Fibers and Polymers 2006, Vol.7, No.4, 328-332

Thermomechanical Properties and Shape Memory Effect of PET-PEG Copolymers Cross-linked with Pentaerythritol

Yong Shik Shim, Byoung Chul Chun*, and Yong-Chan Chung[1]

Department of Polymer Engineering, The University of Suwon, Kyunggi-do 445-743, Intelligent Textile System Research Center, Seoul National University, Seoul 151-742, Korea
[1]Department of Chemistry, The University of Suwon, Kyunggi-do 445-743, Korea
(Received November 2, 2006; Revised November 30, 2006; Accepted November 30, 2006)

Abstract: Poly(ethylene terephthalate) (PET) and poly(ethylene glycol) (PEG) copolymers cross-linked with pentaerythritol, a four-way cross-linker, are prepared to compare their mechanical and shape memory properties with the one cross-linked by glycerol. Composition of PEG and pentaerythritol is varied to search for the one with the best mechanical and shape memory properties. The highest shape recovery rate is observed for the copolymer composed of 30 mol% PEG-200 and 2.5 mol% pentaerythritol. Four-way cross-linking by pentaerythritol significantly improves shape recovery rate and retention of high shape recovery rate after repeated use compared to the one cross-linked by glycerol, a three-way cross-linker, and difference and advantage of additional cross-linking point are discussed.

Keywords: Shape memory, Cross-linking, Shape recovery, Shape retention, Pentaerythritol

Introduction

Smart material is known to respond to change in surrounding and widely researched in such areas as shape memory alloy, semiconductor, polymer, and medical supply. Shape memory material, one of smart material, can detect thermal, mechanical, electrical, or magnetic stimulus, and respond via property changes in shape, location, modulus, damping, and abrasion, together with shape memory and shape retention [1-3]. Shape memory polymer (SMP), being advantageous over other materials in the points of lightness, high shape recovery, easy processing, and high damping, is used in the development of composite laminate with vibration control ability [4-8]. SMPs developed by us have a phase-separated structure in which hard and soft domain is formed due to the difference in intermolecular attraction between hard and soft segment. Hydrogen bonding, together with dipole-dipole interaction, binds hard segments to form hard domain, and hard domain plays an important role in shape recovery. Flexible soft segment absorbs external stress, and keeps the polymer resilient at low temperature. In this study, poly(ethyleneterephthalate) (PET)/polyethyleneglycol (PEG) copolymer is cross-linked with pentaerythritol, a four-way cross-linker, and the effect of additional cross-linking point compared to glycerol, a three-way cross-linker, on mechanical, and shape memory properties is investigated.

Experimental

Materials

Dimethylterephthalate (DMT), PEG, and pentaerythritol were obtained from Aldrich chemical. Ethyleneglycol (EG) was from Duksan Chemical. Calcium acetate and antimony oxide (Hayashi Pure Chemical) were used as the catalyst for esterification, and phosphorous aicd (Kanto Chemical) was added as stabilizer.

Preparation of Cross-linked Copolymer

PET-PEG copolymer was synthesized by melt-condensation method with a custom made reactor [9,10]. Polymerization was carried out in two steps; oligomer was prepared in the first step with DMT, EG, and PEG-200, and the oligomer from the first step was condensed and cross-linked with pentaerythritol in the second step at high temperature and vacuum to shift reaction equilibrium further to product. Detailed synthetic procedure for PET-PEG copolymer can be found in our previous papers [9,10]. Synthetic scheme and characterization of copolymers are shown in the results and discussion section.

Intrinsic Viscosity

Intrinsic viscosity [η] of copolymer dissolved in 1,1,2,2-tetrachloroethane/phenol (4/6, w/w) mixture was measured with Ubbelohde viscometer at 35 °C and 0.5 g/d*l* of concentration.

Thermal Analysis

T_g and T_m were measured by differential scanning calorimeter (DSC, Perkin Elmer Diamond 6). Specimen was heated to 200 °C at 10 °C/min of heating rate, and kept at that temperature for 3 min, and then cooled to −30 °C at 10 °C/min. T_g and T_m were determined from the second heating scan. Dynamic mechanical property was measured by a dynamic mechanical analyzer (DMA-2980, TA instrument), where storage modulus and loss tangent (tanδ) were scanned between −20 °C and 110 °C at the heating rate of 3 °C/min, and 1 Hz.

*Corresponding author: bcchun@suwon.ac.kr

Mechanical Properties and Shape Memory Analysis

Tensile test was performed by universal testing machine (UTM, Lloyd LR 50K) using dumbbell-type specimen prepared according to ASTM D-638 at a crosshead speed of 100 mm/min. Shape memory effect was also checked by tensile test using UTM equipped with temperature-controlled thermal cabinet. For the measurement of shape retention rate, specimen with a length L_0 was strained to 100 % at above T_g but below T_m, and kept at that temperature for 1 min. Specimen under strain was cooled to below T_g, and left at the temperature for 30 min after removal of load, followed by the measurement of deformed length (L_1). For the measurement of shape recovery rate, specimen was heated to the temperature above T_g but below T_m with 10 min stay at the temperature, and cooled back to the temperature below T_g, and the final length (L_2) of specimen after 30 minute of stay at the low temperature was measured (Figure 2). The whole procedure was repeated 3 times consecutively. Shape retention and shape recovery rates can be calculated by the following equation [9,10].

$$\text{Shape retention rate} = (L_1 - L_o) \times 100/L_o \ (\%)$$
$$\text{Shape recovery rate} = (2L_o - L_2) \times 100/L_o \ (\%)$$

Results and Discussion

Thermal Analysis

Glass transition temperature (T_g) of copolymers with different PEG chain length and PEG-200 content is compared in Table 1. All of copolymers in Table 1 contain 2.5 mol% pentaerythritol. Copolymers with PEG-400-25 or PEG-600-25 have too low T_g value to be used as a shape memory polymer, because T_g around room temperature is required for practical application, based on the results from the previous experiments [9,10]. Therefore, PEG-200 is selected and PEG-200 content is changed from 15 mol% to 40 mol% to search for the right T_g range. Although E200-20-25 and E200-25-25 show T_g close to room temperature, strain at break, an important factor in shape memory test, is a little lower than other candidates: E200-20-25 and E200-25-25 are set aside as the SMP candidate. E200-40-25 is excluded due to the low T_g. Now, it is reasonable to select E200-30-25 as the SMP candidate, because it has a good strain and relatively high T_g. After selecting E200-30-25 as the right PEG-200 composition, pentaerythritol content is varied from 0.5 mol% to 3.0 mol% (Table 2 and Figure 3). T_g increases with pentaerythritol content, starting from −5.3 °C of E200-30-05 (0.5 mol%) to 12.3 °C of E200-30-30 (3.0 mol%). E200-30 without or with 0.5 or 1.0 mol% pentaerythritol is not appropriate for SMP because T_g is below 0 °C. E200-30 with 1.5 or 2.0 mol% pentaerythritol also shows very low T_g as a SMP. E200-30 with 2.5 or 3.0 mol% pentaerythritol shows almost same T_g and enough strain for shape memory test. Pentaerythritol content is not raised more than 3.0 mol% due to the hardening of copolymer. The fact that pentaerythritol raises T_g and decreases strain suggests that a compromise between T_g and strain should be made in deciding the SMP candidate. Melting temperature (T_m) of E200-30 series also increases with pentaerythritol content in Figure 4, and T_m of E200-30-25 and E200-30-30 stays around 150 °C. T_g of E200-30-25

Table 1. Physical properties of PET-PEG copolymers cross-linked by 2.5 mol% pentaerythritol

Sample code	[a]PEG (mol%)	Max. stress (N/mm^2)	Strain at break (%)	T_g(°C)	T_m(°C)	[η], dl/g
E400-20-25	20	–	–	−23.5	173.0	0.60
E600-20-25	20	–	–	−33.2	156.8	0.57
E200-15-25	15	19.6	48	33.5	213.5	0.62
E200-20-25	20	14.3	164	29.8	198.1	0.55
E200-25-25	25	13.7	201	27.7	169.4	0.60
E200-30-25	30	1.1	493	12.1	151.7	0.26
E200-40-25	40	0.1	2850	−8.3	145.3	0.41

[a]MW of PEG (200, 400, or 600) is denoted in sample code. 2.5 mol% of pentaerythritol is included for all of the copolymers.

Table 2. Physical properties of E200-30 PET-PEG copolymers cross-linked by variable pentaerythritol content

Sample code	[a]Penta. content (mol%)	Max. stress (N/mm^2)	Strain at break (%)	T_g(°C)	T_m(°C)	[η], dl/g
E200-30-00	0	0.263	3000	−6.2	138.4	0.39
E200-30-05	0.5	0.475	2110	−5.3	141.1	0.45
E200-30-10	1.0	0.751	1559	−3.6	143.6	0.44
E200-30-15	1.5	1.050	739	2.8	145.2	0.37
E200-30-20	2.0	1.057	559	3.7	151.8	0.28
E200-30-25	2.5	1.092	493	12.1	151.7	0.26
E200-30-30	3.0	1.841	380	12.3	156.0	0.69

[a]Pentaerythritol content.

decreases by about 10 °C compared with the previous PET-PEG copolymer with 2.5 mol% glycerol and 20 mol% PEG (T_g of 23.7 °C) [10].

Tensile Property

Synthesis of copolymers and the proposed cross-liked structure is shown Figure 1. Tensile mechanical properties of cross-linked copolymers (2.5 mol% pentaerythritol) with PEG 200, 400, or 600 are shown in Table 1. Copolymers with PEG-400 or 600 easily break down during tensile test, but copolymers with PEG-200 show good stress and strain results. As PEG content is raised, strain at break increases

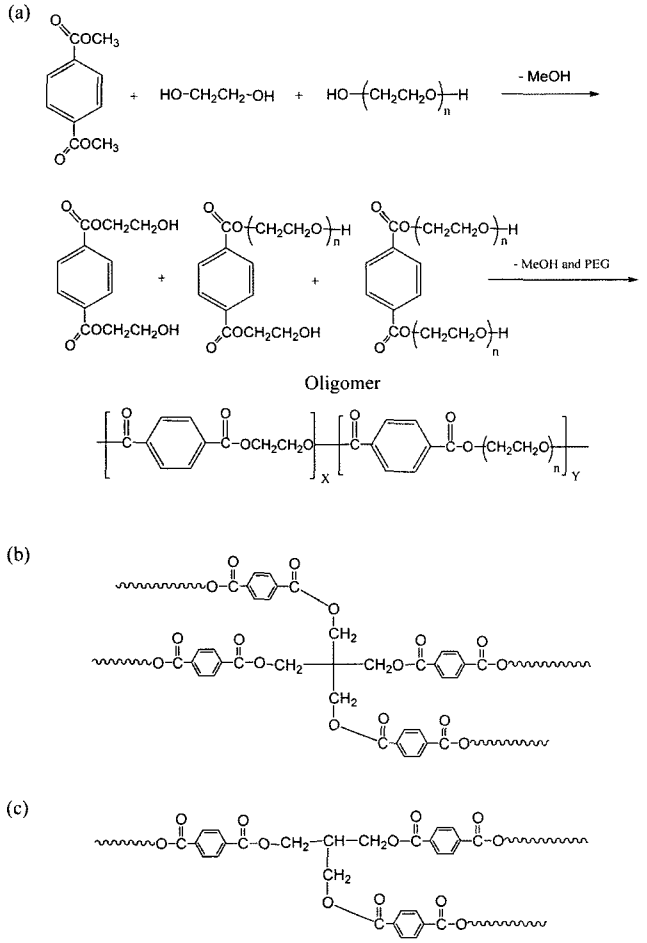

Figure 1. (a) synthetic scheme, (b) pentaerythritol cross-linked structure, and (c) glycerol cross-linked structure.

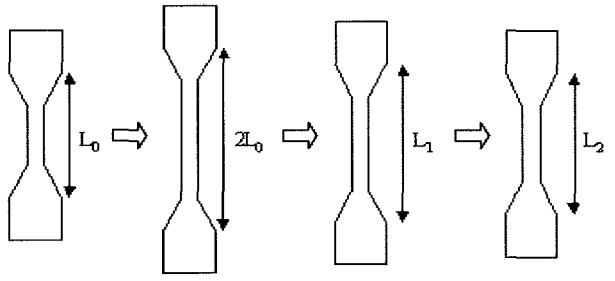

Figure 2. Specimen and method for shape memory test: L_0=initial specimen length, $2L_0$=length of L_0 strained 100 % above T_g, L_1=deformed length below T_g after load removal, and L_2=final specimen length after shape recovery above T_g (L_2 was measured below T_g to freeze the length).

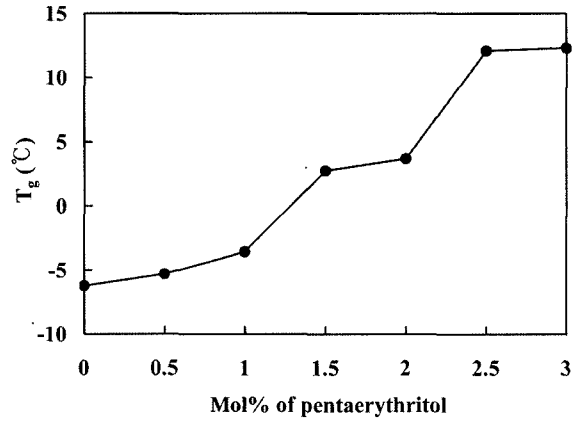

Figure 3. Glass transition temperature vs. pentaerythritol content profile.

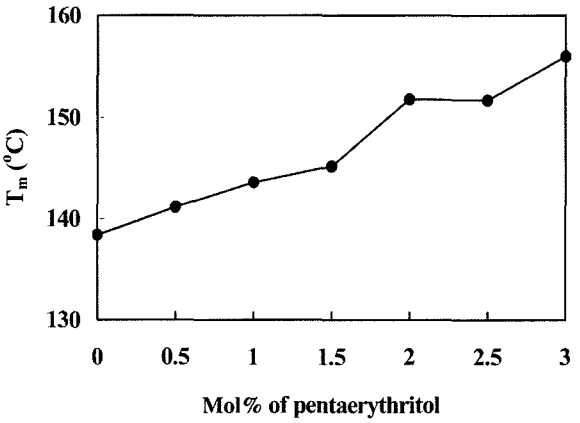

Figure 4. Melting temperature vs. pentaerythritol content profile.

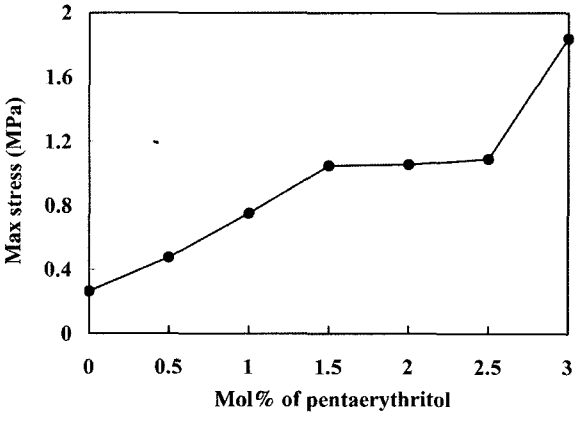

Figure 5. Max. stress vs. pentaerythritol content profile.

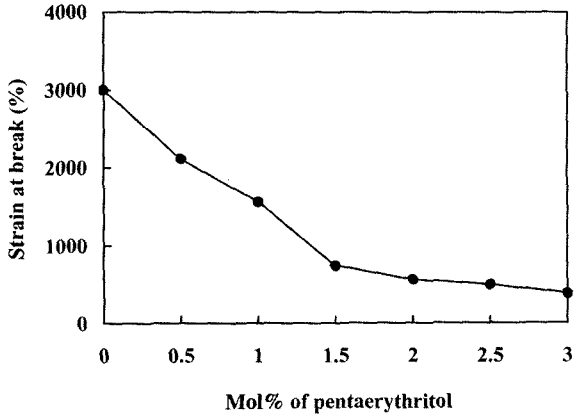

Figure 6. Strain at break vs. pentaerythritol content profile.

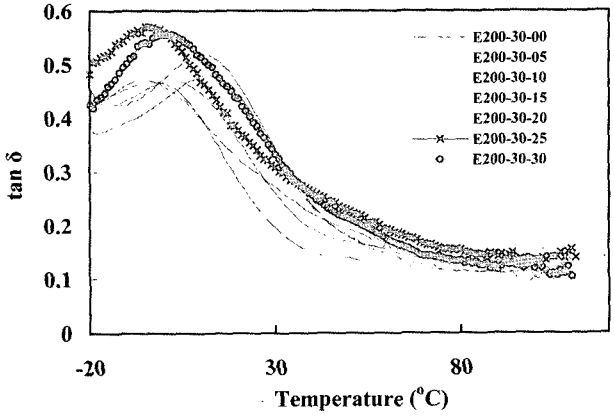

Figure 8. Loss tangent vs. pentaerythritol content profile.

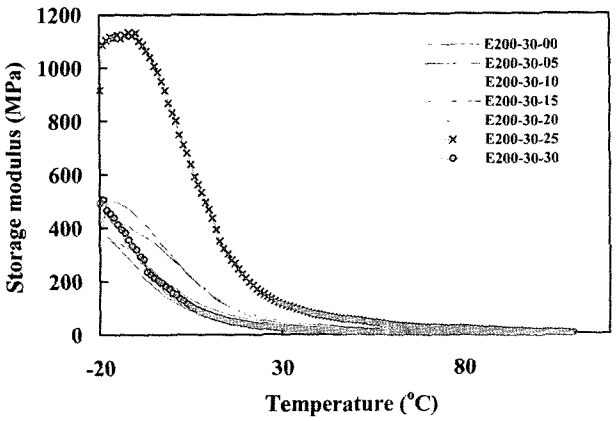

Figure 7. Storage modulus vs. pentaerythritol content profile.

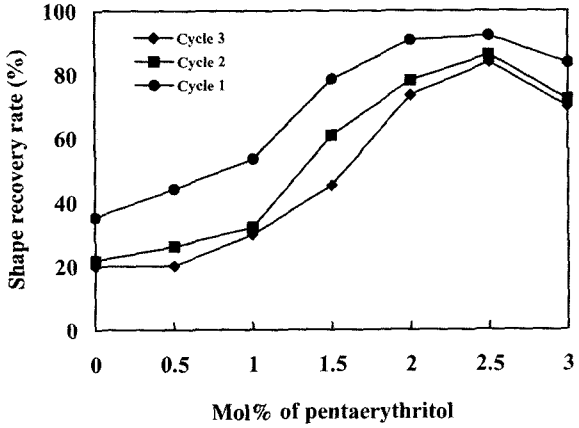

Figure 9. Comparison of shape memory effect of copolymers.

from 48 % (15 mol% PEG) to 2850 % (40 mol%). Instead, maximum stress decreases with the increase of PEG content: maximum stress decreases from 19.6 N/mm^2 (15 mol% PEG) to 0.1 N/mm^2 (40 mol% PEG). As mentioned in thermal analysis section, E200-30 is selected and pentaerythritol content is varied at 30 mol% of PEG-200. Maximum stress gradually increases with pentaerythritol content and reaches the highest one at 3.0 mol% (Figure 5). Strain at break decreases with pentaerythritol content, showing 2110 % at 0.5 mol% pentaerythritol and 493 % at 2.5 mol% pentaerythritol (Figure 6). However, strain at break has improved significantly compared with 48 % of the glycerol cross-linked PET-PEG copolymer (2.5 mol% glycerol and 20 mol% PEG) [10].

Dynamic Mechanical Property

Storage modulus and tanδ of copolymers are compared in Figure 7 and 8. In Figure 7, storage modulus of E200-30-25 is in high contrast with other E200-30 series; the peak storage modulus of E200-30-25 is about 3 times higher than other E200-30 series. The high cross-linking content of E200-30-25 increases storage modulus below glass transition temperature. In Figure 8, tanδ changed around glass transition temperature for all of E200-30 series copolymers. Because tanδ indicates damping ability, the E200-30 series copolymers can be used as vibration-control material.

Shape Memory Effect

Shape retention rate of the copolymers generally maintains above 90 % of the original shape, but shape recovery rate is dependent on pentaerythritol content. In Figure 9, shape memory rate does not decrease much after three cyclic shape memory tests and the highest shape memory rate is observed at 2.5 mol% pentaerythritol. Shape recovery rate of PEG-300-25 is 92 % at the first cyclic test and decreases to 86 % (second cycle) and 83 % (third cycle). The decrease of shape recovery rate is due to the distortion of hard segment interaction after repeated stretch and shrinkage during shape memory test. Previously, we reported about the shape recovery rate of PET copolymer cross-linked by glycerol [10]. Shape recovery rate of copolymer cross-linked by glycerol, in the best case, is 85 % at the first cycle, 82 % at the second cycle, and immeasurable after the third cycle due to break down of copolymer. Comparing the two types of cross-linked copolymers, E200-30-25 improves shape recovery rate, and survives the

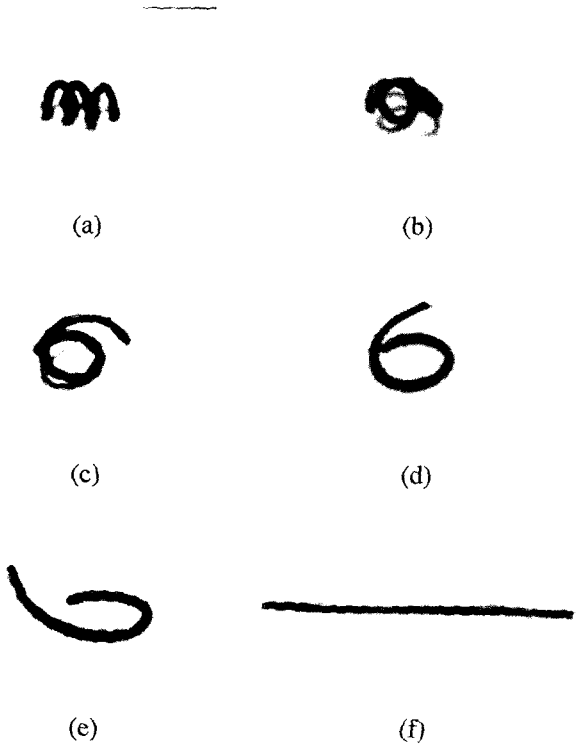

Figure 10. Shape recovery process of the coiled PET-PEG copolymer cross-linked by 2.5 mol% pentaerythritol after (a) 0 s, (b) 5 s, (c) 9 s, (d) 15 s, (e) 20 s, and (f) 30 s.

three test cycle. Extra cross-linking site of pentaerythritol compared to glycerol is responsible for higher shape recovery rate. Although shape recovery rate is satisfactory at this stage, it should stay above 90 % after the third cycle to be useful as a structural material. Lastly, real image of shape recovery process of the coiled copolymer (E200-30-25) is shown in Figure 10, where a linear copolymer is coiled at 20 °C below T_g and shape recovery to original linear shape is done in 30 seconds at room temperature.

Conclusion

Shape memory PET-PEG copolymers cross-linked by pentaerythritol are prepared to test the cross-linker effect on shape memory and mechanical properties. PEG-200 is selected as soft segment due to higher mechanical properties than PEG-400 and PEG-600, and the cross-linker content is controlled at 2.5 mol% that shows the best shape recovery rate. Shape recovery rate of E200-30-25 is 92 % at the first cycle and decreases to 83 % after the third cycle. The four way cross-linking by pentaerythritol significantly improves shape recovery rate, compared to the three way cross-linking glycerol, and extra cross-linking by pentaerythritol is responsible for the improvement.

Acknowledgements

Authors of this paper would like to thank the Korea Science and Engineering Foundation (KOSEF) for sponsoring this research through the SRC/ERC Program of MOST/KOSEF (R11-2005-065).

References

1. T. Takahashi, N. Hayashi, and S. Hayashi, *J. Appl. Polym. Sci.*, **60**, 1061 (1996).
2. Z. G. Wei and R. Sandstrom, *J. Material Science*, **33**, 3743 (1998).
3. C. Park, J. Y. Lee, B. C. Chun, Y. C. Chung, J. W. Cho, and B. G. Cho, *J. Appl. Polym. Sci.*, **94**, 308 (2004).
4. J. H. Yang, B. C. Chun, Y. C. Chung, and J. H. Cho, *Polymer*, **44**, 3251 (2003).
5. T. Takagil, *J. Intelligent Material System and Structure*, **1**, 149 (1990).
6. R. J. Riley and G. Wallace, *J. Intelligent Material System and Structure*, **2**, 228 (1991).
7. P. Akella, X. Chen, and W. Cheng, *Smart Materials and Structures*, **3**, 344 (1994).
8. J. W. Cho, Y. C. Jung, S. H. Lee, B. C. Chun, and Y. C. Chung, *Fibers and Polymers*, **4**, 114 (2003).
9. B. C. Chun, S. H. Cha, Y. C. Chung, and J. W. Cho, *J. Appl. Polym. Sci.*, **83**, 27 (2002).
10. B. C. Chun, S. H. Cha, C. Park, M. J. Park, Y. C. Chung, and J. W. Cho, *J. Appl. Polym. Sci.*, **90**, 3141 (2002).