Sorption Characterization of Poly(vinyl alcohol)/Chitosan Interpenetrating Polymer Network Hydrogels

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ABSTRACT: Poly(vinyl alcohol) (PVA)/chitosan interpenetrating polymer networks (IPN) were prepared by UV irradiation. The water sorption behavior of the IPNs was measured at various temperatures and humidity levels. The water uptake of IPN13 is greater than that of other IPNs. Vapor sorption behavior is more affected by the density of water vapor than by hydrophilic properties with increasing temperature. Equilibrium water uptake increases as humidity increases, and the increase is more noticeable at high humidity. The sorption system of all IPNs is a relaxation-controlled mechanism at a relative humidity (RH) of 90%, but it is a Fickian diffusion-controlled mechanism when the RH is below 50%. With an increase in humidity, the diffusion coefficients were found to increase due to greater penetration of water into the IPNs. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 86–90, 2003

Key words: interpenetrating polymer networks (IPN); hydrogel; kinetics

INTRODUCTION

Since the pioneering work of Wichterle and Lim in 1960 on crosslinked HEMA hydrogels, and because of hydrophilic characteristics and potential to be biocompatible, hydrogels have been of great interest to biomaterial scientists for many years.[1] Hydrogels are polymeric networks that absorb and retain large amounts of water. In a polymeric network, there are hydrophilic groups or domains that are hydrated in an aqueous environment, thereby creating a hydrogel structure. As the term 'network' implies, crosslinking has to be present to avoid dissolution of the hydrophilic polymer chain segments into the aqueous phase.[2]

IPNs are defined as "a combination of two or more polymers in network form, that are synthesized in juxtaposition."[3] They can also be described as crosslinked polymer networks held together by permanent entanglements. The networks are held by 'topological bonds,' essentially without covalent bonds between them.[4–7] By definition, an IPN's structure is obtained when at least one polymer network is synthesized and/or crosslinked independently in the immediate presence of another. As long as the reacting ingredients are blended thoroughly during synthesis, thermodynamic incompatibility can be overcome due to the permanent interlocking of network segments. IPNs with limited phase separation are obtained. It has been reported that polymeric materials with improved mechanical properties can be obtained via IPN structures.[8]

Chitosan is a highly deacetylated derivative of chitin, one of the most widespread polysaccharides in biomass. Consequently, chitosan is necessarily biodegradable and bioresorbable.[9] In addition to these properties, common to every natural polymer, chitosan has biocompatible and bioactive molecules in both polymeric and oligomeric forms.

Poly(vinyl alcohol) (PVA) is used as a basic material for a variety of biomedical applications, including contact lens material,[10] skin replacement material,[11] vocal cord reconstruction,[12] artificial cartilage replacement,[13] etc., because of its inherent non-toxicity, non-carcinogenicity, good biocompatibility and desirable physical properties such as elastic nature and good forming property.[14]

Water sorption is important for biocompatibility because of skin contact, body insertion, food packing, etc. Many researchers have studied the relationship between sorption and polymer films. Sanopoulou et al. reported on non-Fickian sorption kinetics in polymer films.[15] Vachoud et al. reported on the sorption and desorption of solute in chitin, showing that the sorption of the solute depends on electrostatic interactions.[16] Mackin et al. measured the content of amorphous or crystalline regions by moisture sorption.[17] Wadoso et al. studied and compared three methods to determine the vapor activity during hydration and

TABLE I
Composition and Water Uptake of IPNs at Various Temperatures

Sample	Chitosan (wt %)	Equilibrium Water Uptake (g/g IPN)		
		25°C	35°C	45°C
IPN13	25	0.504	0.351	0.285
IPN22	50	0.679	0.477	0.390
IPN31	75	0.882	0.551	0.459

showed that all methods are useful for measuring hydration step activities.[18] Frank et al. studied moisture transport on copolyester thin films.[19]

In this study, IPN hydrogels composed of PVA and chitosan were prepared by UV irradiation. To analyze the water vapor sorption of PVA/chitosan IPN hydrogels as biomaterial, we observed water vapor uptaking behavior, sorption mechanisms, sorption kinetics and activation energy of IPNs at various temperatures and levels of relative humidity.

EXPERIMENTAL

Materials

Chitosan with an average molecular weight of 2.0 $\times 10^5$ and a degree of deacetylation of 76% was submitted from Jakwang Co., Korea and used without purification. PVA with an average molecular weight of 1.5×10^5 and acryloyl chloride were purchased from Aldrich Chemical Co., USA. 2,2-Dimethoxy-2-phenylacetophenone (DMPAP), used as a photoinitiator, and all other chemical reagents used were extra pure grade.

Preparation of the PVA/Chitosan IPN hydrogels

PVA was added to deionized water and heated at 80°C for 1 h to make a solution containing 10 wt % PVA. Acryloyl chloride and DMPAP in tetrahydrofuran (THF) were added to the PVA aqueous solution. Chitosan was dissolved in 4 wt % acetic acid aqueous solution to prepare a 3 wt % chitosan solution. The chitosan solution was then added to the PVA mixture and mixed for 30 min. The mixed solution was poured into a petri dish, stored in a UV box and exposed to a 450 W UV lamp (Ace Glass Co. USA) placed 20 cm above the mould for 1 h under a N_2 atmosphere. The weight ratios of the PVA-to-chitosan mixture were adjusted to 1:3, 2:2 and 3:1. The designation of each sample is listed in Table I. The irradiated samples were dried in an oven at 50°C for 12 h. The dry films were removed from the oven and washed with deionized water to remove any nonreactive materials that were not incorporated into the network.

Sorption experiment of IPN hydrogels

The sorption behavior of the IPN hydrogels was analyzed at various temperatures and relative humidity (RH) levels using a dynamic vapor sorption DVS-1000 instrument (Surface Measurement Systems Ltd., London, UK) with a Cahn D200 microbalance. Prior to analysis, the IPN samples were dried in a vacuum oven at 40°C for a day and then the weights of the IPN samples were measured at 0% RH. The following equation was used to determine the water uptake (W):

$$\text{Water uptake}(W) = \frac{W_s - W_d}{W_d} \qquad (1)$$

where W_s represents the combined weight of a sample and the water absorbed at a given time, and W_d is the weight of the dry state of the sample.

RESULTS AND DISCUSSION

PVA/chitosan IPNs are highly hydrophilic with an equilibrium water uptake (W_∞) that is highly dependent on composition for the experiments carried out at 25°C, as shown in Figure 1. W_∞ was measured for about 15 hours and the values are reported in Table I. IPN13 had the highest water uptake value, while IPN31 had the lowest, and the time required to reach equilibrium state (t_{eq}) was shorter for IPN13 than for the other IPNs. These results show that IPN31 has a complex structure that is more compact than that of other hydrogels and that chitosan is more hydrophilic than PVA because the amount of water uptake increased with an increasing content of chitosan in the IPNs.
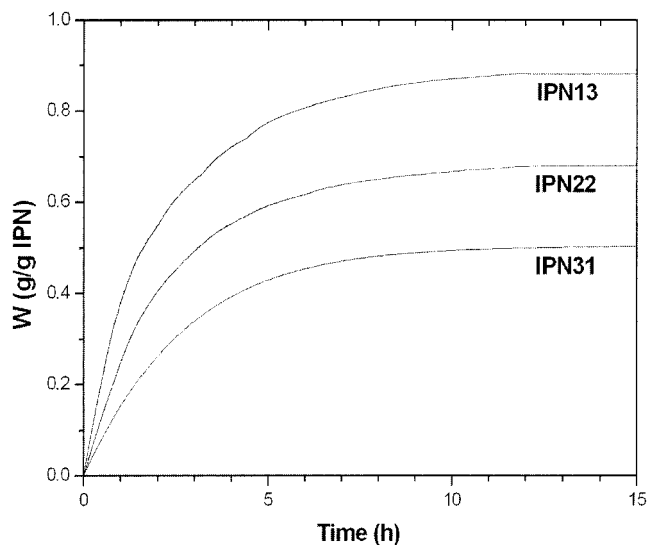

Figure 1 Water uptake of IPN31, IPN22 and IPN13 at 25°C and 90% RH.
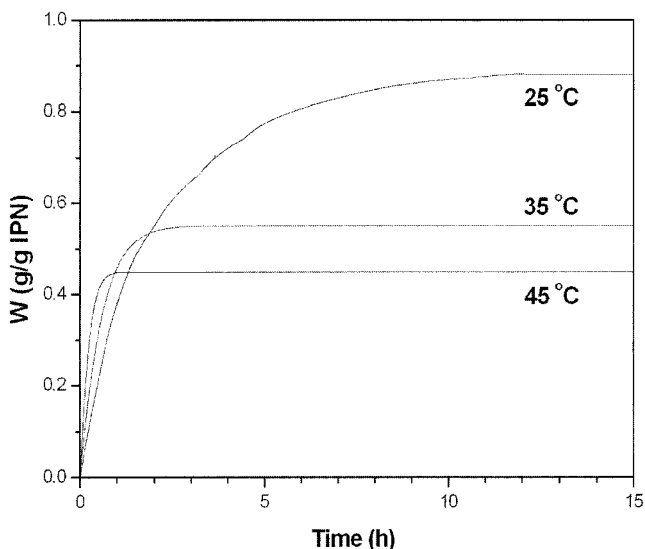
Figure 2 Water uptake of IPN13 at 25, 35 and 45°C.

Figure 2 shows the water uptake of IPN13 at various temperatures. As can be observed, water uptake depends heavily on temperature. Values of W_∞ for IPN13 were 180% at 25°C, 150% at 35°C and 140% at 45°C. The t_{eq} was 1 h at 25°C, 2.5 h at 35°C and 12 h at 45°C. W_∞ was decreased and t_{eq} shortened with increasing temperature. The other IPNs appeared to have similar tendencies. The amount of water uptake for IPN13 was the highest of the hydrogels, resulting in the highest water uptake in all sorption experiments because IPN13 possesses more hydrophilic groups within its structure.

PVA and chitosan are hydrophilic and have upper critical solution temperatures in liquid sorption. Their water uptakes are increased and their t_{eq} values are reached faster with increasing temperature in liquid sorption. In this experiment, t_{eq} appeared to follow this tendency, but W_∞ did not. This result is explained by the fact that the density of water vapor changes greatly with temperature, and the number of water molecules is much smaller in an IPN in the vapor phase than in one in the liquid phase. Therefore, the W_∞ values of our IPNs decreased and their sorption behavior was affected more by the density of water vapor than by their hydrophilic properties with increasing temperature.

Figure 3(a) shows changes in the W_∞ at various levels of RH for IPN samples. The values of water uptake at 30, 50, 75 and 90% RH were 0.010, 0.117, 0.211 and 0.882, respectively. The t_{eq} of IPN samples is shorter with increasing RH. Figure 3(b) shows sorption isotherms. The water sorption isotherm is shown as a sigmoidal curve. Equilibrium water uptake increases as humidity increases, and the increase is more noticeable at high humidity. This type is also called a type II isotherm according to BET classification.[20]

These results prove that the IPN sample is hydrophilic.

Water uptake behavior is related to the sorption mechanism of molecules into the polymer. When a solid polymer is brought into contact with a penetrating liquid or vapor, the penetrant diffuses into the polymer and the polymer swells. Both concentration-gradient-controlled diffusion and relaxation-controlled swelling contribute to the rate and extent of penetrant sorption in the polymer. To analyze the sorption mechanism in this study, we used the following equation:[21]

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left\{ D\frac{\partial C}{\partial x} - vC \right\} \qquad (2)$$
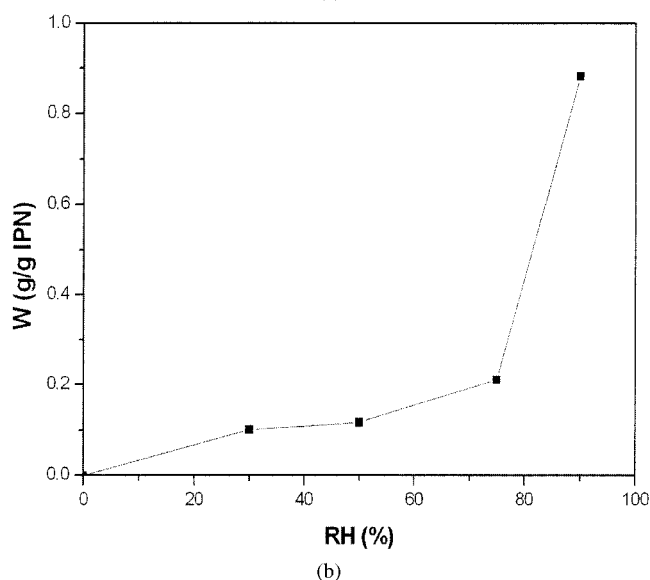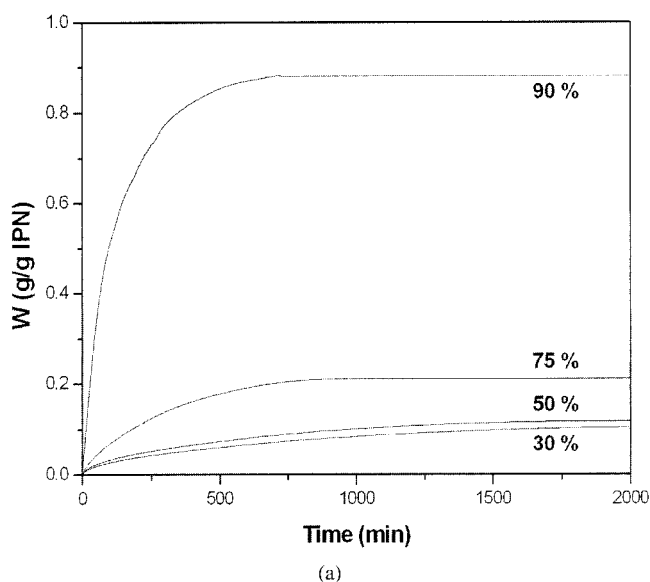

(a)

(b)

Figure 3 (a) Water uptake of IPN13 at various levels of RH, and (b) equilibrium water uptake of IPN13 at various levels of RH.
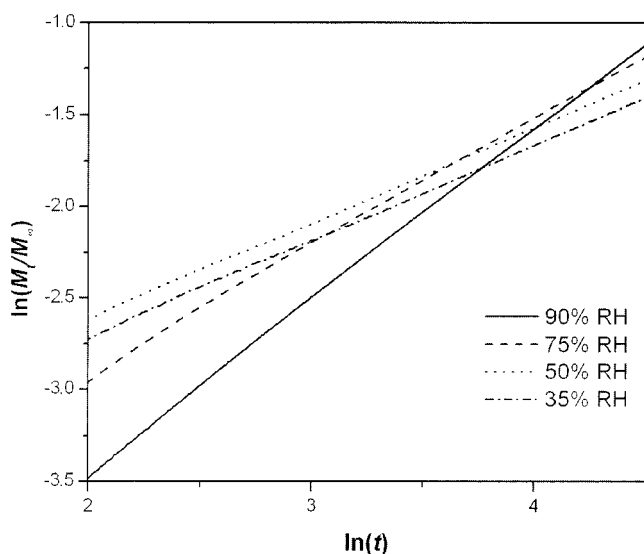
Figure 4 Plots of $\ln(M_t/M_\infty)$ against $\ln t$ at various levels of RH.

Figure 5 Plots of water uptake against $\sqrt{t}$ at various levels of RH.

where C is the concentration of the solute, x is distance, D is the diffusion coefficient, v is the velocity of the swelling front, and t is time. The solution of this equation characterizes diffusion phenomena. For slabs, the solution for this equation, assuming D and v are constant is

$$M_t/M_\infty = K_1 t^{1/2} + K_2 t = kt^n \qquad (3)$$

where M_t and M_∞ represent the amount of water uptake at times t and ∞, respectively; k is a characteristic constant of the hydrogel and n is a characteristic exponent of the mode of transport of the penetrant.[22] This equation has been proposed as a simple method to analyze sorption mechanisms. From this equation, the value of n can be used to determine the mechanism of sorption. When $n = 0.5$, Fickian diffusion will dominate and the sorption mechanism depends on concentration-gradient-controlled diffusion, and when $n = 1$, the system mechanism is anomalous diffusion and depends on relaxation-controlled swelling. For $0.5 < n < 1$, the system mechanism depends on concentration-gradient-controlled diffusion and relaxation controlled swelling. A calculation of the exponent n was achieved by plotting the data in log-log plots according to eq. (4) and using linear regression to determine the slope:

$$\log(M_t/M_\infty) = \log k + n \log t \qquad (4)$$

Figure 4 shows the results of plotting IPN13 water uptake data at various levels of humidity according to eq. (4). The n values of the IPN samples in 30, 50, 75 and 90% RH are 0.527, 0.532, 0.689 and 0.919, respectively. The n value increases with humidity. At 30 and
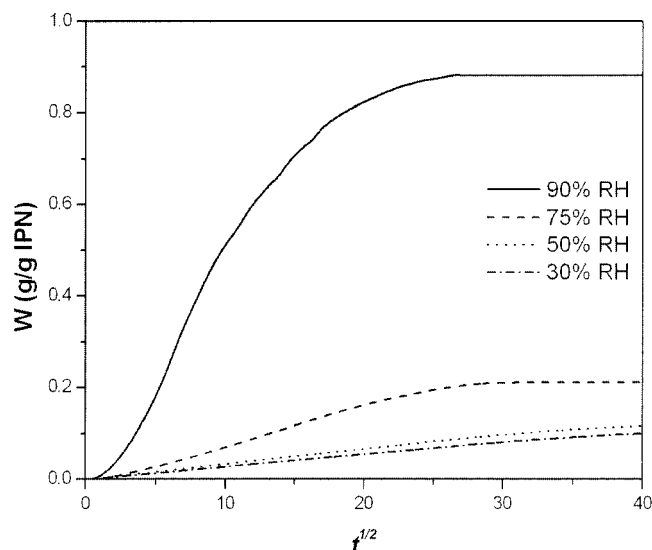
50% RH, their sorption is Fickian transport and depends on concentration-gradient-controlled diffusion because n is about 0.5, but at 75 and 90% RH, their system depends on two mechanisms. Thus, as humidity increases, their system depends on relaxation controlled swelling more than more and is led to anomalous diffusion.

Sorption kinetics were analyzed from diffusion coefficients. The diffusion coefficient for thin films was calculated by utilizing diffusion equations first developed by Crank and Park.[23] A thin film was suspended in the sorption apparatus and the kinetics of sorption for a single step in humidity were recorded in the usual manner. For a single step in controlled humidity, for a double-sided thin film of thickness d, the initial kinetics of sorption into the bulk may be described by the following equation:

$$\frac{M_t}{M_\infty} = \frac{4}{d}\sqrt{\frac{Dt}{\pi}} \qquad (5)$$

where M_t is the amount of water absorbed at time t, M_∞ is the amount absorbed at thermodynamic equilibrium and D is the diffusion coefficient. Eq. (5) is

TABLE II
Diffusion Coefficients and Activation Energy of IPN13 at Various Temperatures and Levels of Relative Humidity

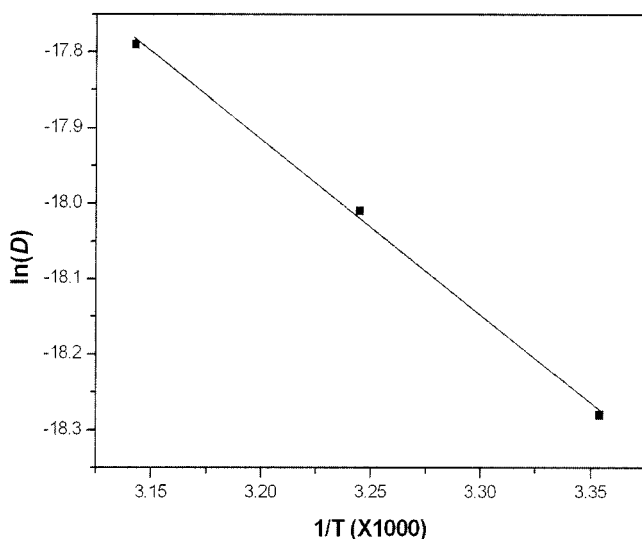| Diffusion Coefficient ($\times 10^8$) (cm^2/s)				Activation Energy (kJ/mol)
Temperature		Relative Humidity		
25°C	1.40	30%	0.63	
35°C	1.51	50%	0.75	
45°C	1.87	75%	1.21	87.12

Figure 6 Plots of ln D against $1/T$ for IPN hydrogels in pure water.

typically valid for values of $M_t/M_\infty < 0.4$, where a plot of M_t/M_∞ against $\sqrt{t}$ should be linear. The diffusion coefficient of IPN13 at various temperatures and levels of humidity was calculated from data presented in Figures 2 and 3. The diffusion coefficients of IPN samples were then calculated from the slope of this line, as shown in Figure 5. The water diffusion coefficients (cm^2/s) of IPN13 were calculated from the slope of the linear line below $M_t/M_\infty < 0.4$. The results of calculating the diffusion coefficients of IPN hydrogels are listed in Table II. With an increase in humidity, the values of the diffusion coefficients were found to increase due to a greater penetration of water into the IPN.

The temperature dependence of the above diffusion coefficients was analyzed on the basis on an Arrhenius-type equation:

$$D = D_0\exp(-E_D/RT) \qquad (6)$$

where E_D is the apparent activation energy for the diffusion process. Analyzing the activation energy of water into the hydrogels determines their hydrophilic ability.[24] As shown in Figure 6, the experimental value of the linear dependence of the logarithm of D versus $1/T$ was obtained. The slope is a straight line and the activation energy is E_D, 4.247 kJ/mol. This value indicates the typical diffusion process of water in a hydrophilic polymer system.

CONCLUSIONS

PVA/chitosan IPNs prepared by UV irradiation demonstrated highly hydrophilic characteristics. Their vapor sorption behavior was more affected by the density of water vapor than by their hydrophilic properties with increasing temperature. The water sorption isotherm as humidity increases can be described by a sigmoidal curve called a type II isotherm according to BET classification. The sorption system of all IPNs is a relaxation-controlled mechanism at 90% RH, but it is a Fickian diffusion-controlled mechanism when the RH is below 50%.

References

1. Hoffman, A. S. Adv Drug Deliver Rev 2002, 43, 3.
2. Hennink, W. W.; van Nostrum, C. F. Adv Drug Deliver Rev 2002, 54, 13.
3. Bischoff, R.; Cray, S. E Prog Polym Sci 1999, 24, 185.
4. Kim, S. C.; Sperling, L. H. IPNs Around the World; Wiley: New York, 1997.
5. Frisch, H. L.; Xu, Q.; Zhou, P. Polym Gel Netw 1994, 2, 257.
6. Barret, L. W.; Sperling, L. H. Trends Polym Sci 1993, 1, 45.
7. Sperling, L. H. Interpenetrating Polymer Networks and Related Materials; Plenum Press: New York, 1981.
8. Hsieh, T. T.; Hsieh, K. H.; Simon, G.. P.; Tiu, C. Polymer 1999, 40, 3153.
9. Li, Y.; Yang, M. J. Sensor Actuat B 2002, 85, 73.
10. Peppas, N. A.; Yang, W. H. Proc IUPAC 1980, 27, 28.
11. Charadack, W. M.; Brueske, D. A.; Santomauro, A. P.; Fazekas, G. Am Surgeon 1962, 155, 127.
12. Peppas, N. A.; Benner Jr., R. E. Biometerials 1980, 1, 158.
13. Peppas, N. A. Biometer Med Dev Artif Org 1974, 7, 421.
14. Bajpai, A. K.; Bajpai, J.; Sandeep Shukla React Func Polym 2001, 50, 9.
15. Sanopoulou, M.; Petropoulos, J. H. Macromolecules 2001, 34, 1400.
16. Vachoud, L.; Zydowicz, N.; Domard, A. Int J Biol Macromol 2001, 28, 93.
17. Mackin, L.; Zanon, R.; Pack, J. M.; Foster, K.; Opalenik, H.; Demonte, M. Int J Pharm 2002, 231, 227.
18. Wadso, L.; Markova, N. Eur J Pharm Biopharm 2001, 51, 77.
19. Frank F. Shi.; James, E. J Polym Sci, B 1998, 36, 1025.
20. Despond, S.; Espuche, E.; Domaed, A. J Polym Sci 2001, 39, 3114.
21. Frisch, H. L. J Polym Sci 1969, 7, 879
22. Franson, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.
23. Crank, J.; Park, G. S. Diffusion in Polymers; Academic Press: New York, 1968.
24. Peppas N. A.; Mikos A.G. In Hydrogels in Medicine and Pharmacy; Peppas, N. A., Ed.; CRC Press: Boca Raton, FL, 1986; Vol. 1, p 1–24.