Effects of a Radiation Crosslinking on a Drawn Microporous HDPE Film with a Nucleating Agent

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Abstract: The effects of crystallinity and radiation crosslinking on the physical properties of a microporous high density polyethylene (HDPE) film with Millad3988 as a nucleating agent were investigated. The pores of the HDPE film were affected by the crystallinity. The crystallinity of the HDPE films increased with increasing Millad3988 amount up to 0.1 wt% but decreased with further addition. The mechanical characteristics of the HDPE containing Millad3988 films improved with increasing irradiation dose up to 50 kGy, but decreased at 75 kGy due to severe degradation. The thermal shrinkage behavior of the HDPE films decreased with increasing radiation dose up to 50 kGy. The porosity of the stretched HDPE/Millad3988 films after γ-ray radiation increased with increasing γ-ray radiation dose up to 50 kGy. The pores of the irradiated films were formed more easily by a stretching due to the formation of a crosslinked structure.

Keywords: microporous polyethylene, thermal-mechanical properties, porosity.

Introduction

A microporous polymer film is required to permeate high ions and be thermally stable and mechanically strong during an assembly operation.[1,2] Also, the crystalline structure of the polymer is important to facilitate the formation of micropores in the stretching step because the stacked lamellas are able to open during the stretching process.[2,3] Polyethylene (PE) is one of the most important thermoplastics due to its abundant supply, low cost, good mechanical properties and resistance to chemicals and harsh environments. Generally, the mechanical properties of PE such as its tensile strength, and storage modulus increase with a density increase.[4,5] High density polyethylene (HDPE) has a very high strength due to its highly crystalline structure.[6] Nucleating agents increase the number of nucleation sites, resulting in an increase in the overall crystallization rate and a decrease in the spherulite size.[7] Both the number and the size of the nucleation sites may affect the crystallization process. Molecular interactions between the polymer and the surface of a nucleating agent must match so as to increase the crystallization rate.[8-11] Also, the mechanical properties and thermal stability of PE can be improved by a crosslinking.[4,12] The crosslinking of PE has been achieved by several methods such as an irradiation, peroxides and a silane crosslinking.[13-15] In this study, we have investigated the role of a nucleating agent and a γ-ray irradiation on the crystallinity and thermal-mechanical properties of a stretched HDPE film. The mechanical properties of the stretched HDPE film were investigated using a dynamic mechanical thermal analysis and a tensile strength. Also, the effect of a γ-ray irradiation on the thermal shrinkable characteristic of the stretched HDPE film was examined. The porosity of the stretched HDPE film as a function of the stretching method was measured with a mercury porosimeter.

Experimental

Materials. A commercial grade of high density polyethylene (HDPE 5200BH) was used throughout this study and was supplied by Honam Petrochemical Corporation (Daejon, Korea). HDPE has a density of 0.964 g/cm^3 and a melting index of 0.35 g/10 min. Nucleating agent Millad3988 was purchased from Milliken Chemical. The structural formula of nucleating agents Millad3988 is shown in Figure 1. Dimethylformamide (DMF) was used as the solvent and supplied by SHOWA Chemical Corporation (Tokyo, Japan).

Sample Preparation. The nucleating agent, Millad3988 was dissolved in DMF and then used to coat the surface of HDPE pellets, which were dried at 80 °C under a vacuum for 24 h. The HDPE pellets coated with Millad3988 were mixed in the extruder (Brabender D-47055). The temperatures of the three zones of the extruder were 190, 220 and 230 °C,

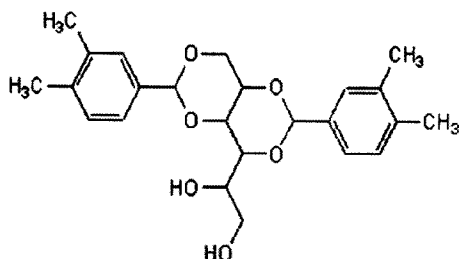*Corresponding Author. E-mail: ycnho@kaeri.re.kr

Figure 1. Chemical formula of the nucleating agent (Millad 3988).

Table I. Preparation Conditions for the HDPE Film with Nucleating Agent (Millad3988)

Sample Name	Amounts of Nucleating Agent (wt%)	Radiation Dose (kGy)
PE-0	0	
PE-01	0.01	
PE-05	0.05	0
PE-10	0.1	
25PE-05	0.05	25
50PE-0	0	
50PE-01	0.01	
50PE-05	0.05	50
50PE-10	0.10	

respectively and the temperature of the die was 100 °C. The screw speed of the extruder was adjusted to 50 rpm. The polymer resins were melt-extruded and uni-axially drawn by roller to obtain the precursor films. Thermal ageing treatment of the HDPE/Millad3988 film was conducted to increase the crystallinity of HDPE in an oven at 125 °C in air for 40 min.[12] The HDPE/Millad3988 films were irradiated by γ-rays to a total dose of 25, 50 and 75 kGy at a dose rate of 5 kGy/h at room temperature. The HDPE/Millad3988 films were uni-axially stretched up to 600% in a heating chamber at 100 °C with a speed rate of 10.8 cm/sec for the formation of pores and then they were slowly cooled at room temperature. The size of the HDPE film was 6×7 cm. The mixing formulations are shown in Table I.

Measurements of the Samples. The crystallinity of the samples was measured by differential scanning calorimetry (DSC, DSCQ100 TA Instrument Company). Heating runs were conducted from 30 to 180 °C at a rate of 10 °C/min in nitrogen. The degree of crystallinity (X_c) can be calculated by the following equation.

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \qquad (1)$$

Where $\Delta H_m^o=290$ J/g is the fusion enthalpy for a totally crystalline polymer and ΔH_m is the fusion enthalpy calcu-

lated from the area of the endothermic melting peak. X-ray diffractometry (XRD; D-MAX-IIIB X-ray diffractometer, Rigaku) in the range $2\theta=5-35°$, was used for a comparison of the crystalline peak of the samples. The dynamic mechanical properties were investigated with a DMA (DMA; DMA Q800, TA Instrument Company), which was varied from 30 to 150 °C at 1 Hz at a heating rate of 5 °C/min. The tensile strength was measured with an Instron443 at room temperature. The size of the specimens was 5×20 mm, the thickness was about 0.02 mm, and the head speed was 10 mm/min. Tensile strength was tested for each sample at least five times. Thermal shrinkage tests of the samples were conducted in an oven at 130 °C for 60 min in air. The percentage of shrinkage (S_h) can be calculated by the following equation.

$$S_h(\%) = \frac{(A_o-A_a)}{A_o} \times 100 \qquad (2)$$

Where A_o is the original area of the samples before a heating and A_a is the area of the samples after heating. The porosity of the samples was measured with a mercury porosimeter (Autopore IV 9500, Micromeritics). In the case of the porosity, at least three specimens were tested from each sample. The morphological changes of the samples were observed using a scanning electron microscope (SEM, JSM6390 JEOL Company). Specimen surfaces were coated with a thin layer of gold palladium alloy by sputtering to provide a conductive surface.

Results and Discussion

Figure 2 shows the crystallinity of the HDPE films with increasing amounts of Millad3988. The crystallinity of the HDPE films increased with the amounts of Millad3988 but decreased above the addition of 0.1 wt% of Millad3988 as shown in Figure 2. The temperature dependencies of the
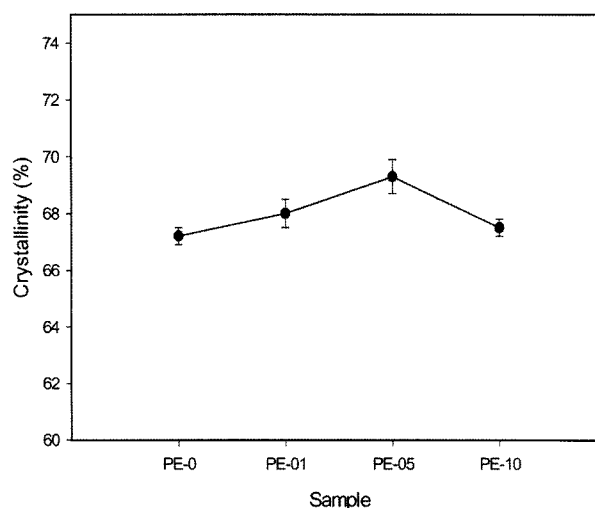

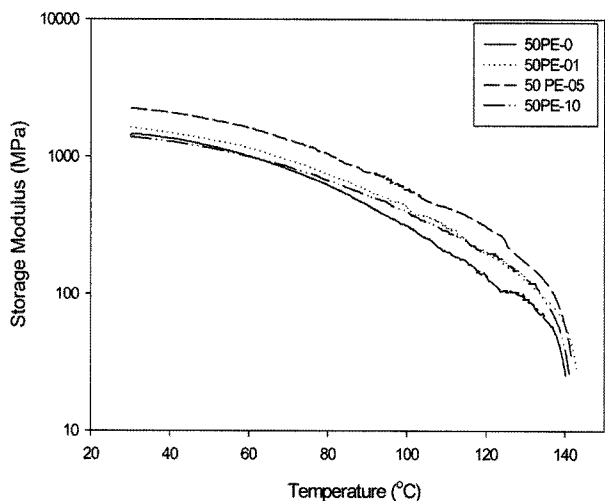**Figure 2.** The crystallinity of the HDPE films as a function of Millad3988.

Figure 3. The storage modulus of the irradiated HDPE films as a function of Millad3988; the irradiation dose is 50 kGy.

Figure 5. The XRD analysis of the HDPE containing Millad3988 (0.05 wt%) films as a function of γ-ray radiation dose.

storage modulus for the irradiated HDPE films with increasing amounts of Millad3988 are shown in Figure 3. The storage modulus of the irradiated HDPE film increased with the amounts of Millad3988 but decreased above the addition of 0.1 wt% of Millad3988 as shown in Figure 3. This result is very similar to the crystallinity trend of Figure 2. The probable reason for these results is that proper nucleating agent content may maintain the formation ability of the crystal nucleus and the rate of the crystallization of the polymer due to the molecular interactions between the polymer and the surface of a nucleating agent.[11]

The temperature dependencies of the storage modulus for HDPE/Millad3988 (0.05 wt%) with an increasing radiation dose are shown in Figure 4. Non-irradiated HDPE/Millad3988 film exhibited the lowest storage modulus in this study. By a γ-ray irradiation, there was an increase in the storage modu-
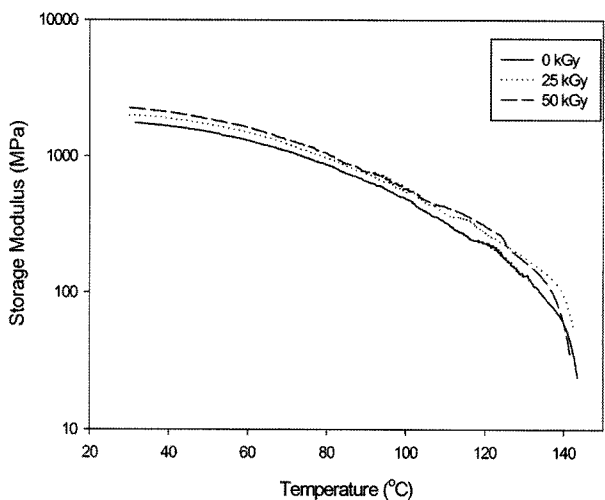
lus of the films. The increase in the storage modulus of the HDPE/Millad3988 films with an increasing γ-ray radiation dose is due to the crosslinking of the polymer.

Figure 5 shows a comparison of the XRD patterns for the irradiated HDPE films and the non-irradiated HDPE films. No changes of the crystalline peaks were observed in the irradiated samples compared with that in the non-irradiated sample. This XRD result indicates that the crystallinity of the polymer was little affected by the crosslinking induced by a γ-ray irradiation. It was reported that a 100% crosslinked part of an irradiated HDPE is composed of an amorphous phase rather than a crystalline phase.[16,17]

A microporous film should be resistant to severe conditions such as a high temperature. For example, the thermal shrinkage rate of a microporous film should be minimized.[1] Thermal shrinkage tests of the samples were conducted in an oven at 130 °C for 60 min in air. Figure 6 shows the ther-

Figure 4. The storage modulus of the HDPE containing Millad3988 (0.05 wt%) with an increasing γ-ray radiation dose.
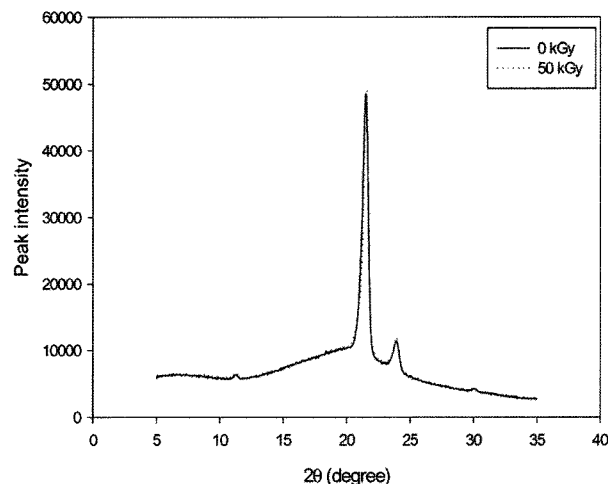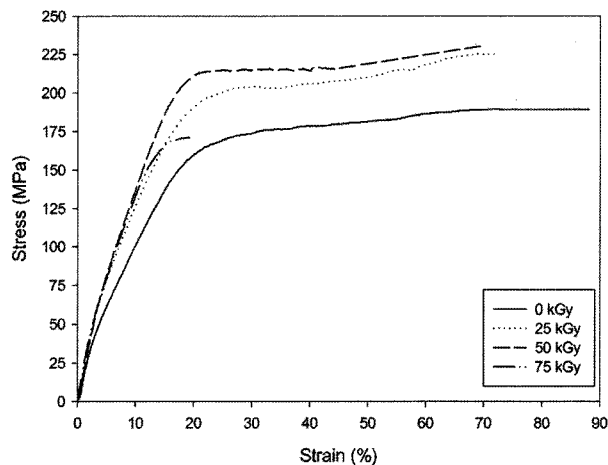

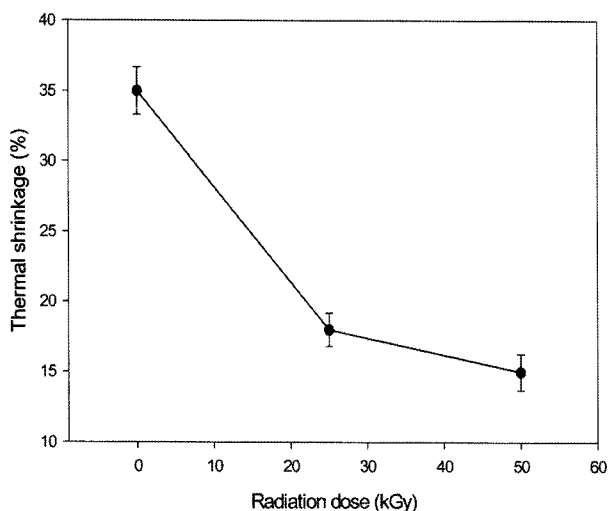**Figure 6.** The strain-stress curves of the HDPE/Millad3988 (0.05 wt%) films with an increasing γ-ray radiation dose.

Figure 7. The thermal shrinkage of the HDPE/Millad 3988 (0.05 wt%) films according to an increasing radiation dose.

Figure 8. The porosity of the HDPE/Millad3988 films as a function of the nucleating agents with an increasing γ-ray radiation dose.

mal shrinkage rate of the HDPE/Millad3988 (0.05 wt%) films according to an increasing γ-ray radiation dose. The shrinkage behavior decreased with an increasing radiation dose.

Figure 7 represents the stress versus strain curves of the HDPE/Millad3988 (0.05 wt%) film with an increasing γ-ray radiation. The maximum strength of the HDPE/Millad3988 (0.05 wt%) film increased with an irradiation dose up to 50 kGy. When the radiation dose is 50 kGy, the maximum strength of the film is about 225 MPa. Also, Young's modulus of the HDPE/Millad3988 (0.05 wt%) film had the same trend as the maximum strength. On the other hand, the strain at a break of the HDPE/Millad3988 (0.05 wt%) film was decreased with an increasing γ-ray radiation. However, the maximum strength of the film irradiated at 75 kGy had the lowest value and the strain at a break was only 20%. This result showed that the film irradiated at 75 kGy was degraded due to the high radiation dose. As shown in Figure 7, the high doses of irradiation induce a severe degradation rather than a crosslinking of the materials. However, the optimum dose of an irradiation induces a further crosslinking of the materials and improves the thermal and mechanical characteristics of the materials.

The porosity is expressed by the percent share of pores in a sample volume. A mercury porosimetry was used in this study. The porosity of the HDPE/ Millad3988 films as a function of the nucleating agent with an increasing γ-ray radiation dose is shown in Figure 8. The HDPE/Millad3988 films were irradiated by γ-rays to a total dose of 25 kGy and 50 kGy at a dose rate of 5 kGy/h at room temperature and then uni-axially stretched up to 600%. The porosity of the stretched HDPE/Millad3988 films increased with increasing amounts of the nucleating agent but decreased above the addition of 0.1 wt% of the nucleating agent. This result is very similar to the crystallinity trend of Figure 2. From this
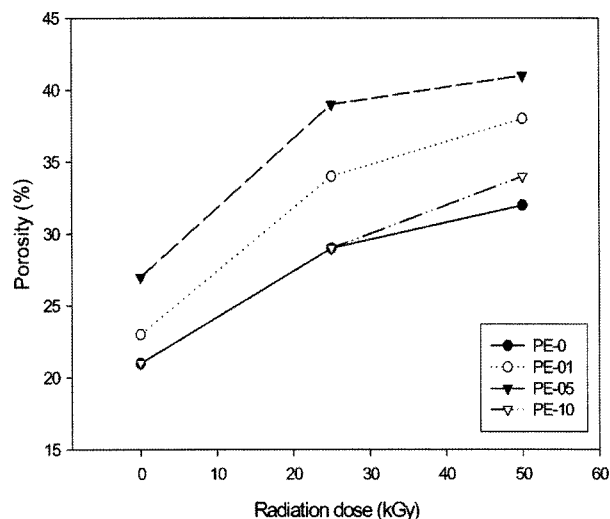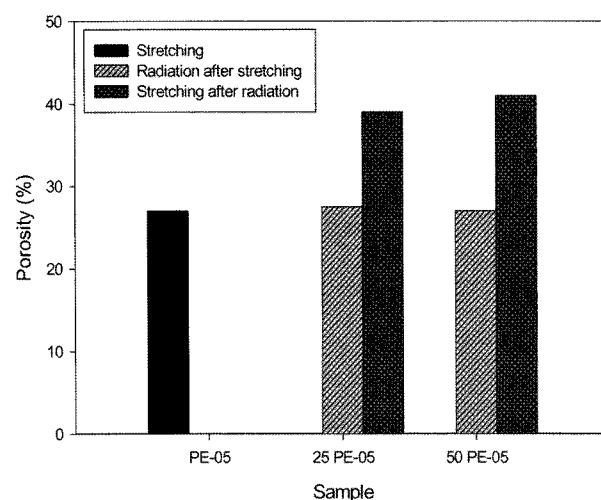

Figure 9. Comparison of the porosity by the stretching method.

result, it is found that the porosity of the films is directly related to the crystallinity of the polymer because a pore can be formed easily due to the lamellar structures. Also, the porosity of the HDPE/Millad3988 films increased with an increasing γ-ray radiation dose.

Figure 9 shows the porosity of the HDPE/Millad3988 (0.05 wt%) films when the HDPE/Millad3988 films were irradiated by γ-rays after a uni-axial stretching, and were uni-axially stretched after a γ-ray radiation. The porosity of the stretched HDPE/Millad3988 films after a γ-rays radiation is higher than that of the irradiated HDPE/Millad3988 films after a stretching. The porosity of the stretched HDPE/ Millad3988 films after a γ-rays radiation increased with an increasing γ-ray radiation dose, but the porosity of the irradiated HDPE/Millad3988 films after a stretching was not really changed with an increasing γ-ray radiation dose. Figure 10 shows the SEM micrographs of the surface of 50PE-05
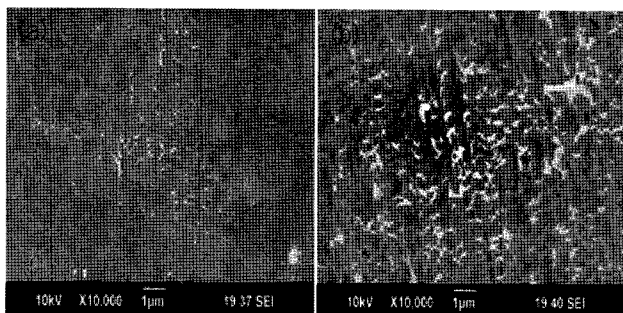
Figure 10. SEM micrographs of the surface of 50PE-05 by the stretching method: (a) radiation after stretching; (b) stretching after radiation.

by the stretching method. It is clearly observed that the pores are more uniformly distributed for the stretched 50PE-05 after a γ-rays radiation and less uniform for the irradiated 50PE-05 after a stretching. Also, the pore volume of the stretched 50PE-05 after a γ-rays radiation was larger than that of the irradiated 50PE-05 after a stretching. As shown in Figure 8, Figure 9 and Figure 10, it can be seen that the porosity and pore distribution of the stretched HDPE films are associated with a crossinking of the materials caused by a γ-ray radiation. The probable reason for these results is that the pores of the irradiated films could be formed easily by a stretching due to a crosslinked structure.

Conclusions

A microporous polymer film is required to permeate high ions and be thermally stable and mechanically strong. The purposes of this paper were to study the role of a nucleating agent and a γ-ray irradiation on the crystallinity and thermal-mechanical properties of a microporous HDPE film. The crystallinity of the HDPE films were increased with the amounts of Millad3988 but decreased above the addition of 0.1 wt% of Millad3988. Also, the porosity of the stretched HDPE/Millad3988 films was very similar to the crystallinity trend. The thermal shrinkage behavior decreased with an increasing radiation dose up to 50 kGy. The mechanical characteristics of the HDPE containing Millad3988 films improved with an irradiation dose up to 50 kGy. However, the maximum strength of the membrane irradiated at 75 kGy had the lowest value and its strain at a break was only 20%. The high doses of irradiation induced severe degradation

rather than a crosslinking of the materials. However, the optimum dose of an irradiation induced a further crosslinking of the materials. The porosity and pore distribution of the stretched HDPE films after a γ-rays radiation were higher than that of the irradiated HDPE/Millad3988 films after a stretching due to a crosslinked structure.

References

(1) D. W. Ihm, J. G. Noh, and J. Y. Kim, *J. Power Sources*, **109**, 388 (2002).

(2) S. S. Zhang, *J. Power Sources*, **164**, 351 (2007).

(3) H. S. Park, J. H. Lee, J. D. Nam, S. J. Seo, Y. K. Lee, Y. S. Oh, and H. C. Jung, *Macromol. Res.*, **14**, 430 (2006).

(4) H. S. Yang, K. Park, J. S. Son, J. J. Kim, D. K. Han, B. W. Park, and S. H. Baek, *Macromol. Res.*, **15**, 256 (2007).

(5) S. Kim, K. Cahr, J. Hahn, J. K. Lee, D. Y. Yoon, H. W. Rhee, and M. Y. Jin, *Macromol. Res.*, **15**, 1 (2007).

(6) A. A. Min, T. G. Chuah, and T. R. Chantara, *Mater. Design*, **29**, 992 (2008).

(7) H. D. Keith, F. J. Padden, and R. G. Vadimsky, *J. Polym. Sci. Part A2-4: Polym. Phys.*, **4**, 267 (1966).

(8) J. C. Wittmann and B. Lotz, *Prog. Polym. Sci.*, **15**, 909 (1990).

(9) B. J. Chisholm, P. M. Fong, J. G. Zimmer, and R. J. Hendrix, *Appl. Polym. Sci.*, **74**, 889 (1999).

(10) J. P. Mercier, *Polym. Eng. Sci.*, **30**, 270 (1990).

(11) B. Li, G. H. Hu, G. P. Cao, T. Liu, L. Zhao, and W. K. Yuan, *J. Supercritical Fluids*, **44**, 446 (2008).

(12) C. S. Lee, S. H. Yoo, J. Y. Jho, K. Choi, and T. W. Hwang, *Macromol. Res.*, **12**, 112 (2004).

(13) H. A. Khonakdar, J. U. Morshedian, U. Wagenknecht, and S. H. Jafari, *Polymer*, **44**, 4301 (2003).

(14) D. S. Kim, M. D. Guiver, M. Y. Seo, H. I. Cho, D. H. Kim, J. W. Rhim, G. Y. Moon, and S. Y. Nam, *Macromol. Res.*, **15**, 412 (2007).

(15) D. K. Lee, J. T. Park, J. K. Choi, D. K. Roh, J. H. Lee, Y. G. Shul, and J. H. Kim, *Macromol. Res.*, **16**, 549 (2008).

(16) S. O. Han, D. W. Lee, and O. H. Han, *Polym. Degrad. Stabil.*, **63**, 237 (1999).

(17) S. M. Lee, H. J. Jeon, S.W. Choi, H. H. Song, Y. C. Nho, and K. Cho, *Macromol. Res.*, **14**, 640 (2006).