed from the solution, blotted with laboratory tissue, and weighed. After 24-h testing, the sample was then transferred to a pH 4.0 buffer and weighed periodically for another 24 h. This concludes a typical testing cycle.

The extent of swelling was expressed as $SR(t)$, the weight percentage of water in the swollen gels,

$$SR(t) = [w(t) - w(0)]/w(0) \times 100\% \quad (1)$$

where $w(t)$ is the weight of swollen gels at time t and $w(0)$ is the weight of dry gels.

DMTA

DMTA data were evaluated with a Rheovibron DDV-II dynamic viscoelastometer (Toyo Baldwin Co.). Samples were tested in a temperature range beginning at -80°C with a heating rate of 2°C/min until sample failure at 110 Hz. The data were collected every 2 or 3 min.

DSC

DSC thermograms were recorded over a temperature range beginning at 123 K and terminating at 473 K. Samples of 15 ± 3 mg mass were run at a heating rate of 20 K/min with a Perkin-Elmer DSC2-C interfaced to a model 3600 data station.

SAXS and WAXD

SAXS and WAXD experiments were performed with a Rigaku D/MAX-RA rotating anode X-ray generator with a copper target at 40-kV cathode potential and 150- or 50-mA emission current, respectively. The X rays were collimated into a beam (10 mm × 70 μm) with a Kratky camera, and the scattered X rays were detected with a

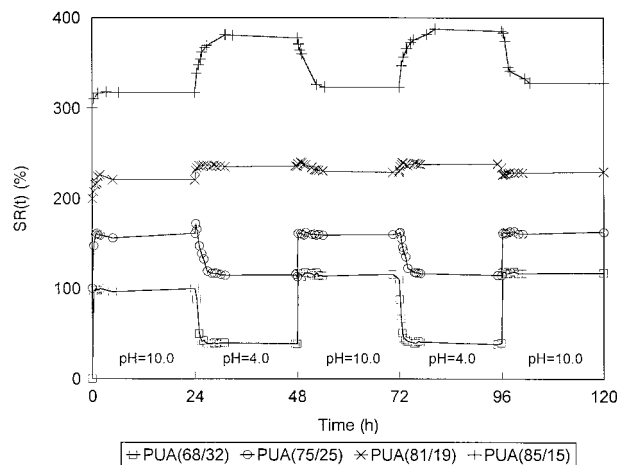


Figure 1 Swelling and deswelling of polyacrylate-polyurethane hydrogels at pH 4 and 10. Note that each curve has been successively shifted by 100% on the Y axis for clarity.

SC-30 scintillation counter probe. $\text{CuK}\alpha$ X rays were selected by detector pulse-height analysis.

SAXS data were corrected for sample transmittance and scattering from the empty camera, then placed on a relative and logarithmic scale expressed as \bar{I} versus q , where \bar{I} is the smeared relative intensity and q is the scattering vector.

$$q = 4\pi \sin \theta / \lambda \quad (2)$$

where θ is half of the scattering angle and λ is the wavelength of the $\text{CuK}\alpha$ radiation.¹⁹ WAXD data were placed on a relative scale expressed as \bar{I} versus 2θ .

RESULTS AND DISCUSSION

pH-Sensitive Swelling-Deswelling Behaviors

The swelling-deswelling behaviors of PUA networks are shown in Figure 1. It can be clearly observed that all the samples could swell and deswell rapidly and almost reversibly. Moreover, it should be noted that the composition could influence the pH-sensitive behaviors significantly. In describing the copolymers, the first number describes the weight percentage of PU segments and the subsequent number is the weight percentage of the copolymer of AA and HPA. When the weight percentage of PU is relatively low [PUA(68/32) and PUA(75/25)], gels swelled at pH 10 and deswelled at pH 4, exhibiting the typical

pH sensitivity of polyacid gels, which is consistent with previous literature.¹⁰ However, when the PU content was increased to a certain extent [PUA(81/19) and PUA(85/15)], gels exhibited “abnormal” pH responses, which means that the hydrogels expanded at pH 4 and contracted at pH 10.

DSC

To try to explain the observed abnormal pH-sensitive behaviors, a “simple-balance” mechanism was proposed, which will be interpreted in detail. PUAs consist of both PA-grafted urethane hard segments and polyether soft segments; thus, it is easy to understand that PA-grafted urethane hard segments contribute to the typical pH sensitivity of polyacid gels because of their pendant carboxylic groups. If polyether soft segments could exhibit the pH sensitivity of polybasic gels, which means that polyether oxygen atoms might be protonated and deprotonated as basic groups, a simple balance should exist between polyacid gels and polybasic gels in this system. As a result, when the PU content is relatively low [PUA(68/32) and PUA(75/25)], the pH sensitivity might be dominated by the typical pH sensitivity of PA. However, when the PU content reached a certain degree [PUA(81/19) and PUA(85/15)], the pH sensitivity of polybasic gels might exceed that of polyacid ones. Consequently, the swelling-deswelling behaviors characteristic of polybasic hydrogels should be exhibited.

If the simple-balance mechanism mentioned above really existed in our studied systems (when immersed into an acid buffer solution) due to the protonation process, the PUA(81/19) or PUA(85/15) samples should experience an obvious glass transition temperature (T_g) increase because the electrostatic repulsion was assumed to “stiffen” the protonated segments.¹⁸ However, as indicated by the DSC results, the T_g value of PUA(81/19) (216.2 K), which had been immersed in an acid buffer and dried in a vacuum oven, was quite comparable to that of the dry control (216.1 K), which means that polyether oxygen atoms should not participate in the protonation process, thus excluding the possibility of the simple-balance mechanism, which is consistent with previous studies.²⁰

DMTA

Because the simple-balance mechanism failed to explain the abnormal pH-sensitive behaviors, a

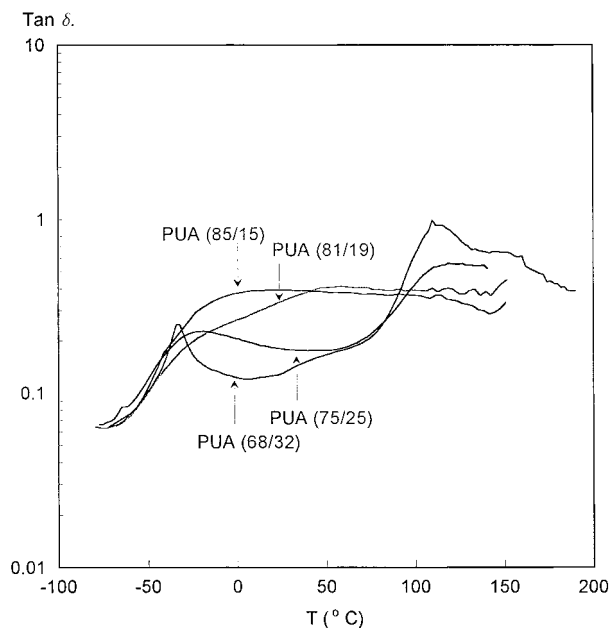


Figure 2 DMTA spectra of polyacrylate-polyurethane networks: $\tan \delta$ - T curves.

multiphase-transition mechanism was proposed as another speculation. It has been widely accepted that a certain degree of phase separation always exists between urethane hard domains and polyether soft segments in segmented PU systems and the different compositions always define different morphologies. Because the PA segments were directly attached on the urethane

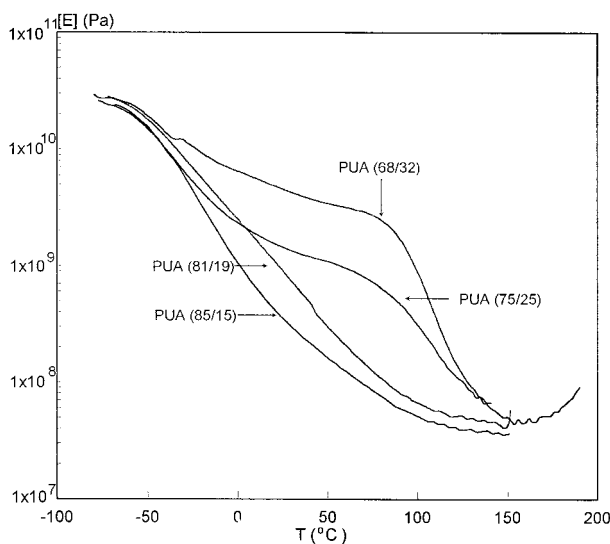


Figure 3 DMTA spectra of polyacrylate-polyurethane networks: $|E|$ - T curves.

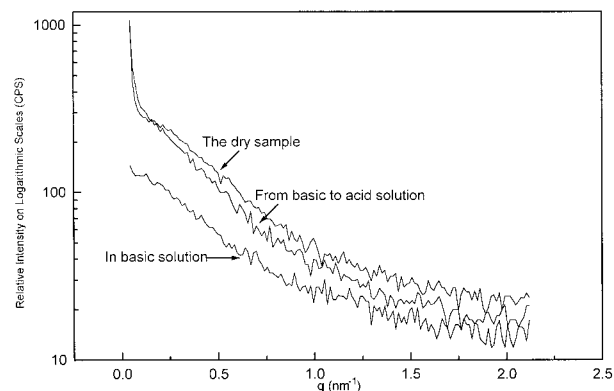


Figure 4 SAXS pattern of polyacrylate-polyurethane network. Note that PUA(85/15) was taken as an example.

hard domains in the studied systems, if a high enough phase mixing degree could be achieved, the interaction between hard and soft segments might become so strong that the pH sensitivity of the hard domains could cause the polyether soft segments to passively respond to pH changes and significantly influence them. Conversely, the passive pH responses of polyether segments might also have a great effect on the original pH-sensitive behaviors of hard segments, thus resulting in a closer interaction between hard domains and polyether soft segments, which is a prerequisite of the multiphase-transition process. The multiphase-transition process would determine the abnormal pH sensitivity, which will be discussed in detail.

The DMTA results, expressed as loss tangent ($\tan \delta$) versus T and absolute modulus ($|E|$) versus T on logarithmic scales are shown in Figures

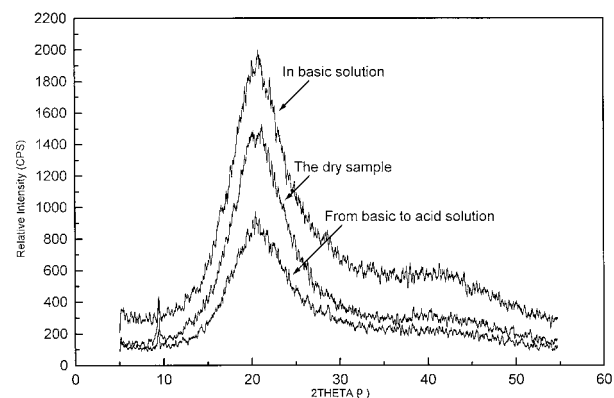


Figure 5 WAXD pattern of polyacrylate-polyurethane network. Note that PUA(85/15) was taken as an example.

Table I Data Extracted from SAXS Curves of PUA(85/15)

	Dry Sample	In Basic Solution	From Basic to Acid Solution
Absolute value of slope	423.3 ± 10.9	181.2 ± 5.9	442.8 ± 14.7

Note that the linear regression calculation was used to estimate the slope of the SAXS curves in a range of q from 0.2 to 0.5 nm⁻¹, and the reliability of the calculated results was beyond 99%. A smaller slope value should be considered as evidence that the “tail” of the SAXS curve drops more slowly.¹⁹

2 and 3, respectively. As shown in Figure 2, two separate glass transition peaks could be clearly noted in the PUA(68/32) and PUA(75/25) samples, one corresponding to the glass transition of the PTMO segments and the other corresponding to the glass transition of the PA-grafted urethane segments, which indicated a certain degree of phase separation between polyether soft segments and PA-grafted urethane hard segments. However, with the ratio of PU/PA raised [PUA(81/19) and PUA(85/15)], these two glass transitions became close to each other gradually and eventually developed into a broad endotherm band, which suggested a better phase mixing morphology. As shown in Figure 3, the $[E]$ curves of PUA(68/32) and PUA(75/25) were dropped by a two-step procedure. In contrast, the $[E]$ curves of PUA(81/19) and PUA(85/15) exhibited a single-step decrease, which reaffirmed the phase-mixing morphology.²¹

Although the observed better phase-mixing structure supplies a close interaction between hard and soft segments and meets the prerequisite of the multiphase-transition mechanism, direct hard evidence for such a mechanism is still required, which will be supplied in the following SAXS and WAXD discussion section.

SAXS and WAXD

SAXS and WAXD always present the strongest evidence for morphological studies. Generally

speaking, SAXS can suggest morphological changes on urethane hard domains¹⁹ and WAXD can supply important phase information on amorphous polyether soft segments.²² To directly determine whether the multiphase-transition process took place during pH-sensitive measurements, the SAXS and WAXD were applied simultaneously to study the changes on hard and soft segments, which is indicated in Figure 4 and Figure 5.

As shown in Figure 4, a peak at about 0.3 nm⁻¹ could be noted, which is typically observed for PU hard domains.¹⁹ Figure 5 shows that the WAXD testing resulted in a diffraction peak at $2\theta \approx 20^\circ$, indicating a spacing of 4.5 Å, which was characteristic of the amorphous polyether soft segments.²² All the data extracted from SAXS and WAXD curves are listed in Table I and Table II.

It could be clearly observed that compared with the dry sample of PUA(85/15) when soaked in the basic buffer, hard domains tended to dissociate, which is indicated by the decreased SAXS peak intensity. The fact that the “tail” of the SAXS curve dropped more slowly also reaffirmed the dissociation.¹⁹ The initial swelling behavior should be attributed to such a physical linkage dissociation. It should also be noted that at the same time polyether soft segments experienced a mutation from an amorphous state to a more aggregated phase, which could

Table II Data Extracted from WAXD Curves of PUA(85/15)

	Dry Sample	In Basic Solution	From Basic to Acid Solution
Ratio of peak height to width at half-height	98.7	113.3	62.3

Note that the values were acquired from the WAXD peak at $2\theta \approx 20^\circ$. The larger ratio suggested a sharpened peak and should be considered as evidence for a more aggregated state of the polyether soft segments.

be best supported by the much sharpened WAXD peak at $2\theta \approx 20^\circ$.

Such a synergism also took place when the sample was removed from the basic solution and immersed in the acid solution. It could be detected that the polyacid gel properties of PA-grafted urethane hard segments caused the hard domains to form again under the stimulus of the acid environment, which is suggested by the retrieval of the SAXS peak intensity. However, in the PUA(81/19) and PUA(85/15), because of their low PA content, the effect of polyacid gels should be quite low, meaning that hard segments could only contract to a very limited degree. Meanwhile, it was obvious that the formerly aggregated polyether segments were dissociated into an amorphous state that is much more mixed than the dry sample, which could be confirmed by the broader WAXD band. Because the PU content is relatively high, such a relaxation movement should become a decisive factor in the swelling ratio, thus causing the continued swelling behaviors in the acid buffer.

This accomplished a typical multiphase-transition process, as well as concluded a testing cycle, and therefore made the mechanism of the abnormal pH sensitivity explicit.

CONCLUSION

The abnormal pH sensitivity of PUA was observed when the ratio of PU/PA increased to a certain level. The DSC, DMTA, SAXS, and WAXD showed that a multiphase-transition mechanism dominated the abnormal phenomenon.

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REFERENCES

1. T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).
2. B. G. Kabra, M. K. Akhtar, and S. H. Gehrke, *Polymer*, **33**, 990 (1992).
3. T. G. Park and A. S. Hoffman, *J. Appl. Polym. Sci.*, **46**, 659 (1992).
4. K. K. Lee, E. L. Cussler, M. Marchetti, and M. A. McHugh, *Chem. Eng. Sci.*, **45**, 766 (1990).
5. B. A. Firestone and R. A. Siegel, *J. Appl. Polym. Sci.*, **43**, 901 (1991).
6. R. A. Siegel and B. A. Firestone, *Macromolecules*, **21**, 3254 (1988).
7. L. Brannon-Peppas and N. A. Peppas, *Biomaterials*, **11**, 635 (1990).
8. P. Y. Yeh, P. Kopeckova, and J. Kopecek, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 1627 (1994).
9. B. Keszler and J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 3153 (1994).
10. M. Y. Yu and W. H. Zhang, *Polym. Bull.*, **30**, 719 (1993).
11. P. H. Corkhill, C. J. Hamilton, and B. J. Tighe, *Biomaterials*, **10**, 3 (1989).
12. S. Nishi and T. Kotaka, *Macromolecules*, **19**, 978 (1986).
13. K. F. Mueller and S. J. Heiber, *J. Appl. Polym. Sci.*, **27**, 4043 (1982).
14. K. Ishihara, M. Kobayashi, N. Ishimaru, and I. Shinohara, *Polym. J.*, **16**, 625 (1984).
15. A. S. Hoffman, *Polym. Prepr.*, **3**, 220 (1990).
16. S. Nishi and T. Kotaka, *Polym. J.*, **21**, 393 (1989).
17. L. Y. Chou, H. W. Blanch, and J. M. Prausnitz, *J. Appl. Polym. Sci.*, **45**, 1411 (1992).
18. K. Kataoka, H. Koyo, and T. Tsuruta, *Macromolecules*, **28**, 3336 (1995).
19. X. Wei and X. Yu, *J. Polym. Sci., Part B: Polym. Phys.*, **35**, 225 (1997).
20. M. B. Armond, J. M. Chabagno, and M. J. Duclot, in *Fast Ion Transport in Solids, Electrodes and Electrolytes*, P. Vashishta, J. N. Mundy, and G. K. Shenoy, Eds., Elsevier North Holland, New York, 1979, p. 131.
21. S. Nishi and T. Kotaka, *Macromolecules*, **18**, 1519 (1985).
22. X. He, X. Jia, and X. Yu, *J. Appl. Polym. Sci.*, **54**, 207 (1994).