Polymer Bulletin 58, 401–409 (2007)
DOI 10.1007/s00289-006-0672-6

Polymer Bulletin

Radiation Grafting of N-Isopropylacrylamide onto Poly(vinyl chloride) tubes by Gamma Irradiation

Ever Arenas[1], Emilio Bucio[1] (✉), Guillermina Burillo[1], and Gabriel P. Lopez[2]

[1]Instituto de Ciencias Nucleares; UNAM, Ciudad Universitaria, 04510 México, D. F.
[2]Center for Biomedical Engineering, Dept. of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque NM 87131

E-mail: ebucio@nucleares.unam.mx

Received: 24 April 2006 / Revised version: 2 August 2006 / Accepted: 2 August 2006
Published online: 23 August 2006 –

Summary

Grafted copolymer of poly(vinyl chloride) (PVC) with N-isopropylacrylamide (NIPAAm) was prepared by radiation-grafting method using γ-ray source. NIPAAm was graft polymerized from its aqueous solution onto PVC tubes by preirradiation method, all samples were exposed in the presence of air at room temperature to ^{60}Co. Conditions for achieving maximum grafting yield were observed between 0.5 and 1 moldm^{-3} of monomer concentration, pre-irradiation dose of PVC from 5 to 110 kGy, and reaction temperature of 323 and 333 K. Characterization of the grafted copolymer was conducted by various methods: FTIR-ATR, TGA, and SEM. The temperature-responsive behavior of grafted copolymer was studied by swelling at various temperatures and pH 6.8.

Introduction

In industry, technology, biology and medicine, it is often necessary to change and/or to improve some of the polymeric surface properties without modifying the bulk properties of the material [1]. Poly(vinyl chloride) (PVC) is one of the most widely used polymers in the world, because it exhibits a good price / performance balance that allows penetration into many applications such as pipes, cable insulation, packaging foils, and medical products [2]. PVC has many applications due to its attractive physical characteristics such as flexibility, softness, and transparency. Some of its surface characteristics such as morphology, wettability, adhesion, and biocompatibility within biological environments can be modified by different methods [3]. Patients undergoing medical procedures such as blood transfusion, hemodialysis or nutritional support may be exposed to plasticizers, such as di(2-ethylhexyl) phthalate (DEHP), from PVC medical devices. In 2001, the US Food and Drug Admistration published the results of the safety assessment of DEHP released from PVC medical devices [4]. Furthermore, in direct contact with blood, these polymers are prone to initiate the formation of clots; platelets and other components of the blood coagulation system are activated. It is well known that the formation of a thrombus depends on the behavior of platelets at or near the surface of an artificial

material and on the protein-based coagulation cascade. Recently, flexible PVC materials have also been used in neurosurgical implants [5, 6]. In these applications, it is necessary to use materials having morphological, chemical, and physical surface properties which exhibit minimal adverse reactions in biological environments, and are, additionally, stable in time [7]. Over the past few years a class of polymers that have shown promise in dynamic control of surface properties in a variety of biological applications have been the so called "smart" or stimuli responsive polymers. One important and well studied class of "smart" or 'intelligent' polymers are water soluble polymers and hydrogels that exhibit relatively large changes in their chemical and physical properties in response to small changes on environmental stimuli [8]. One of the most well-known thermo-responsive polymers is poly(N-isopropylacrylamide) (PNIPAAm), which exhibits a lower critical solution temperature (LCST) at around 32°C in an aqueous solution [9, 10]. Graft polymerization is one of the most effective methods to produce environment-sensitive composite materials or membranes, and has been used for example, in applications where a thermo-responsive polymer is capable of controlled drug release upon slight temperature change (an example of an intelligent biomaterial) [11]. Recently, new NIPAAm derivatives were designed with the goals of effectively controlling the phase transition of temperature by adding hydrophilic or hydrophobic comonomers. Additionally, some new stimuli responsive properties were also developed in NIPAAm derivatives around the critical temperature [12]. Radiation grafting of PVC with different monomers has some advantages compared to conventional grafting methods and has been a well-known process for many years [13, 14]. In this paper, we investigate, for the first time, grafting of NIPAAm onto the surfaces of small diameter PVC tubes by a pre-irradiation method using gamma rays. We examine the effects of irradiation time, dose and characterized the grafted tubes by infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy and water swelling measurement as a function of temperature.

Experimental

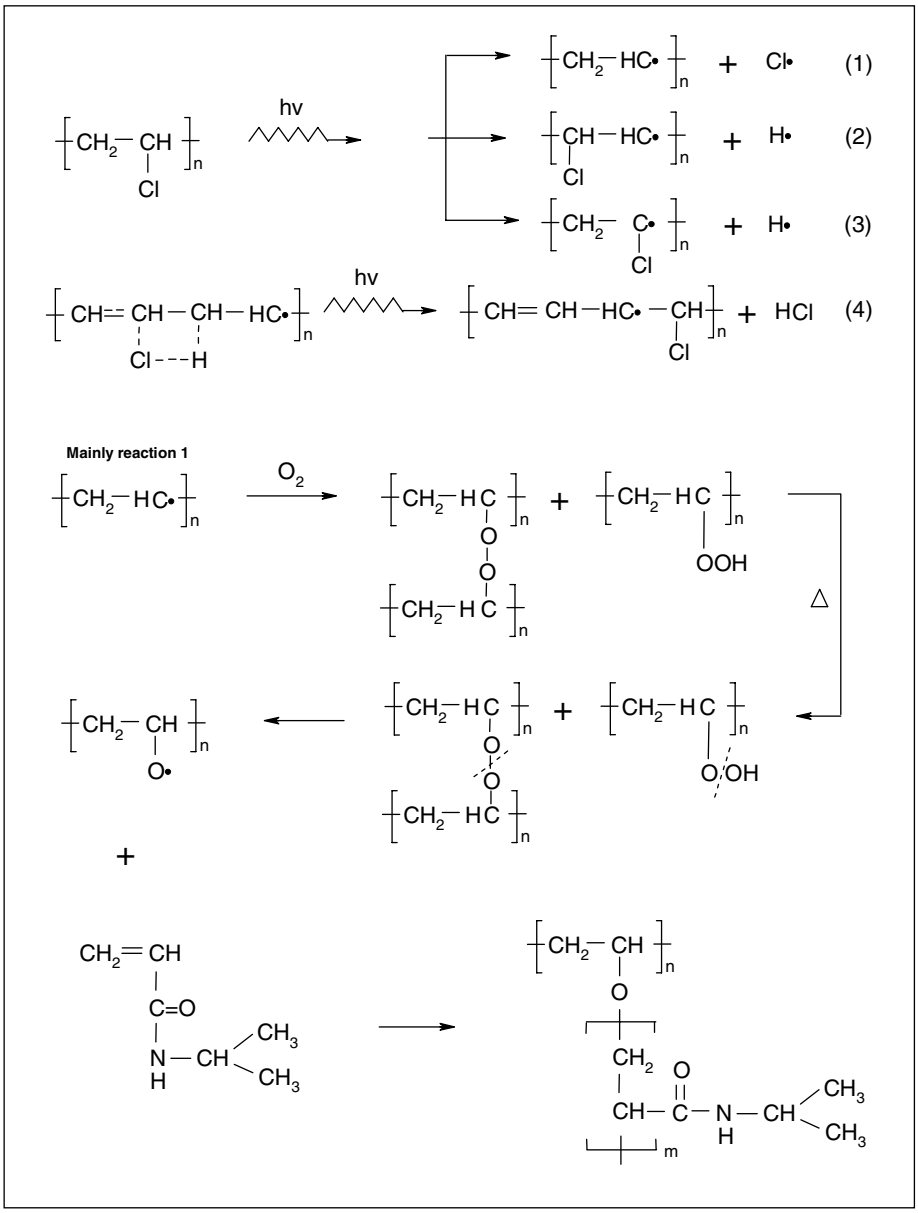
Materials

Flexible, colorless, poly(vinyl chloride) tubes (PVC) with phthalate as additive were kindly supplied by Spectra Hardware Inc. (inner diameter of 2.54 mm and thickness of 0.9 mm) and used as received. N-isopropylacrylamide supplied by Aldrich Co, USA (NIPAAm) was recrystallized from hexane/toluene 50/50 vol. hexane and toluene from Baker were used as received.

Grafting

The PVC tubes were gamma irradiated with a ^{60}Co Gamma-Beam 651-PT source with an activity of 9.25 x 10^{14} Bq, in the presence of air by preirradiation method, at room temperature, dose rate of 1.4 and 3 kGy/h and pre-irradiation dose from 5 to 110 kGy. The irradiated PVC tubes were placed in glass ampoules which contained aqueous solutions at two different monomer concentration of NIPAAm (0.5 and 1 moldm^{-3}), and the ampoules were sealed off in vacuum after degassing by repeated freeze/thaw cycles. Reaction temperatures were 323 and 333 K, at reaction time between 2 and 25 h. The ungrafted PNIPAAm formed during the graft copolymerization was

removed by washing with water for 24h. The grafting yield (Yg) was calculated by the equation: Yg (%) = 100[(Wg-Wo) / Wo], where Wg and Wo are the weights of the grafted and initial tubes, respectively.
The radiation effects on PVC are very complex since many reactions take place simultaneously (Scheme 1).



Scheme 1. Graft copolymer of N-isopropylacrylamide onto poly(vinyl chloride) by radiation-grafting method using γ-ray source.

Characterization

FTIR-ATR (attenuated total reflection) spectra of the starting and modified PVC tubes were analyzed using a Perkin-Elmer PARAGON 500 spectrometer, in the horizontal attenuated total reflectance mode, a SeZn glass was used as contact with the sample surface. The decomposition temperatures were determined in nitrogen atmosphere by thermogravimetric analysis, in a TGA Q50 (TA Instruments, New Castle, DE). The scanning electron microscopy (SEM) of the cross section of the films was performed using an apparatus of JEOL model JSM 5200. The low critical solution temperature (LCST) of the grafted tubes was determined by measuring equilibrium changes of swelling of the samples immersed in distilled water at different temperatures between 298 and 310 K for 3 h at neutral pH.

The percentage swelling was determined gravimetrically by the following equation: Swelling (%) = 100[(Ws-Wo) / Wo], where Ws and Wo are weights of the swollen and initial tube respectively. The thermosensitivity is expressed as T = Mt / M∞; where Mt is the swelling at 298 K and M∞ is the swelling at 310 K (equilibrium).

Results and Discussion

The increase in grafting yield as a function of reaction time for PVC samples by pre-irradiation method at a dose of 20 kGy and constant monomer concentration is shown in Figure 1. The general tendency follows the expected increased efficiency of the grafting process from 2 to 10 h, after this reaction time grafting was constant because pre-irradiated method conducted in air-saturated tubes results in an efficient decomposition of all oxidative products, in this case maximum grafting was 18%.

Grafting yield as a function of pre-irradiation dose is shown in Figure 2; the graft percentage increases with absorbed dose and temperature. High dose allows a high formation of active centers that were reacting with monomer forming of Poly(N-isopropylacrylamide) (PNIPAAm) and increasing the graft percentage. The temperature of 333 K allows an increase the probability of reaction compared to 323 K.

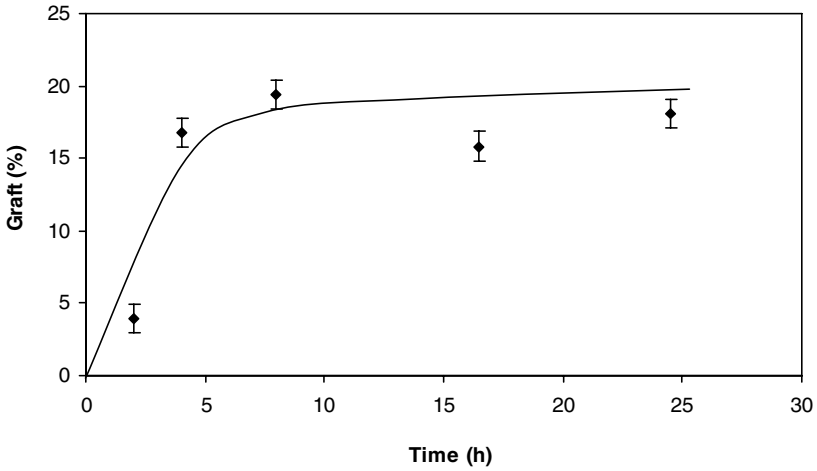


Figure 1. Grafting yield of poly(NIPAAm) onto pre-irradiated PVC tubes with increasing reaction time. Monomer concentration of 1 moldm^{-3}, reaction temperature 333 K, dose rate 3 kGy/h, and a pre-irradiation dose of 20 kGy.

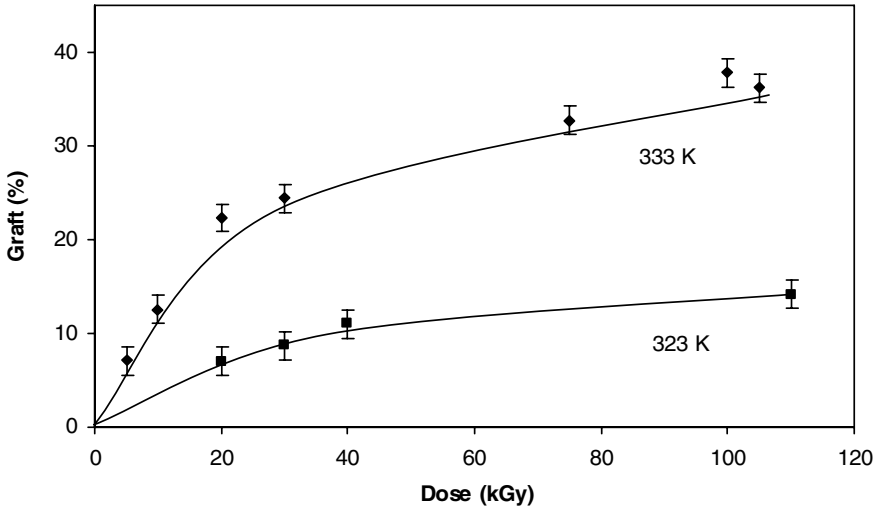


Figure 2. Grafting yield of poly(NIPAAm) onto pre-irradiated PVC tubes with increasing pre-irradiation dose, at different temperatures 323 and 333 K, monomer concentration 1 moldm^{-3}, reaction time 20h, and dose rate 3 kGy/h.

The effect of monomer concentration on the grafting as a function of preirradiation dose is shown in Figure 3, at reaction time of 20 h, reaction temperature 333 K and dose rate of 3 kGy/h. Grafting yield increases with monomer concentration from 0.5 to 1 moldm^{-3}; concentration of NIPAAm above 1 moldm^{-3} favors the "gel effect", this effect results from a slow termination step owing to the lack of mobility of the growing chains, increasing the yield of grafting.

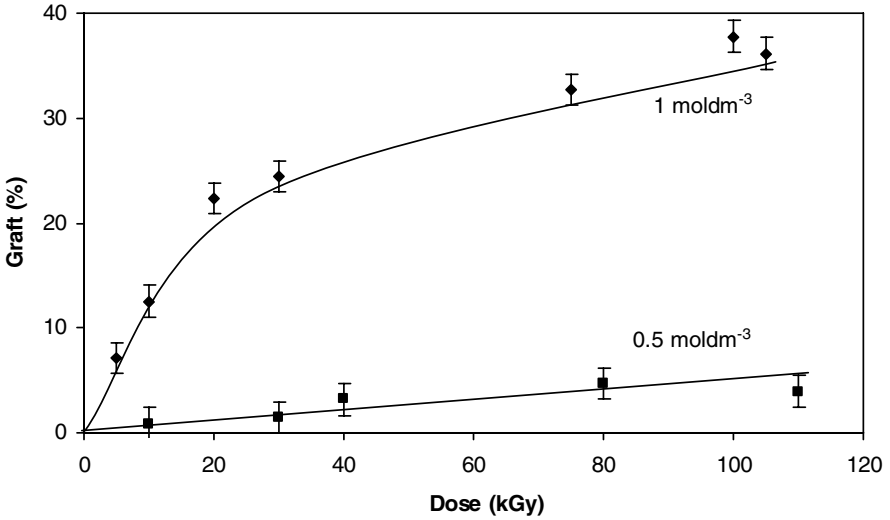


Figure 3. Grafting yield of poly(NIPAAm) onto pre-irradiated PVC tubes as a function of pre-irradiation dose at different monomer concentration, reaction temperature 333 K, reaction time 20h, and dose rate 3 kGy/h.

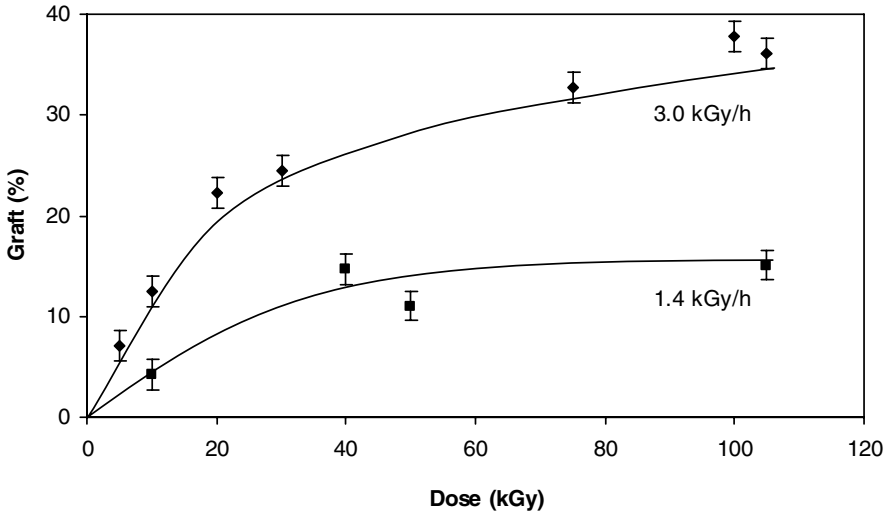


Figure 4. Grafting yield of NIPAAm onto PVC tubes as a function of pre-irradiation dose, at different dose rate, monomer concentration 1 moldm^{-3}, reaction time 20h, and reaction temperature 333 K.

Figure 4 shows higher yield of NIPAAm grafting onto PVC tubes at dose rate of 3.0 kGy/h as compared with 1.4 kGy/h. The high dose rate increases the formation of radicals to initiate the grafting process.

The FTIR-ATR of samples, PVC, NIPAAm monomer, and grafted PVC are shown in Figure 5. The absorption bands of PVC tubes are clear CH_2 (2925 cm^{-1}), and CH-Cl

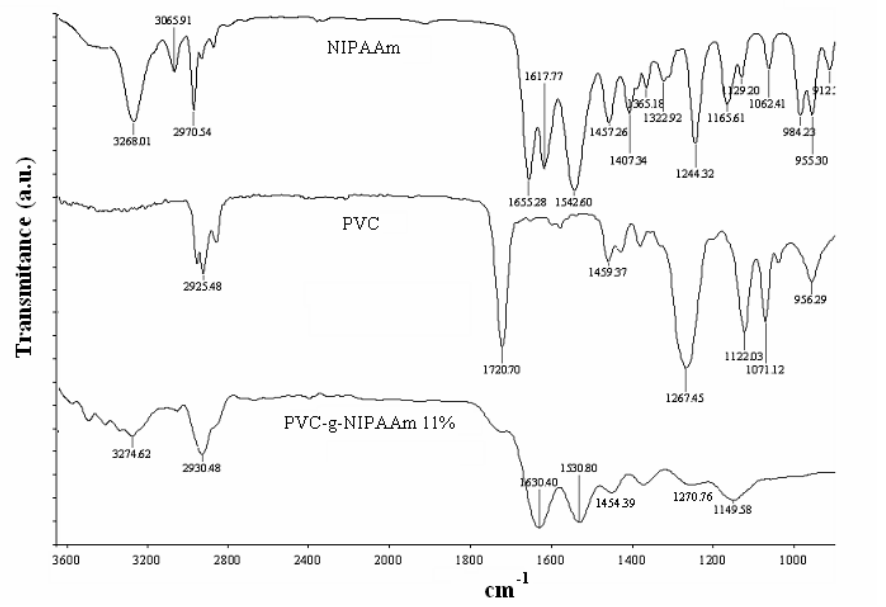


Figure 5. FTIR-ATR spectra of NIPAAm, PVC alone, and PVC-g-NIPAAm (11% graft).

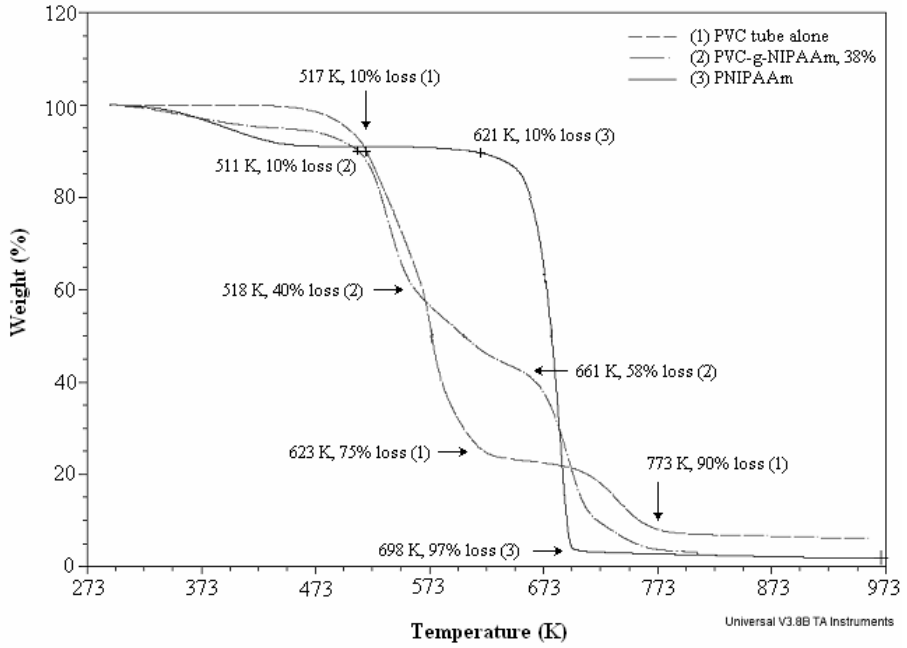


Figure 6. Thermogravimetric analysis of: PVC tube alone (1), PVC-g-NIPAAm (38% graft) (2), and PNIPAAm (3).

(1459 and 1267 cm^{-1}). Additionally a band at 1720 cm^{-1} due to phthalate additive is present. The NIPAAm monomer shows C=O (1655 cm^{-1}), N-H (3268 and 1542 cm^{-1}) and CH_3 (2970 cm^{-1}) peaks. Graft copolymer samples show peaks characteristic of both polymers, PVC and poly(NIPAAm). This characterization confirms grafting of NIPAAm onto the PVC tubes.

The thermal behavior of PVC tubes was characterized by thermogravimetic analysis in a nitrogen atmosphere from room temperature to 973 K at 10 $Kmin^{-1}$ (10°$Cmin^{-1}$). The PVC sample showed two decomposition temperatures, the first one attributed to dehydrochlorination at about 517 K and the second one at 743 K, due to the polymer decomposition. The decomposition temperature of PNIPAAm occurs to 685 K, and PVC-g-NIPAAm (38% graft) shows two decomposition temperatures, the fist one due to dehydrochlorination of PVC and the second one to decomposition of the PNIPAAm grafted onto the PVC tubes.

Scanning electron microscopy (SEM) of PVC of tubes indicated a flat surface for the PVC samples (Figure 7a); homogenous grafting in PVC-g-NIPAAm surface (Figure 7b) and the cross-section of PVC-g-NIPAAm tubes, grafting surface was observed (Figure 7c). These micrographs were strong evidence of NIPAAm grafted onto PVC tubes. PVC tubes exhibit a gradual increase of their thickness on NIPAAm grafting at 5.5, 15 and 38 % graft, thickness increased 8.8, 13 and 32 % respectively, and there is not increase in length. These results indicated that the grafting were obtained mainly in surface.

Equilibrium swelling of PVC-g-NIPAAm tubes in water was found at 3h. Typical swelling profile of PVC-g-NIPAAm tubes are plotted in Figure 8 and LCST was measurement for graft contents of 38%; it was observed at 303 K. Termosensitivity results was 2.23 for 38% graft.

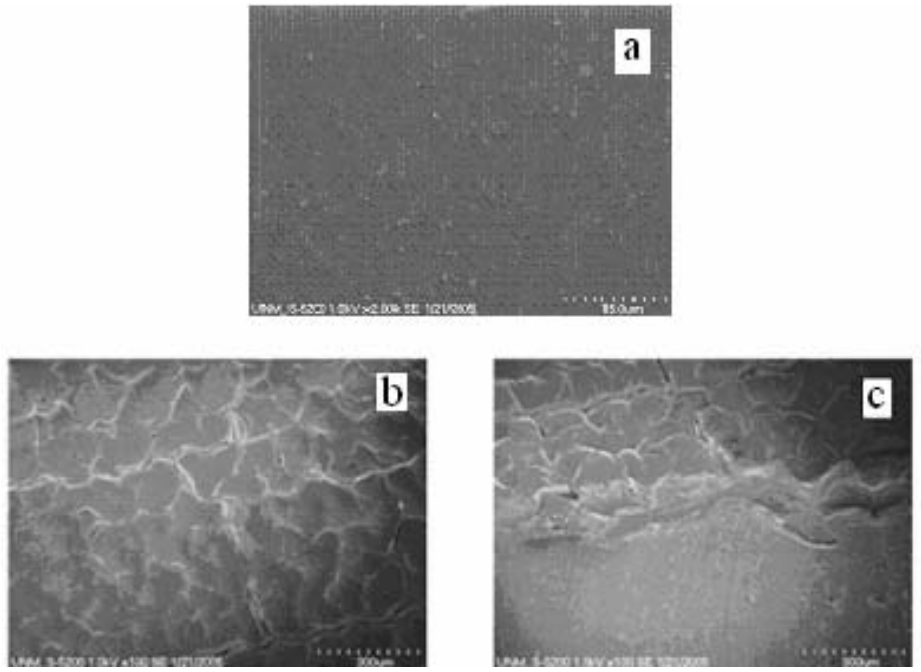


Figure 7. Scanning electron microscopy micrographs of the poly(NIPAAm)-grafted PVC (38% yield); PVC alone (a), graft on surface (b), and cross-section of tubes (c). Magnification of 5200X.

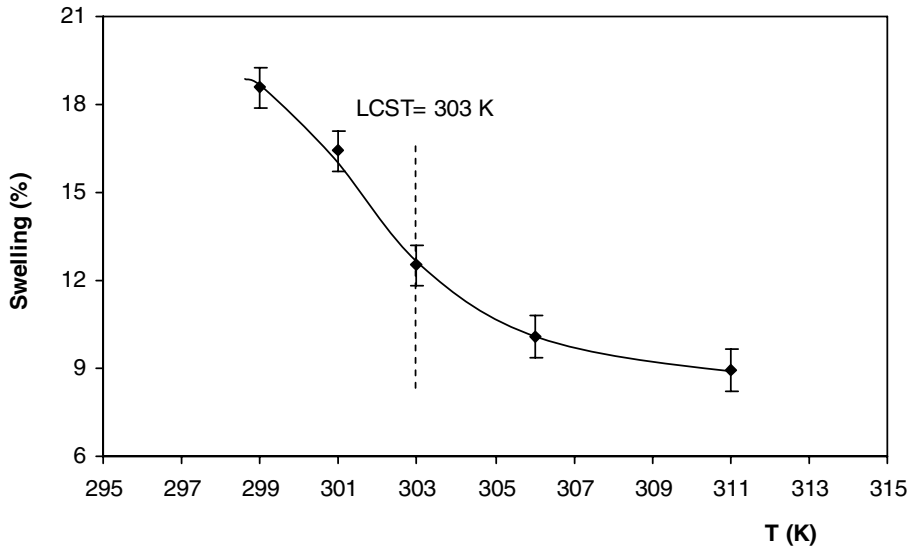


Figure 8. Temperature dependence of the swelling ratio in water as function of temperature for poly(NIPAAm)-grafted PVC tubes 38% graft.

Conclusions

Thermosensitive tubes (PVC-g-NIPAAm) were obtained by pre-irradiation method in air. Factors influencing the degree of grafting such as pre-irradiation dose, dose rate, monomer concentration, reaction time and reaction temperature, were optimized to obtain a maximum grafting degree of 38%, at this grafting percentage, the surface of the tubes were homogeneously covered whit PNIPAAm. The grafted tubes could respond to environmental temperature changes, and present a sharp volume transition around the LCST at 303 K (30°C). Thermosensitivity of these films was 2.23 at grafting of PNIPAAm of 38 %.

Acknowledgements. The authors thank to E. Cervera from FQ-UNAM, F. García, A. Ramírez and S. Castillo-Rojas from ICN-UNAM for technical assistance. We are grateful for the financial support of the Universidad Nacional Autónoma de México, DGAPA (project IN200306) and the Office of Naval Research, USA.

References

1. Dumitrascua N., Balaub T., Tasca M., and Popa G. (2000) Materials Chemistry and Physics 65: 339.
2. Sung K., Seung-Yeop K., and Takenori S. (2006) Polymer 47: 3005.
3. Zhang W., Chu P.K., Ji J., Zhang Y., and Jiang Z. Applied Surface Science, In Press.
4. Inoue K., Kawaguchi M., Yamanaka R., Higuchi T., Ito R., Saito K., and Nakazawa H. (2005) Clinica Chimica Acta 358: 159.
5. Rhodes N.P., Kumary T.V., and Williams D.F. (1996) Biomaterials 17:1995.
6. Mao C., Zhao W. B., Zhu A. P., Shen J., and Lin S. C. (2004) Process Biochemistry 39: 1151.
7. Nomura S., Lundberg F., Stollenwerk M., Nakamura K., and Ljungh A. (1997) J. Biomed. Mater. Res.(Appl. Biomater.) 38:35.
8. Shtanko N. I., Kabanov V. Y., Apel P.Y., Yoshida M., Vilenskii A. I. (2000) Journal of Membrane Science 179: 155.
9. Trong-Ming D., Hann-Ru C. (2005) Carbohydrate Polymers 61: 334.
10. Gümüşderelioğlu M., Topal I. U. (2005) Radiat. Phys. and Chem. 73: 272.
11. Mazzei R., Smolko E., Tadey D., Gizzi L. (2000) Nucl. Inst. and Meth in Phys Research B 170: 419.
12. Chia-Lung L., Wen-Yen C., Chia-Fen L. (2005) Polymer 46: 10092.
13. Chapiro A. (1962) Radiation Chemistry of PolymericSystems. Inc. New York.
14. Wilson J. E. (1974) Radiation Chemistry of Monomers, Polymers, and Plastics. Marcel Dekker, Inc. New York.
15. Mayer J., Szadkowska-NiczeM. (2006) Journal of Photochemistry and Photobiology A: Chemistry 177: 185.