

Mechanical Properties of Poly(acrylamide-sodium acrylate) Hydrogels Synthesized under Direct Current Electric Fields with High Voltages

Jun Shan,* Jie Chen, Xu Shen, and Ronghua Chen

Department of Chemistry, Tongji University, Shanghai 200092, P.R. China

(Received January 5, 1999; CL-990011)

The poly(acrylamide-sodium acrylate) hydrogels were synthesized by free polymerization under externally imposed electric fields. The mechanical properties of hydrogel were measured by tensile test. The results indicate that the Young's modulus of hydrogel is increased with electric field strength. It is shown that the polymerization of polar monomer molecules with ordered arrangement in the direction of electric field results in the formation of orientated network structure hydrogel.

Polymer hydrogel is a kind of intelligent polymer material which can modulate its volume in response to environmental stimuli such as changes in solvent composition,¹⁻⁵ pH,⁶⁻⁹ temperature,¹⁰⁻¹³ electric field,^{14,15} and light irradiation.¹⁶ It has many potential applications in various fields of the drug release and delivery system,^{17,18} the biotechnology¹⁹ and the chemomechanical system^{20,21} for smart actuator, artificial muscle, sensor, tissue engineering.

So far, many polymer hydrogel samples using different monomers have been synthesized by the various methods such as the aqueous solution polymerization, the radiation polymerization and the photopolymerization. However, these hydrogel samples have two defects, *i.e.*, the weak mechanical strength and the slow stimulus response, which greatly limit the practical applications of polymer hydrogels.

Much effort has been made to improve the mechanical strength and the stimulus response of polymer hydrogels by use of the graft^{22,23} and interpenetrating polymer methods.^{24,25}

In our previous work,²⁶⁻²⁸ the micromorphology of poly-(acrylamide-sodium acrylate) P(AM-NaA) hydrogels with different molar ratios of monomers AM and NaA was studied, and displayed the nonhomogeneous bubble-film network structure. In addition, the solvent composition greatly affected the micromorphology.

P(AM-NaA) hydrogel samples were synthesized under the direct current electric fields with different high voltages and by the copolymerization of AM with NaA at a molar ratio of 8.0/2.0 in water (total monomer concentration 0.7034 M) containing crosslinking agent N, N'-methylene bisacrylamide MBA 0.1330 g. The aqueous solution was poured into a plastic container, degassed with high purity nitrogen gas, sealed and put into the electric field. Then, the redox initiator including $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaHSO_3 was injected above solution, respectively. And the high voltage was immediately imposed on two parallel plate electrodes. The copolymerization of AM and NaA was carried out at room temperature for 4 h (see Figure 1). The hydrogel samples were still colorless and transparent, and looked to have better strength and elasticity compared with those synthesized under no externally imposed electric field. The electric field strength $E=V/d$, where V is the electric pressure and d the distance between two parallel plate electrodes.

As the hydrogel is a kind of quite soft, elastic and moist material, its mechanical strength is very weak compared with those of most of polymer materials. We measured its mechanical properties by using the device of tensile test shown in Figure 2. The direction of extension is perpendicular to the direction of imposed electric field.

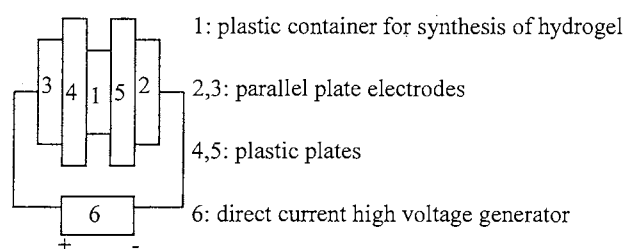


Figure 1. The device of synthesis of poly(acrylamide-sodium acrylate) hydrogel.

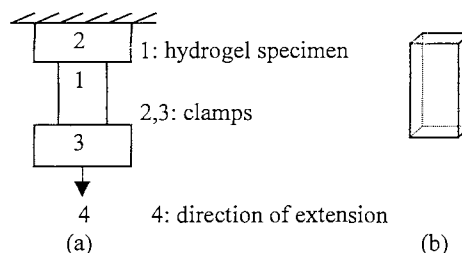


Figure 2. (a) Advice of tensile test; (b) The size of strip-shaped tensile specimen of hydrogel: $30 \times 15 \times 5$ mm, and the gauge length 20 mm.

For each of hydrogel sample synthesized under corresponding electric field strength, we repeatedly do its tensile test.

The stress-strain behaviours of different hydrogel samples were shown in Figure 3. The mechanical properties of hydrogel samples were listed in Table 1, where E_y represents the tensile elastic modulus (*i.e.*, Young's modulus), σ_p the proportional limit, σ_b the tensile strength (*i.e.*, the tensile stress at break) and ϵ_b the percentage elongation at break. It is evident that the mechanical properties (except for ϵ_b) all increase with the electric field strength E . Especially, the Young's modulus $E_y = 5.20 \times 10^3$ N/m² of hydrogel sample under the external electric field of $E = 3.28 \times 10^6$ V/m grows 2.6-fold as $E_y = 2.0 \times 10^3$ N/m² at $E = 0$ V/m (*i.e.*, no external electric field). It is clear that the mechanical strength of hydrogel can be greatly improved by use of above synthetic method.

Note that the values of σ_b and ϵ_b in Table 1 cannot represent the real ones of hydrogel samples. In fact, they are always lower or may be quite lower than the corresponding real values because all of the breaking points in the tensile tests of

hydrogel specimens are at one of two damping ends. This is because the damping force weakens the strength of specimen at damping end, no matter which shape of hydrogel specimen.

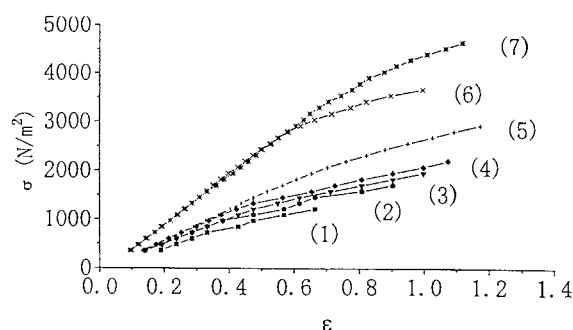


Figure 3. The stress-strain curves of P(AM-NaA) hydrogel samples. $E(\text{V/m}) = (1) 0; (2) 2.30 \times 10^5; (3) 3.28 \times 10^5; (4) 6.57 \times 10^5; (5) 1.97 \times 10^6; (6) 2.63 \times 10^6; (7) 3.28 \times 10^6$.

Table 1. The mechanical properties of P(AM-NaA) hydrogels

No.	$E(\text{V/m}) \times 10^5$	$E_Y(\text{N/m}^2) \times 10^3$	$\sigma_p(\text{N/m}^2)$	$\sigma_b(\text{N/m}^2)$	$\epsilon(\%)$
1	0.00	2.00	651.7	1232	66.2
2	2.30	2.55	969.5	1669	89.9
3	3.28	2.60	1232	1929	99.8
4	6.57	2.98	1320	2192	108
5	19.7	3.18	1465	2918	117
6	26.3	4.90	2665	3674	102
7	32.8	5.20	3093	4662	112

The P(AM-NaA) hydrogels mentioned above have identical FT-IR spectra including main characteristic absorption peaks of amide group at 1640 cm^{-1} and carboxy anion at 1576 cm^{-1} . It indicates that the composition of P(AM-NaA) hydrogels does not vary as the imposed electric field strengths. And nor do the crosslinking densities of P(AM-NaA) hydrogels because of the weight of crosslinking agent MBA being kept constant in each of pregel solutions.

It is well known that the polar small molecules in a static electric field tend to orient themselves in the direction of the externally imposed field. In other words, AM and NaA

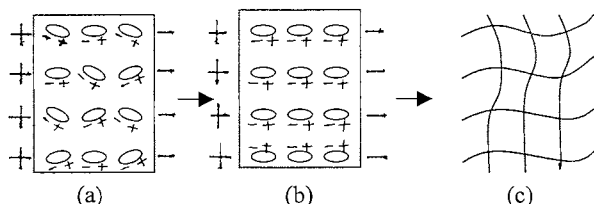


Figure 4. (a) weak electric field; (b) strong electric field; (c) orientated network structure of hydrogel.

monomer molecules in pregel solution under the externally electric field surely form the ordered (or orientated) arrangement. So it can be foreseen that the polymerization of ordered monomer molecules certainly results in the formation of orientated network structure of hydrogel, which is conducive to the increase of mechanical strength of P(AM-NaA) hydrogel.

The order degrees of both network structure of hydrogel and monomer molecules greatly depend on the imposed electric field strength and the temperature. At the room temperature they are proportional to the externally imposed electric field strength E . So the Young's modulus E_Y of hydrogel increases with the electric field strength E (see Figure 3).

We can use the following model to describe the formation of orientated network structure of hydrogel (see Figure 4).

References and Notes

- 1 T. Tanaka, *Polymer*, **20**, 1404 (1979).
- 2 M. Ilavsky, *Macromolecules*, **15**, 782 (1982).
- 3 Y. Hirokawa and T. Tanaka, *J. Chem. Phys.*, **81**, 6379 (1984).
- 4 S. Katayama and T. Tanaka, *Macromolecules*, **17**, 2641 (1984).
- 5 M. Ilavsky, J. Hrouz, and K. Bouchal, *Polym. Bull.*, **14**, 301 (1985).
- 6 T. Tanaka, D. Fillmore, S. Sun, I. Nishio, G. Swislow, and A. Shah, *Phys. Rev. Lett.*, **45**, 1636 (1980).
- 7 T. Tanaka, *Sci. Am.*, **244**, 110 (1981).
- 8 R. X. Zhuo and X. Z. Zhang, *Acta Polymerica Sinica*, **4**, 500 (1997).
- 9 X. Chen, W. J. Li, W. Zhong, C. J. Ge, H. F. Wang, and T. Y. Yu, *Chem. J. Chinese Universities*, **17**, 968 (1996).
- 10 T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).
- 11 M. Ilavsky, J. Hrouz, and I. Havlicek, *Polymer*, **26**, 1514 (1985).
- 12 X. Zhou and Q. W. He, *Acta Polymerica Sinica*, **1**, 74 (1992).
- 13 M. R. Jin and C. F. Wu, *Acta Polymerica Sinica*, **3**, 321 (1995).
- 14 T. Tanaka, I. Nishio, S. Sun, and S. Ueno-Nishio, *Science*, **218**, 467 (1982).
- 15 Y. Osada, H. Okuzaki, and H. Hori, *Nature*, **355**, 242 (1992).
- 16 A. Suzuki and T. Tanaka, *Nature*, **346**, 3455 (1990).
- 17 N. A. Peppas and R. Langer, *Science*, **263**, 1715 (1994).
- 18 B. Jeong, Y. H. Bae, D. S. Lee, and S. W. Kim, *Nature*, **388**, 860 (1997).
- 19 T. Okano, N. Yamada, H. Sakai, and Y. Sakurai, *J. Biomed. Mater. Res.*, **27**, 1243 (1993).
- 20 Y. Osada and J. P. Gong, *Prog. Polym. Sci.*, **13**, 187 (1993).
- 21 Z. Hu, X. Zhang, and Y. Li, *Science*, **269**, 525 (1995).
- 22 H. T. Pu, Z. L. Ding, and Z. T. Ma, *J. Appl. Polym. Sci.*, **62**, 1529 (1996).
- 23 P. S. Stayton, T. Shimoboji, C. Long, A. Chilkoti, G. Chen, J. M. Harris, and A. S. Hoffman, *Nature*, **373**, 49 (1995).
- 24 A. S. Hoffman, A. Affrassibi, and L. C. Dong, *J. Control. Release*, **4**, 213 (1986).
- 25 K. Mukae, Y. H. Bae, T. Okano, and S. W. Kim, *Polym. J.*, **22**, 206 (1990).
- 26 J. Shan, J. Chen, Z. J. Liu, and M. S. Zhang, *Polym. J.*, **28**, 886 (1996).
- 27 J. Shan, Z. J. Liu, F. Q. Li, and J. Ji, *Polym. J.*, **29**, 580 (1997).
- 28 J. Shan, Z. J. Liu, and J. Chen, *Polym. J.*, **30**, 585 (1998).