

# pH- and Thermal Characteristics of Graft Hydrogels Based on Chitosan and Poly(dimethylsiloxane)

IN YOUNG KIM,<sup>1</sup> SEON JEONG KIM,<sup>1</sup> MI-SEON SHIN,<sup>1</sup> YOUNG MOO LEE,<sup>2</sup> DONG-IC SHIN,<sup>3</sup> SUN I. KIM<sup>1</sup>

<sup>1</sup> Department of Biomedical Engineering, Hanyang University, Seoul 133-791, Korea

<sup>2</sup> School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

<sup>3</sup> Department of Biomedical Engineering, Asan Medical Center, Korea

Received 21 June 2001; accepted 8 October 2001

**ABSTRACT:** Graft copolymerization of epoxy-terminated poly(dimethylsiloxane) (PDMS) onto chitosan was reacted without using a catalyst. pH-sensitive hydrogels were obtained that are based on two different components: a natural polymer and a synthetic polymer. These PDMS substituents provide the basis for hydrophobic interactions that contribute to the formation of hydrogels. Various graft hydrogels were prepared from different weight ratios of chitosan and PDMS. Swelling behavior of these hydrogels was studied by immersion of the gels in various buffer solution. Photocrosslinked hydrogels exhibited a high equilibrium water content (EWC). Particularly, the sample CP31 of the highest chitosan–PDMS weight ratio showed the highest EWC in time-dependent, temperature-dependent, and pH-dependent swelling behavior. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2661–2666, 2002

**Key words:** hydrogel; swelling; thermal properties

## INTRODUCTION

Hydrogels are water-swollen, crosslinked polymeric structures produced by the simple reaction of one or more monomers. Hydrogels, especially, have become excellent carriers for release of drugs and bioactive macromolecules either in their swollen equilibrium state or as dynamically swelling systems.<sup>1,2</sup> They are used for variety either by crosslinking, by formation of interpenetrating networks, or by crystallization that induces crystallite formation and drastic reinforcement of their structure.

Graft copolymerization is one of the best methods to bring together synthetic and natural poly-

mers to retain the good properties of natural polymers such as biodegradation, bioactivity, etc. In this work, chitosan and PDMS were used to synthesize the graft copolymer with hydrophobic, synthetic side chains and hydrophilic, natural main chains by direct polycondensation without using catalysis. Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment, which are as “intelligent materials.” For example, the water uptake of these materials may be sensitive to temperature,<sup>3</sup> pH,<sup>4</sup> or to the ionic strength<sup>5</sup> of the swelling solutions or even to the presence of a magnetic<sup>6</sup> or ultraviolet.<sup>7</sup>

Qu et al.<sup>8–10</sup> reported graft hydrogels composed of chitosan and D,L-lactic acid or glycolic acid and studied their swelling mechanisms, state of water, and thermal analysis. Also, Sakai et

Correspondence to: S. I. Kim (sunkim@hanyang.ac.kr).

*Journal of Applied Polymer Science*, Vol. 85, 2661–2666 (2002)  
© 2002 Wiley Periodicals, Inc.

al.<sup>11</sup> reported a hydrogel sensor using the graft method.

Recently, attention has been focused on employing natural polymers such as cellulose,<sup>12</sup> starch,<sup>13</sup> gelatin,<sup>14,15</sup> and chitosan<sup>16,17</sup> to compose hydrogels with a specific response to a biological environment.

Chitosan, especially, possesses an excellent biocompatibility and mechanical property, and has been used as biomedical materials. In recent literature, Lee et al.<sup>18</sup> reported an IPN hydrogel-composed chitosan and poly(acrylic acid) (PAAc), and studied their swelling behaviors and thermal analysis. Yao<sup>19,20</sup> reported on the chitosan semi-IPNs hydrogels crosslinked with glutaraldehyde and studied their swelling kinetics. Wang et al.<sup>21</sup> blended chitosan and PAAc, and used glutaraldehyde to crosslink chitosan. Reports of hydrogel using silicone were not in abundance. However, Lopour et al.<sup>22</sup> reported silicone rubber–hydrogel composites as polymeric biomaterials. In their report, they showed the relations between the properties and the influence of the interaction of polymeric phases on their mechanical properties in the silicone rubber–hydrogel composite materials.

Generally, the water in hydrogels can be classified into three species: freezing water (namely free water), nonfreezing water (namely bound water), and freezing bound water. A study on the physical state of water in the hydrogels might provide useful information on their microstructure and behavior.

We prepared hydrogels based on grafting chitosan (CS) with PDMS, and investigated their structure, pH sensitivity, and swelling properties. The structural change of the hydrogels in different pH buffers was analyzed. The effect of hydrophobic side chains on the water state in hydrogels is discussed.

In this study, we would like to report on the preparation and swelling properties of novel time- and pH-dependent hydrogels. In addition, differential scanning calorimeter (DSC) studies were performed to understand the state of water for the swollen and dry gel in graft hydrogels.

## EXPERIMENTAL

### Materials

The chitosan was offered from Jakwang Co., Korea, and used without purification. Silicone and

epoxy-terminated poly(dimethylsiloxane) (PDMS) were obtained from Shinetsu Co., Japan.

### Preparation of Graft Hydrogels

The synthesis of the hydrogel was carried out by direct grafting of PDMS onto chitosan in the absence of catalyst. Chitosan solution 2 wt % (dissolved in 1% acetic acid aqueous solution) and PDMS were mixed and heated at 80°C for 2 h. Various graft hydrogels were prepared from different compositions (1 : 1, 1 : 3, 3 : 1 wt/wt) of chitosan/PDMS. The solutions were poured onto a Petri dish. UV irradiation was conducted using a 450 W UV lamp (Ace Glass Co.) for 2 h at a distance 20 cm and at room temperature until gelation occurred. Samples were dried at 50°C for 16 h. After 16 h, the dry films were obtained and washed with deionized water to remove any unreacted materials that were not incorporated into the network.

### Characterization

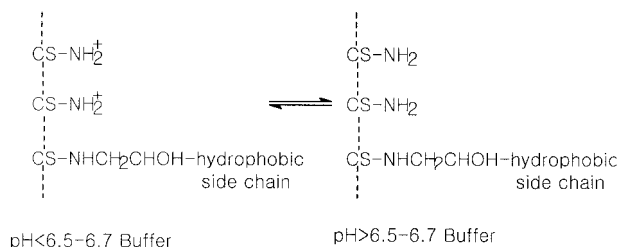
Fourier transform infrared (FTIR) spectroscopy (Bruker Model EQUINOX 55) was used to confirm the chemical structure of graft hydrogels. To measure the equilibrium water content (EWC), preweighed dry samples were immersed in various buffer solutions. After excess water on the surface was removed with the filter paper, the weight of the swollen samples was measured at various time intervals. The procedure was repeated until there was no further weight increase and five times. EWC was determined according to the following equation:

$$\text{EWC}(\%) = ((W_s - W_d)/W_s) \times 100$$

where,  $W_s$  and  $W_d$  represent the weight of swollen and dry states samples, respectively. To investigate the melting endotherm of hydrogels, the measurement of differential scanning calorimeter was conducted by TA Instruments DSC 2010, in aluminum pans at a 5°C/min scanning rate under  $N_2$  flow.

## RESULTS AND DISCUSSION

Graft copolymerization of PDMS onto chitosan was attempted without using a catalyst. Scheme 1 shows a structure change of the CS graft co-



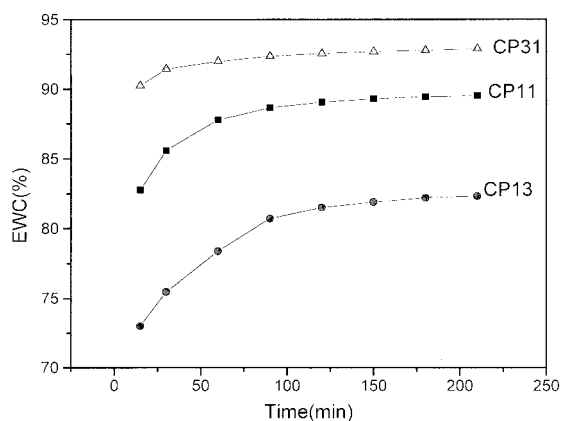
**Scheme 1** Structure change of CS graft copolymer in acidic and alkaline buffer.

polymer according to the pH value of the buffer solution in acidic and alkaline buffer.

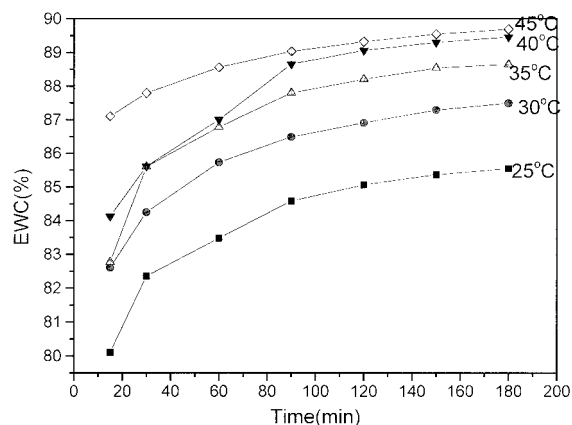
In FTIR spectra, characteristic peaks of chitosan are located at  $3450\text{ cm}^{-1}$  for the hydroxyl group, and  $1650$  and  $1550\text{ cm}^{-1}$  for amide I and II, respectively;  $1300\text{ cm}^{-1}$  is an Si—C group in silicone.

All swelling behaviors are plotted on the average of five times. Time-dependent swelling behavior of graft hydrogels in pH 7 buffer solution at  $35^\circ\text{C}$  is plotted in Figure 1. All hydrogels swelled rapidly and reached to equilibrium within 2 h. The sample, CP31, appeared at the highest swelling ratio in time-dependent swelling behaviors, and on the EWC of the sample, CP13 was lowest among swollen samples.

Also, in the temperature-dependent swelling behavior, stepwise swelling behavior at pH 7 with temperatures alternating between  $25$  and  $45^\circ\text{C}$  was investigated to confirm the swelling process with temperature by measuring the swelling ratio with a time term. Temperature-dependent swell-



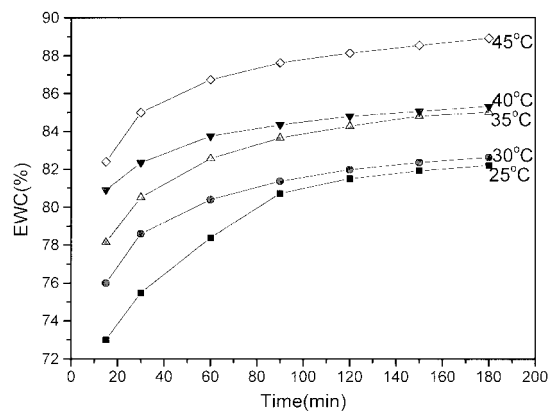
**Figure 1** Time-dependent swelling behavior of graft hydrogels in pH 7 at  $35^\circ\text{C}$ ; CP11, CP13, CP31 (weight ratio of chitosan and PDMS; 1 : 1, 1 : 3, 3 : 1, respectively).



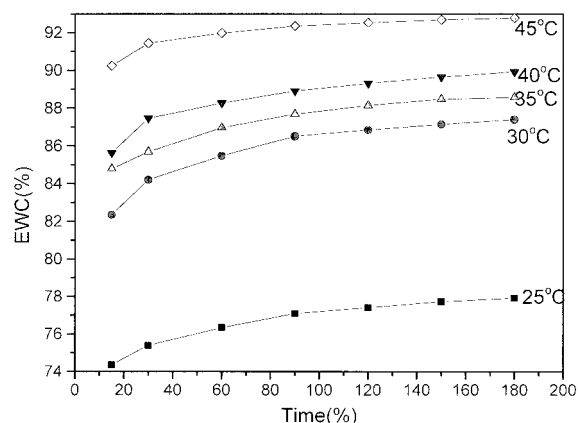
**Figure 2** Temperature-dependent swelling behavior of CP11.

ing behaviors of graft hydrogels are shown in Figures 2–4. The EWC increased with an increment of temperature- and time-dependent behaviors, and the CP31 sample appeared at the highest swelling ratio in temperature-dependent swelling behavior. The EWC of the CP13 sample was the lowest.

To investigate swelling behavior in variation to pH, the disk samples were swollen in several buffer solutions of pH 2, 4, 7, 9, and 10 at  $35^\circ\text{C}$ . Figure 5 shows the pH-dependent swelling behaviors of fully swollen hydrogels. The hydrogels show a lower specific solution content at basic pH compared with acidic pH. It is known that a high concentration of the charged ionic group in the gel increases swelling due to osmosis and charge repulsion. Thus, when the degree of ionization of the gel bound groups is decreased, swelling decreases. Because the swelling process of gels in-



**Figure 3** Temperature-dependent swelling behavior of PC13.



**Figure 4** Temperature-dependent swelling behavior of CP31.

volves the ionization of amino groups at the acid in acidic (pH 2) buffer solution, the acid would be attached to the gels by the ionic bonds. Therefore, the weight of the gels increased in the acidic (pH2) buffer.

At high pH, because the aggregation and intermolecular interactions and the protonation of amino groups have already reached their maximum, the swellability of the hydrogel becomes unchanged when the buffer pH is higher than 7. This pH-sensitive behavior is typical of ionic hydrogels. Because the graft hydrogel, the CP31, possesses more chitosan in its structure, the swelling degree may be the highest among the other hydrogels, resulting in the highest total water content at all conditions of experiments. Besides, the content of chitosan and PDMS in hydrogels, of course, affected EWC. For example, the CP31 that contained the highest content of chitosan among samples showed the highest EWC value due to the ionization of chitosan at all pHs. Meanwhile, the CP13 that containing the lowest content of chitosan among samples showed the lowest EWC value at all pHs. In summary, the EWC of graft hydrogel depended on pH and the amount of complex that is the content of chitosan and PDMS.

DSC thermograms exhibit the melting endotherms of PDMS and graft hydrogel. Graft hydrogel showed melting peaks in Figure 6. Chitosan is very rigid, and we cannot detect any noticeable transition temperature in the DSC thermogram because of the characteristics of natural polymer similar to cellulose. The weight ratio of chitosan to PDMS decreased from 3 : 1 to 1 : 3. Figure 7 shows the DSC thermogram of fully swollen graft

hydrogels. The endothermic peak of swollen gel appeared between 2 to 6°C. The fraction of free water is approximately estimated by the ratio of endothermic peak, integrated between these ranges, to the melting endothermic peak of heat of fusion for pure water. Bound water is expressed as the difference between total water and free water. EWC values, free water contents, and bound water contents, respectively, are calculated and listed in Table I. Free water contents in the graft hydrogel of CP11, CP13, and CP31 were 87.44, 79.53, and 88.19 at pH 7, respectively. The CP13 shows the lowest EWC and free water content. This result confirmed that CP13 had more compact structure than CP11 or CP31.

The fraction of free water in total water is approximately calculated as the ratio of the endothermic peak area for water of swollen hydrogel to melting endothermic heat of fusion (79.9 cal/g) for pure water:

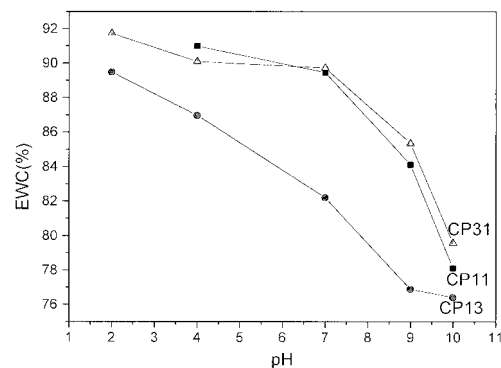
$$W_b = W_t - (W_f + W_{fb}) = W_t - Q_{\text{endo}}/Q_f$$

where  $Q_{\text{endo}}$  is the heat of fusion for ice (equal to 79.9 cal/g) and  $Q_f$  is the heat of fusion for the sample.

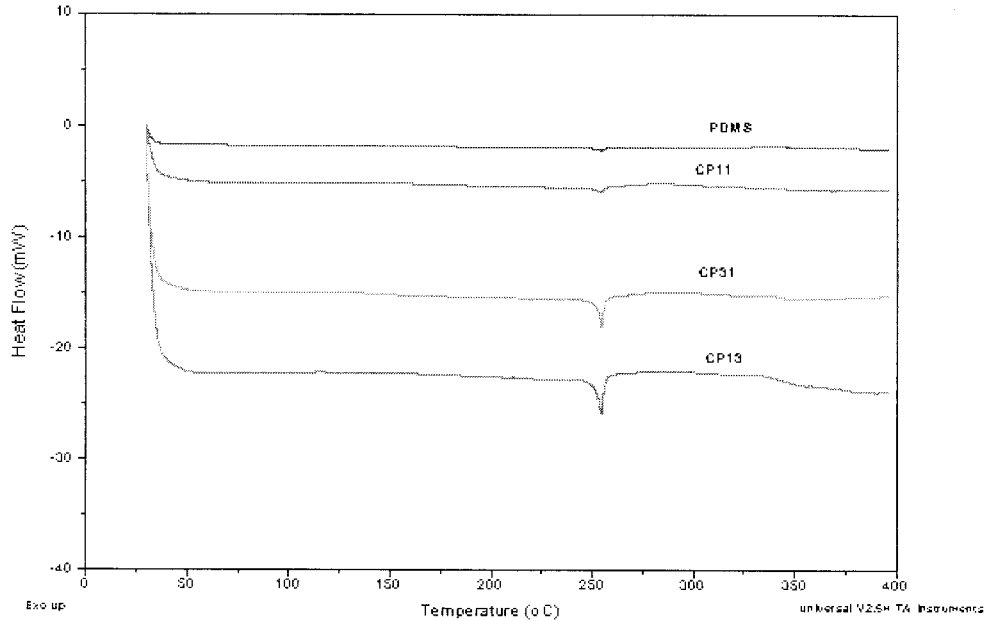
In the present study, the EWC in DSC test was calculated in pH7 buffer solution at 35°C. The free water has good mobility because it has no interaction with polymer chains. However, the bound water is involved in the hydrogen bonding with polymer.

## CONCLUSIONS

Graft hydrogels were prepared by the UV irradiation technique. Chitosan dissolved in aqueous



**Figure 5** pH-dependent swelling behavior of CP11, CP13, and CP31.

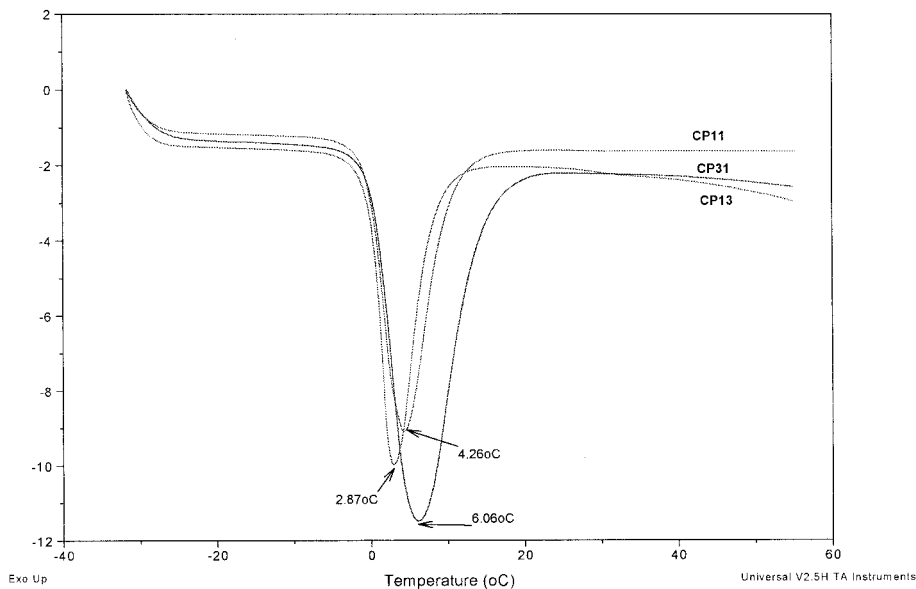


**Figure 6** DSC thermograms of graft hydrogels and PDMS: PDMS, CP11, CP13, CP31.

acetic acid solution to give a homogeneous viscous polyelectrolyte solution. By heating the solution, the reaction occurred. These samples could form hydrogels in aqueous solutions and change their swellability according to the buffer pH, temperature, and time. No chemical crosslinking will occur in this grafting reaction. The pH-sensitive

and biodegradable hydrogels was synthesized by grafting PDMS to chitosan.

All hydrogels exhibited a high EWC in the range 82–92%. Prepared hydrogels were characterized and confirmed by FTIR and DSC. The pH-sensitive characteristics of hydrogels were studied by a swelling test under various pH con-



**Figure 7** DSC thermograms of hydrogels that were fully swollen in pH 7; CP11, CP13, CP31.

**Table I Water State of Graft Hydrogels Calculated by Using DSC**

Sample <sup>a</sup>	Ewc (%)	Free Water (%)	Bound Water (%)
CP31	92.89	88.19	4.70
CP11	89.52	87.44	2.08
CP13	82.33	79.53	2.80

<sup>a</sup> All samples were swollen in pH 7 at 35°C.

ditions at 35°C. Chitosan content determined the behavior for swelling. Therefore, the CP31 sample appeared as the highest swelling ratio in pH- and time-dependent swelling behavior. The CP13 exhibited the lowest EWC value among three graft hydrogels due to low free water content and relatively high content of bound water, as evidenced by DSC analysis. These pH-sensitive hydrogels have potential use in biomedical application, such as controlled release systems.

We are continuing our preparation of full IPN systems. Further work including the electrostatic interactions is under way in our laboratory, and this will be reported in the near future.

This work is the result of research activities of Basic Research Grant (2000-2-31400-002-3) and Advanced Biometric Research Center (ABRC) supported by Korea Science and Engineering Foundation.

## REFERENCES

- DeRossi, D.; Kajiwara, K.; Osada, Y.; Yamauchi, A. *Polymer Gels; Fundamentals and Biomedical Applications*; Plenum Press: New York, 1991.
- Klempner, O.; Utracki, L. A.; Sperling, L. H. *Adv Chem Ser* 1991, 239.
- Dong, L. C.; Hoffman, A. S.; *ACS Symp Series* 1987, 350, 236.
- Brannon-Peppas, L.; Peppas, L. A. *J. Control Rel* 1989, 8, 267.
- Siegel, R. A.; Fireston, B.A. *Macromolecules* 1988, 21, 3254.
- Grodzinsky, A. J.; Weiss A. M. *Sep Purif Method* 1985, 14, 1.
- Irie, M. *Adv Polym Sci* 1990, 94, 28.
- Qu, X.; Wirsen, A.; Albertsson, A. C. *J Appl Polym Sci* 1999, 74, 3186.
- Qu, X.; Wirsen, A.; Albertsson, A. C. *Polymer* 2000, 41, 4589.
- Qu, X.; Wirsen, A.; Albertsson, A. C. *ACS Polym Mater Sci Eng* 1998, 79, 242.
- Sakai, Y.; Rao, V. L.; Sadaoka, Y.; Matsuguchi, M. *Polym Bull* 1987, 18, 501.
- Oliverira, W. D.; Glasser, W. G. *J Appl Polym Sci* 1996, 61, 81.
- Pascual, B.; Castellano, I.; Vazquez, B.; Gurruchaga, M.; Goni, I. *Polymer* 1996, 37, 1005.
- Rathna, G. V. N.; Rao, D. V. M.; Chatterji, P. R. *JMS-Pure Appl Chem A* 1996, 33, 1199.
- Vazquez, B.; Gurruchaga, M.; Goni, I. *Polymer* 1995, 36, 2311.
- Guan, Y. L.; Shao, L.; Liu, J.; Yao, K. D. *J Appl Polym Sci* 1996, 61, 2325.
- Guan, Y. L.; Shao, L.; Liu, J.; Yao, K. D. *J. Appl Polym Sci* 1996, 62, 1253.
- Lee, J. W.; Kim, S. Y.; Kim, S. J.; Lee, Y. M. *J Appl Polym Sci* 1999, 73, 113.
- Yao, K. D. *J Polym Sci Part A Polym Chem* 1994, 32, 1213.
- Yao, K. D.; Liu, J.; Cheng, G. X.; Zhao, R. Z.; Wang, W. H.; Wei, L. *Polym Int* 1998, 45, 191.
- Wang, H.; Li, W.; Li, Y.; Wang, Z. *J Appl Polym Sci* 1997, 65, 1445.
- Lopour, P.; Plichta, Z.; Volfova, Z. *Biomaterial* 1993, 14, 1051.