

Thermal and Mechanical Properties of the Polymers Synthesized by the Sequential Polymerization of Propylene and 1-Hexadecene

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ABSTRACT: The block copolymer of poly(1-hexadecene) (PHD) and polypropylene (PP) was effectively synthesized by the sequential polymerization of propylene and 1-hexadecene by using highly isospecific $\text{TiCl}_3/\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ (Cp = cyclopentadienyl). The block copolymers had two separate melting temperatures of constituent blocks. The modulus of PHD-PP block copolymer was enhanced as the content of sequentially polymerized PP block was increased. The elongation at break showed positive deviation at the intermediate compositions from the simple additive values of constituent homopolymers. Shape memory effect which utilizes the crystalline PHD block as a reversible phase and the crystalline PP block as a fixed structure was examined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1709–1715, 2002; DOI 10.1002/app.10551

Key words: polypropylene; block copolymers; thermal properties; mechanical properties

INTRODUCTION

Poly(1-alkenes) are the polymers of a homologous series with regularly spaced side chains of varying length. The properties of these polymers vary dramatically depending on stereo-regularity and the length of the alkyl substituent at the double bond in an 1-alkene molecule.^{1–3} Poly(1-alkenes) with longer linear side chains derive their crystallinity from the side chain rather than from the polymer backbone.^{2–5} They usually have two melting points attributed to the crystallization of side chains of atactic and isotactic poly(1-alk-

enes), respectively. For example, hexane-soluble atactic poly(1-octadecene) has a melting point at 41.5°C and hexane-insoluble isotactic poly(1-octadecene) has a melting point at 68.0°C.⁶ Therefore, if we use a highly isospecific catalyst, the lower melting peak due to atactic polymer can be minimized.⁴

Most poly(1-alkenes) are not mechanically strong solid plastics, so they are commercially used as glues or as a drag reducer of nonpolar organic liquids.² Random copolymerization of 1-alkenes with ethylene or propylene can diversely modify the physical properties of polyethylene (PE) and polypropylene (PP), so much of 1-alkenes are used commercially as comonomers.^{2,7}

It can be anticipated that some mechanical properties of poly(1-alkenes) can be improved by

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Table I Characteristics of the Polymers Used in This Study

Designation	Polymerization Time (min)		Content of Propylene Repeating Unit (wt %)	Polymers Soluble in <i>n</i> -Heptane at 40°C (wt %)	[η] (dL/g)
	First Stage	Second Stage			
PHD	—	240	0	100	2.02
C16PP11	5	180	10.8	21	1.33
C16PP19	15	180	18.6	27	1.34
C16PP32	30	180	32.5	30	1.58
C16PP47	60	180	46.9	22	2.00
C16PP59	90	180	59.2	7	1.81
PP	240	—	100	0	1.43

the sequentially polymerized crystalline PE or PP block. However, to the best of our knowledge, detailed published articles about heterophase block copolymers of 1-alkene with ethylene or propylene are not easily available. In this study, we synthesized the heterophase block copolymers of 1-hexadecene and propylene by sequential polymerization with highly isospecific $\text{TiCl}_3/\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ (Cp = cyclopentadienyl) catalyst. The heterogeneous block copolymers with two separate melting points of constituent blocks can be used as a shape-memory polymer.^{8,9} Therefore, the thermal and the mechanical properties, including shape memory behavior, of the block copolymers were examined in this study.

EXPERIMENTAL

Materials

1-Hexadecene (Janssen Chimica, USA) and *n*-heptane (Junsei Chemical, Japan) were purified by passing it through the columns of molecular sieve 4 Å and distillation over sodium metal under nitrogen prior to use. Propylene (Korea Petrochemical Ind. Co., Ltd.) of polymerization grade was purified by passing it through the column of Fisher RIDOX catalyst and molecular sieve 5A/13×. 1,2,4-Trichlorobenzene (Aldrich, USA) and methanol (Aldrich) were used as received. TiCl_3 (Engelhard Corp., USA) was used without further treatment. $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ was prepared by reacting Cp_2TiCl_2 (Aldrich) with a slight excess of methyl lithium (Aldrich), dissolved in diethyl ether at -20°C under a nitrogen atmosphere. After the temperature was raised up to 0°C , the reaction mixture was hydrolyzed with cold deaerated water. The organic layer was separated and dried over sodium sulfate, and the solvent was removed

by distillation under vacuum to give orange $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$ crystals.⁶

Polymerization

The polymerization was carried out at 40°C in *n*-heptane as diluent. The diluent and catalyst were added into a 1-L three-necked flask equipped with mechanical stirrer, reflux condenser, and thermometer. At the first stage, propylene was continuously fed into the reactor with a pressure of 103.3 KPa to get PP block. At the second stage, after the unreacted propylene was evacuated, 1-hexadecene was fed into the reactor to get sequentially polymerized poly(1-hexadecene) (PHD) block. The times carried out for each stage are shown in Table I. After the completion of polymerization, the acidic methanol was added to quench the polymerization and was poured into a 10-fold excess of methanol to get the precipitate of polymer. The precipitate was filtered, washed with methanol, and dried under vacuum at room temperature.

Characterization

The PHD homopolymer was soluble in *n*-heptane at 40°C . However, PP homopolymer was not soluble in *n*-heptane at 40°C . In Table I, we can see that the polymers soluble in *n*-heptane at 40°C are much less than the content of PHD block. This shows that much of PHD block was effectively linked to PP block.

Films for the measurement of thermal and mechanical properties were prepared by the casting of polymer solution in 1,2,4-trichlorobenzene at 135°C on a glass plate under vacuum. Clean film with even thickness was obtained with all the polymers in Table I. However, it was not possible to get a clean film with even thickness from the

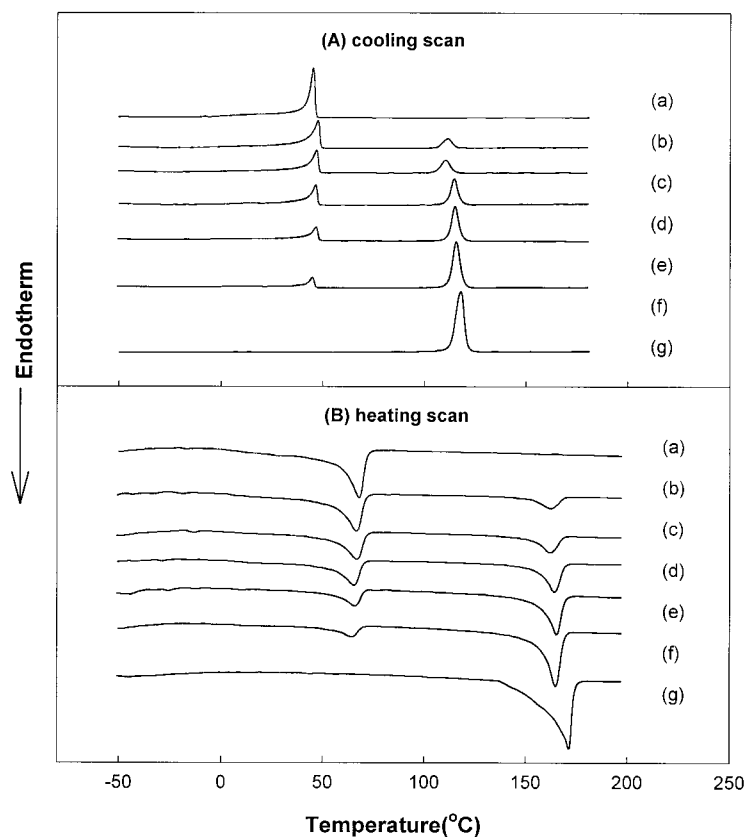


Figure 1 DSC thermograms obtained (A) on cooling scan and (B) on subsequent heating scan; (a) PHD, (b) C16PP11, (c) C16PP19, (d) C16PP32, (e) C16PP47, (f) C16PP59, and (g) PP.

polymer solution containing both PHD homopolymer and PP homopolymer, both separately synthesized. This seems to be due to the macrophase separation between PHD homopolymer and PP homopolymer which are incompatible. Therefore, these results suggest that PHD-PP block copolymer which reduces macrophase separation was effectively synthesized by sequential polymerization.

The content of the propylene repeating unit in the synthesized polymer was determined by comparing the IR absorbance at 720 cm^{-1} of PHD and 1168 cm^{-1} of PP with a Bruker FTIR spectrophotometer (Germany). The sample designation code in Table I indicates the content of the propylene repeating unit in the synthesized polymer. For example, C16PP47 indicates that the content of the propylene repeating unit in this polymer is about 47 wt %.

The intrinsic viscosity, $[\eta]$, of synthesized polymer was determined in 1,2,4-trichlorobenzene at 135°C .

Differential scanning calorimetry (DSC) was carried out with a TA Instruments DSC-2910

(USA) at a heating rate and a cooling rate of $10^\circ\text{C}/\text{min}$. All runs were carried out with a sample of $\sim 5\text{ mg}$. The DSC thermograms in Figure 1 and the thermal properties in Table II were determined as follows. After melting for 1 min at 200°C , the crystallization temperature (T_{ch}) and the heat of crystallization (ΔH_{ch}) of PP segment, and the crystallization temperature (T_{cs}) and the heat of crystallization (ΔH_{cs}) of PHD segment, were measured on cooling scan to -70°C . On the subsequent heating scan after staying 1 min at -70°C , the melting temperature (T_{ms}) and the heat of fusion (ΔH_{ms}) of the PHD segment and the melting temperature (T_{mh}) and the heat of fusion (ΔH_{mh}) of the PP segment were measured.

Dynamic mechanical properties were determined with a dynamic mechanical thermal analyzer (Rheometric Scientific DMTA MK-III, USA) by using a bending mode at a heating rate of $3^\circ\text{C}/\text{min}$ and 20 Hz.

Tensile tests were done at a rate of 10 mm/min by using a tensile tester (Tinius Olsen Series 1000, USA), attaching a constant temperature heating chamber. The microtensile test speci-

Table II Thermal Properties

Sample	Polypropylene Segment					Poly(1-hexadecene) Segment				
	T_{mh} (°C)	T_{ch} (°C)	$T_{mh} - T_{ch}$ (°C)	ΔH_{mh} (J/g-PP segment)	ΔH_{ch} (J/g-PP segment)	T_{ms} (°C)	T_{cs} (°C)	$T_{ms} - T_{cs}$ (°C)	ΔH_{ms} (J/g-PHD segment)	ΔH_{cs} (J/g-PHD segment)
PHD	—	—	—	—	—	68.1	45.3	22.8	62.3	95.5
C16PP11	162.3	111.4	50.9	134.8	149.5	66.7	47.6	19.1	59.6	82.4
C16PP19	161.9	110.0	51.9	108.2	134.7	66.9	46.9	20.0	53.9	67.6
C16PP32	164.3	114.6	49.7	105.9	113.6	65.5	46.5	19.0	54.1	72.8
C16PP47	165.4	115.1	50.3	105.5	112.2	66.0	47.0	19.0	42.7	69.0
C16PP59	164.9	115.7	49.2	104.3	111.1	64.3	45.0	19.3	36.6	37.2
PP	171.4	117.9	53.5	108.3	102.6	—	—	—	—	—

mens had the dimensions of 30 mm length, 10 mm width, and 0.3 mm thickness.

RESULTS AND DISCUSSION

Thermal Properties

Figure 1 shows the DSC thermograms of the synthesized polymers obtained on cooling and subse-

quent heating scans. All the sequentially polymerized polymers show two separate crystallization peaks on the cooling scan and two separate melting temperatures on subsequent heating scan. These results show that PHD and PP segments crystallize separately. Figure 1 and Table II show that both the melting temperature of PHD and the PP segment in sequentially polymerized polymers are decreased compared with

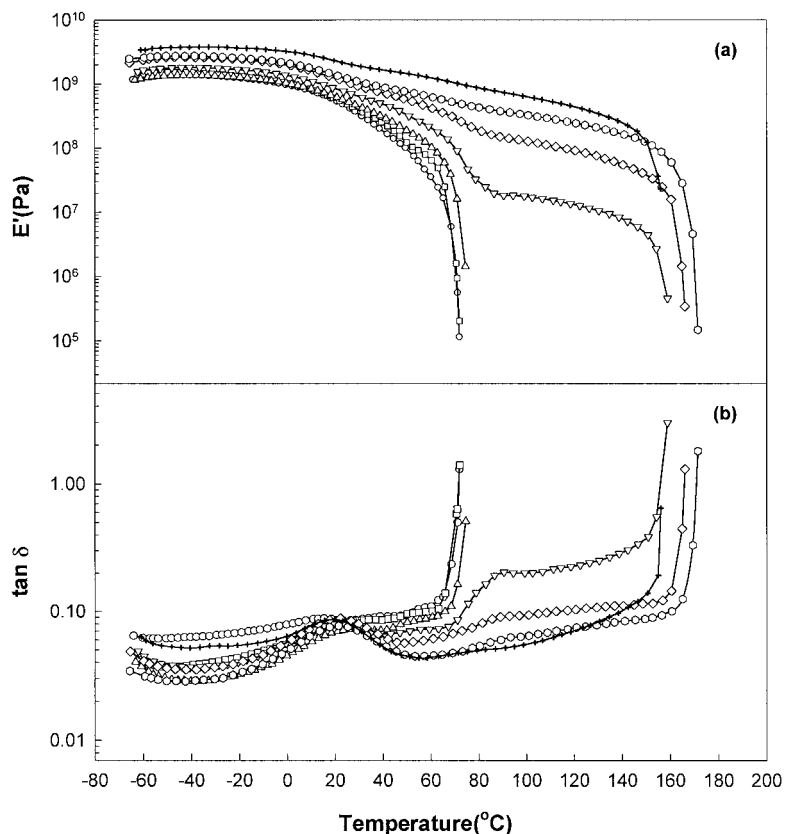


Figure 2 (a) Tensile storage modulus and (b) $\tan \delta$ of (○) PHD, (□) C16PP11, (△) C16PP19, (▽) C16PP32, (◇) C16PP47, (⊙) C16PP59, and (+) PP.

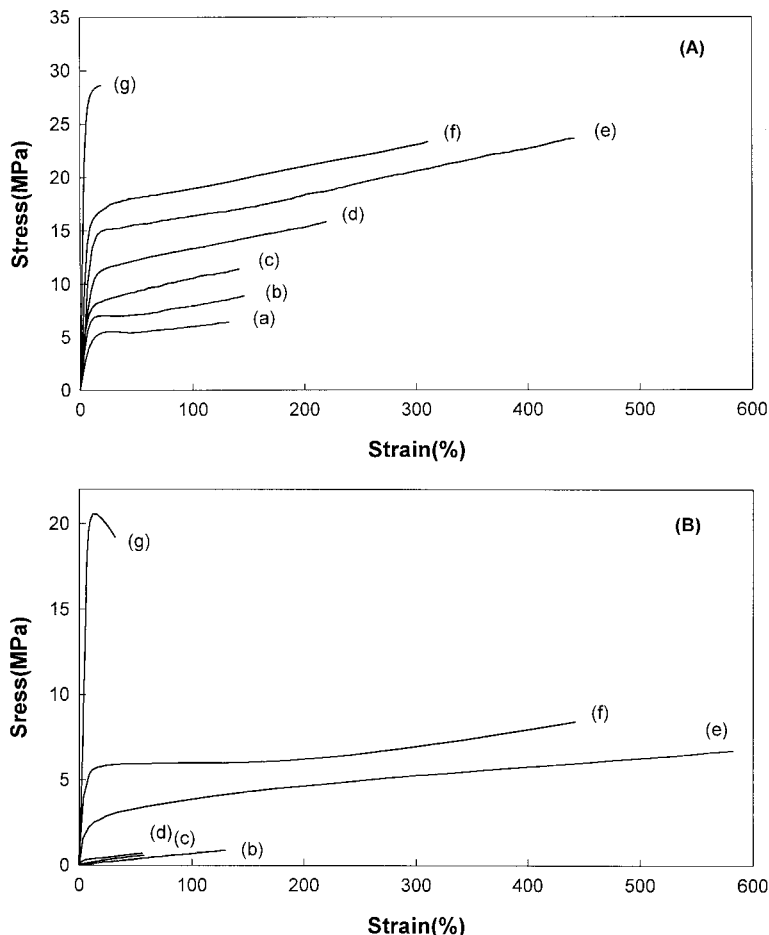


Figure 3 Stress–strain curves at (A) 25°C and (B) 80°C of (a) PHD, (b) C16PP11, (c) C16PP19, (d) C16PP32, (e) C16PP47, (f) C16PP59, and (g) PP.

those of homopolymers. These results suggest that there is partial miscibility between PHD and PP segment, because melting temperature decreases in blends when the constituent polymers are miscible in amorphous domain.¹⁰

The supercooling necessary for the crystallization of both PHD segments ($T_{ms} - T_{cs}$) and PP segment ($T_{mh} - T_{ch}$) decrease in sequentially polymerized polymers compared with those of homopolymers. These results suggest that the primary nucleation for crystallization is promoted because of the presence of interface in our heterophase system.¹¹

The ΔH_{mh} and ΔH_{ch} do not vary so much compared with PP homopolymer until the content of PHD segment is more than 80 wt %. However, ΔH_{ms} and ΔH_{cs} evidently decrease even when the content of the PP segment is < 50 wt %. This shows that crystalline PP segment which crystallized previously on cooling restricts the movement for the crystallization of PHD segments.¹²

Mechanical Properties

The change of tensile storage modulus, E' , observed on heating of all the polymers examined in this study are shown in Figure 2. All the polymers show $\tan \delta$ peaks around 20°C because of glass transition.¹³ PHD homopolymer flows after the melting around 65°C. However, a rubbery plateau persists up to about 150°C, when the content of the sequentially polymerized PP block is > 32 wt %. These results show that the crystalline PP domain does its role as physical crosslinker or reinforcing filler until melting. It can also be observed that E' generally increases as the content of PP block is increased and is more evident at a rubbery plateau.

The stress–strain curves obtained at 25 and 80°C are shown in Figure 3, and the quantitative values of tensile properties are summarized in Table III. We can see that modulus and tensile strength generally increase as the content of PP

Table III Tensile Properties

Sample	Tensile Properties at 25 °C			Tensile Properties at 80 °C		
	5% Secant Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	5% Secant Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
PHD	59	6.4	133	—	—	—
C16PP11	94	8.9	148	1	0.9	130
C16PP19	117	11.5	144	3	0.6	58
C16PP32	134	15.8	221	6	0.6	56
C16PP47	154	23.6	444	36	6.7	587
C16PP59	243	23.4	311	93	8.5	443
PP	479	28.6	19	250	19.2	32

block is increased. The fact that block copolymers have larger values of elongation at break than homopolymers suggests that synergistic properties of elongation or impact strength can be obtained in the block copolymer synthesized by the sequential polymerization of propylene and 1-hexadecene, compared with homopolymers.

Shape Memory Behavior

Thermal-responsive shape memory polymers basically consist of the fixed structure for memoriz-

ing original shape and the thermally reversible phase for maintaining transient shape.^{8,14} Crystal, glassy state, entanglement, or crosslinking can be used as a fixed structure. Thermally reversible phase is generally designed to have a large drop in elastic modulus above shape recovery temperature (T_s ; i.e., glass transition temperature or melting temperature).

In this respect, PHD-PP block copolymers of our study have the potential to be used as a shape memory polymer. That is, when a cast or molded

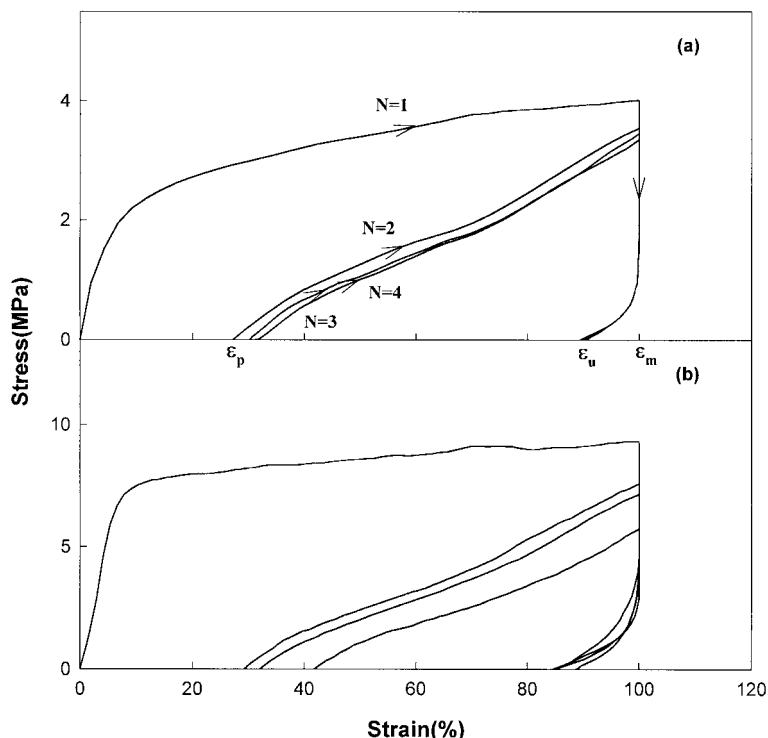


Figure 4 Cyclic tensile behavior of (a) C16PP47 and (b) C16PP59.

specimen is heated above T_{ms} but below T_{mh} , it changes from a rigid crystalline state to a rubbery state at which it is highly flexible, allowing it to be deformed to a new shape that can be frozen in by cooling below T_{ms} . If the deformed specimen is subsequently heated above the T_{ms} , the specimen will remember its original shape and spontaneously return to that shape.

The result of cyclic tensile test to examine the shape memory effect of C16PP47 and C16PP59, which have rubbery plateaus (Fig. 2) and can be elongated more than 100% at 80°C, are shown in Figure 4.¹⁵ The sample was elongated at 80°C to 100% strain (ϵ_m) at a constant elongation rate of 10 mm/min. Although maintaining the strain at ϵ_m , the sample was cooled to 25°C and unloaded. Upon removing the constraint at 25°C, small recovery of strain to ϵ_u occurs. The sample was subsequently heated to 80°C in 5 min and stayed at that temperature for the next 10 min, allowing recovery of strain. This completes one thermomechanical cycle ($N = 1$) leaving a residual strain, ϵ_p , where the next cycle ($N = 2$) starts.

In Figure 4, we can see that cyclic tensile test curves of C16PP47 maintain their shapes almost identically after the first tempering cycle; however, ϵ_p values of C16PP59 slowly increase upon repeating cycle. These results suggest that the probability of permanent deformation of fixed structure is raised as the content of fixed structure is increased. In our previous study, the ϵ_p values of thermoplastic polyurethane,⁹ poly(caprolactone)-polyamide block copolymer,⁸ and poly(methylene-1,3-cyclopentane)-polyethylene block copolymer¹⁶ were < 20%. Compared with these results, the ϵ_p values of Figure 4 are somewhat larger.

CONCLUSION

1. The heterophase PHD-PP block copolymer with two separate melting temperatures of constituent blocks was effectively synthesized by the sequential polymerization of propylene and 1-hexadecene.

2. The modulus of block copolymer was increased as the content of PP block was increased. However, synergistic values of elongation at break compared with homopolymers were observed in the block copolymer at intermediate compositions.

3. When the PHD block was used as a thermally reversible phase for maintaining transient shape and when PP block was used as a fixed structure memorizing original shape, shape memory effect was observed.

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