Metallocene-Based Branch−Block Thermoplastic Elastomers

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Received June 22, 2000; Revised Manuscript Received September 19, 2000

ABSTRACT: Long chain branched (LCB) polyethylene block copolymers having thermoplastic elastomer character were made using mixed metallocene catalysts. Conceptually, the synthesis can be divided into two steps. Step 1 involves the generation of vinyl-terminated, crystallizable macromonomers, and step 2 involves the incorporation of these macromonomers into an amorphous or plastomeric copolymer backbone. In practice, the two steps may be conducted sequentially or simultaneously. The polymer properties depend on the catalyst pair and the process conditions selected, which determine the populations of reactive macromonomer and the probability of incorporating them into the backbone. One such useful pair is the mixture of Cp_2ZrCl_2 and $(C_5Me_4SiMe_2NC_{12}H_{23})TiCl_2$, activated with MAO. In the presence of a mixed ethylene/butene feed the Cp_2ZrCl_2 catalyst, by virtue of its low comonomer incorporating capability, will produce primarily crystalline polyethylene macromonomers. The titanium catalyst, on the other hand, has a higher affinity for comonomers and will consume comonomer and macromonomers during the polymerization which produces plastomeric backbone containing, in one case, over 20 mol % butene. Microtensile test on the polymers showed good elastic recovery and good high-temperature tensile strength. The properties of the resultant comblike polymers will be governed by the topological details of the branched polymer as well as the LCB distribution. To study the latter distribution, branched model polymers having dissimilar LCB and backbone compositions were synthesized. GPC-FTIR analysis provided the LCB distribution pattern, revealing a progression of statistically branched polymers with the highest molecular weight molecules containing the highest levels of branching. Upon cooling from the melt, the crystalline segments (primarily in the LCB portions) would cocrystallize to form crystalline domains embedded in an amorphous matrix, as confirmed by transmission electron microscopy.

Introduction

Metallocene catalysts have enabled the fine control of polyolefin size dimensions and microstructure[1] as well as the synthesis of novel products ranging from cyclic olefin copolymers[2] to syndiotactic polystyrene[3] and ethylene−styrene interpolymers.[4] Full optimization of mechanical and flow properties has often been difficult, particularly when dealing with a single catalyst that produces linear polymer chains; flow properties are often improved at the expense of mechanical properties, and vice versa. The use of mixed catalysts[5] and long chain branching approaches[6] provide additional degrees of freedom for the design of polymers with unprecedented balance of properties. The challenge is to define the rules that determine properties. Long chain branching would allow not only the synthesis of polymers having improved processability and melt strength[7] but also the synthesis of in-reactor block copolymers,[8] some displaying characteristics of thermoplastic elastomers (TPE).

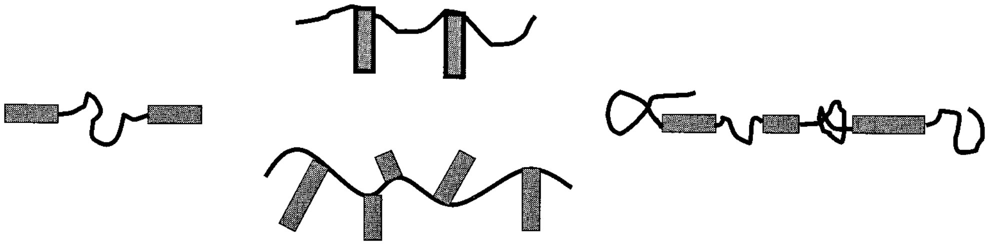
A thermoplastic elastomer consists of hard and soft segments.[9,10] The hard segments—which are typically glassy but could also be semicrystalline—could be interconnected to the soft segments in topologically distinct architectures, yielding linear block, branch−block (graft), or multiblock structures,[11] as illustrated in Figure 1. Styrene−isoprene−styrene linear triblock copolymer (Shell's family of Kraton rubbers) is an example of a TPE produced using anionic polymerization.

The morphological details of a block copolymer depend on the composition of block segments, segment sizes, the copolymer topology, and the thermodynamic interaction parameters for each block segment.[12,13] When self-assembled, these copolymers can produce cylindrical, spherical, lamellar, or more complicated morphologies[14] that determine individual property profile.[15] To design block copolymers, one must be able to control block copolymer composition and topological details.

Beside anionic, cationic, or radical polymerization techniques that have been the main polymerization routes to controlled architectures,[16,17] metallocene-catalyzed routes are also being explored. In one approach, Chung uses metallocene polymerization to introduce a borane functionality on a polyolefin backbone; the borane is then converted to oxygen functionality which is subsequently grafted with methyl methacrylate.[18] In another approach, Stehling uses a combination of metallocene and "living" free-radical polymerization to synthesize polyolefin-based functionalized graft copolymers.[19] Markel et al. have shown that polymerization of olefins using mixed metallocenes also has the potential to produce branch−block copolymers with themoplastic elastomer character.[8] Unlike the compositionally uniform materials such as triblock copolymers from ionic polymerization, a long chain branching distribution pattern describes the metallocene-derived compositions. The compositional and structural heterogeneities of these systems can be probed using hyphenated analytical techniques (e.g., GPC-FTIR)[20] or modeled using graft copolymer statistics[21] and kinetic theory.[22,23]

In this work, branch−block copolymers with crystalline branches and plastomer backbones were synthesized using mixed metallocene catalysts in a solution polymerization.[24,25] The resulting polymers exhibited good thermoplastic elastomeric properties.

10.1021/ma001087b CCC: $19.00



A linear triblock Comb Branch-blocks Amultiblock

Figure 1. Schematic examples of block copolymer structures with the potential for elastomeric properties (solid blocks represent crystalline or semicrystalline portions; lines represent amorphous portions of the polymer molecules).

Experimental Section

Materials. Polymerization grade ethylene, propylene, and solvents were supplied by pipeline directly from the ExxonMobil chemical plant and purified by passing through activated basic alumina and molecular sieves. Norbornene (purchased from Aldrich Chemical Co.) was purified by sublimation and dissolved in toluene to make an 80% stock solution. All other reagents were obtained commercially and used as received.

Catalyst Preparation. All catalyst preparations were performed in an inert atmosphere with <1.5 ppm H_2O content. Metallocene catalyst precursors were activated with either methylalumoxane (MAO, 10% in toluene, from Albemarle Inc.) or dimethylanilinium tetrakis(perfluorophenyl)borate (Boulder Scientific Co.). The catalyst was added to a stainless steel tube by pipet and transferred to the reactor.

Macromonomer Synthesis. Macromonomer synthesis was conducted in a 1 L Zipperclave reactor equipped with a water jacket for temperature control. The reactor was purged with nitrogen and pressure tested (to 300 psi) using ethylene. High-purity (>99.5%) solvent (toluene or hexane, 600 mL) was measured into the reactor using calibrated sight glasses, and comonomer (butene, 10 mL) was added as required. The reactor temperature controller was set to 90 °C, and the system was allowed to reach the equilibrium. The ethylene pressure regulator was set to 20 psi above the reactor pressure (ΔP = 20 psi), and ethylene was added to the reactor until a steady state was achieved as measured by zero ethylene uptake. Catalyst was injected using a catalyst tube, and the ethylene supply manifold was immediately opened to the reactor in order to maintain a constant reactor pressure as ethylene was consumed. The reaction medium was mixed using a flat-paddle stirrer rotating at 750 rpm. The reaction was terminated by methanol injection after 15−30 min. The product was poured into an excess of isopropyl alcohol to precipitate the polymer, which was then evaporated to dryness.

Synthesis of Block Copolymer. (A) Assembly of Branch−Block Structures in a Sequential Process. The polymerization was conducted in a 2 L autoclave reactor. Typically, the reactor was charged with toluene (300 mL), macromonomer (5−30 g), and triisobutylaluminum (0.5 mL of 1 M solution in 2 mL of toluene). Appropriate monomer and comonomer were then added to the reactor. Generally, comonomer (butene (60 mL) or norbornene (60 mL of 80% solution in toluene)) was introduced into the reactor followed by addition of ethylene to reach 100 psi above original reactor pressure (ΔP of ethylene = 100 psi). The reactor was heated to the desired temperature and equilibrated for 5 min. Then the catalyst and activator (in 3 mL of toluene) were injected using a catalyst tube. After 15−20 min, the reactor was cooled to 25 °C and vented. The product was poured into an excess of isopropyl alcohol to precipitate the polymer, which was then dried in air overnight.

(B) Simultaneous Synthesis of Macromonomer and Backbone. This process involves the simultaneous production of the macromonomer and the backbone in the presence of mixed metallocene catalysts. The reactor was purged with nitrogen and pressure tested using ethylene. Solvent (toluene, 600 mL) and comonomer (butene, 20 mL) were added to the reactor. The reactor temperature controller was set to 90 °C, and the system was allowed to reach equilibrium. The ethylene pressure regulator was next set to 100 psig, and ethylene was added to the system until a steady state was achieved as measured by zero ethylene uptake. The catalyst (Cp_2ZrCl_2 and $(C_5Me_4SiMe_2NC_{12}H_{23})TiCl_2$) activated with 10% methylalumoxane (MAO) solution in toluene was injected with a catalyst tube. The 100 psig ethylene supply manifold was immediately opened to the reactor in order to maintain a constant reactor pressure as ethylene was consumed by reaction. Reaction was terminated by methanol injection after 7 min. The product was poured into an excess of isopropyl alcohol and evaporated to dryness.

Characterization. Molecular weight characteristics were analyzed by high-temperature (135 °C) gel permeation chromatography (GPC) using a Waters 150C high-temperature system equipped with Shodex AT-806MS columns and a differential refractive index detector. The separation columns were calibrated using a broad molecular weight distribution, high-density polyethylene standard (NBS 1475) supplied by the National Institute of Standards and Technology (NIST). GPC-FTIR results were obtained on a Lab Connections unit. In this instrument, a portion of the eluent from the GPC is deposited on a germanium disk as it is slowly rotated. The net result is an arc of polymer on the disk, the rotational angle of which corresponds to the measured molecular weight. A series of FTIR spectra are recorded from the arc of polymer, and the molecular composition is calculated as a function of molecular weight. To measure the butene content in macromonomers and branch−block copolymer, the FTIR was calibrated with a series of ethylene−butene copolymers with known ethylene content as determined by ^1H NMR. The ethylene content was measured using absorbency at 1378 cm^{-1} (normalized for thickness using absorbency at 4323 cm^{-1}).

The melt rheology data were obtained using a Rheometric Scientific RMS-800 in parallel plate oscillatory shear mode at 180 °C from 0.1 to 400 rad/s. The polymers were stabilized with 0.1−0.2 wt % of BHT.

Prior to physical property testing, samples were compression-molded in a Carver hydraulic press to form plaques approximately 0.03 in. thick. Tensile properties were measured on an Instron 4505 instrument at room temperature and 80 °C. Standard tensile testing was performed on microtensile dog bones with dimensions specified in ASTM method D1708. Crosshead speed was 2 in./min with a data collection rate of 10 points/s. To determine elastic recovery, microtensile dog bones were elongated to 150% strain at a crosshead speed of 20 in/min, at which strain they were held for 10 min before the load was removed. Sample length was measured after 1 h, and the recovery was calculated according to

$$\text{recovery (\%)} = 100 \times \frac{\text{stretched length} - \text{recovered length}}{\text{stretched length} - \text{original length}}$$

Transmission electron micrographs (TEM) of selected materials were obtained using a JEOL 2000-FX electron microscope using an accelerating voltage of approximately 160 kV. Mor-

Table 1. Polymerization Parameters and Characterization of Macromonomer Samples

								GPC		^{1}H NMR		
sample	catalyst^a	cat. amt (mg)	Al/metal ratio	solvent	butene (mL)	temp (°C)	yield (g)	M_n	M_w	M_w/M_n	vinyl (%)	butene (mol %)
M 1	A	4	21.5	toluene		90	34	25 154	55 516	2.21	91.4	
M 2	A	8	21.5	toluene		90	58	24 619	54 085	2.20	94.6	
M 3	A	8	21.5	hexane		90	19	12 933	46 941	3.63	89.5	
M 4	A	32	21.5	hexane		90	2	1 744	4 710	2.70	85.4	
M 5	A	32	21.5	hexane	50	90	31	6 964	35 992	5.16	64.3	3.9
M 6	B	8	34.4	toluene		90	17	22 124	125 359	5.67	89.6	
M 7	B	32	34.4	hexane		90	12	3 655	13 117	3.59	86.1	
M 8	B	16	34.4	toluene	10	90	22	48 611	173 905	3.58	84.6	5.8
M 9	C	5	158	toluene	50	90	36	7 014	23 431	3.34	56.3	12.5

[a] Catalyst: A = bis(pentadienyl)zirconium dichloride activated with methylalumoxane (MAO, 10% in toluene). B = dimethylsiladiyl(tetramethylcyclopentadienyl)(cyclododecamido)titanium dichloride activated with methylalumoxane (MAO, 10% in toluene). C = dimethylsiladiylbis(indenyl)hafnium dichloride activated with methylalumoxane (MAO, 10% in toluene).

Table 2. Polymerization Parameters and Characterization of Branch−Block Copolymers

											GPC	
sample	cat.^{a}	cat. amt (mg)	macromonomer type	macromonomer amt (g)	monomer	monomer amt	comonomer	solvent	temp (°C)	yield (g)	M_w	M_w/M_n
BB 1	B	1	ethylene/butene	20	ethylene	100 psi	butene (60 mL)	toluene	90	42.6	192 778	4.44
BB 2	B	1	ethylene/ norbornene	30	ethylene	100 psi	norbornene (60 mL, 80%)	toluene	60	91.9	198 049	6.23
BB 3^b	A/B	0.25/0.25			ethylene	100 psi	butene (60 mL)	toluene	80	23.9	245 495	2.23
BB 4^b	A/B	0.25/0.25			ethylene	100 psi	butene (60 mL)	toluene	90	18.5	315 303	2.45
BB 5	D	2	ethylene	10	propylene	150 mL		toluene	90	40	53 844	2.37
BB 6	D	2	ethylene	10	propylene	150 mL		toluene	50	53	164 395	3.78
BB 7	E	2	ethylene	10	propylene	150 mL		toluene	90	40	76 278	2.07
BB 8	E	2	ethylene	5	propylene	150 mL		toluene	50	68	201 141	1.79

[a] Catalyst: D = dimethylsiladiylbis(2-methylindenyl)zirconium dichloride activated with methylalumoxane (MAO, 10% in toluene). E = dimethylsiladiylbis(indenyl)hafnium dimethyl complex activated with dimethylanilinium tetrakis(perfluorophenyl)borate. [b] Simultaneous synthesis of macromonomer and backbone using mixed metallocene catalyst.

phological contrast was obtained by staining samples with ruthenium tetroxide prior to cryomicrotoming to obtain sections approximately 800−1000 Å thick.

Results and Discussion

1. Macromonomer Synthesis. Most syntheses for ethylene copolymers produce ∼30% vinyl chain ends, the balance being made up of the less reactive vinylene and vinylidene.[24] In this work, low molecular weight macromonomers having high vinyl chain end selectivity were made using high concentrations of metallocene catalyst and low Al:M ratios at 90 °C. Some polymerization parameters and characterization data are listed in Table 1. The molecular weight of the macromonomers can be regulated by reaction temperature and catalyst concentration. Generally, higher catalyst concentration leads to lower molecular weight. A possible chain termination mechanism may involve zirconocene−zirconocene interactions, as postulated by Kaminsky and others.[26] Under the conditions employed in this work, high populations of vinyl termini could be obtained. The percentage of vinyl chain ends was determined by ^{1}H NMR analysis. ^{1}H NMR can readily distinguish olefin chain ends such as vinyl, vinylene, vinylidene, and trisubstituted groups. Thus, the percentage of vinyl chain ends may be calculated assuming every chain has one unsaturated end. Generally, the vinyl chain end population declined with increasing comonomer content in the macromonomer, as shown in Table 1.

2. Synthesis of Branch−Block Copolymers. Production of branch−block copolymers involves the synthesis of vinyl-terminated macromonomers and their incorporation into polymer backbones. This may be achieved either through a sequential process or in a simultaneous synthesis with mixed-metallocene catalyst. Some typical branch−block copolymers with various compositions made under these conditions are listed in Table 2.

In the sequential process, macromonomers were isolated prior to use in the second step. The macromonomer compositions include polyethylene and ethylene−butene and ethylene−norbornene copolymers. Reaction variables tested include comonomer concentration, macromonomer concentration, and reaction temperature. A sequential process in which the macromonomer is used without isolation was also investigated. In such a process, catalyst deactivation is needed since different catalysts are used for macromonomer synthesis and incorporation. Typically, 5 min at 150 °C of thermal deactivation was sufficient to kill the catalyst (as measured by zero ethylene uptake), but a 15 min kill step was used to ensure complete deactivation. Addition of a 10-fold excess of methanol (relative to metallocene precursors) as a means of killing the catalyst was also tested. Note that the reactivation was possible in this case by the addition of excess levels of MAO. It is believed that the methanol complexes with metallocene catalysts to render them inactive, while MAO may partially reverse this physical interaction.

Branch−block copolymers may also be synthesized with the simultaneous production of the macromonomer and the backbone in the presence of mixed metallocene catalysts and a mixed monomer stream at 90 °C. In such a case one catalyst is responsible for generating vinyl-terminated, crystallizable majority ethylene macromonomers while the other incorporates the macromonomers into noncrystallizable ethylene−butene copolymer backbones. The mixed metallocene system used in this study consists of Cp_2ZrCl_2 and $(C_5Me_4SiMe_2NC_{12}H_{23})TiCl_2$ activated with MAO. While the Cp_2ZrCl_2 catalyst is producing vinyl-terminated macromonomers, the ($C_5Me_4SiMe_2NC_{12}H_{23}$)$TiCl_2$ catalyst is incorporating them into growing noncrystallizable ethylene/butene copolymer backbones, producing branch–block compositions. Conceptually, the relative ratio of these two metallocenes may be adjusted to achieve the desired level of branching for property control, but this requires further experimental and kinetic modeling effort.[22]

The reactivity ratios of ethylene, butene, and macromonomer were not measured under the process conditions employed. However, based on reactivity ratios of closely related systems, literature indicates Cp_2ZrCl_2 catalyst to have less tendency to incorporate comonomers compared to ($C_5Me_4SiMe_2NBu$)$TiCl_2$ catalyst. For example, one reference gives a r_1 of ~22 and an r_2 of ~0 for the copolymerization of ethylene and hexene at 40 °C using Cp_2ZrCl_2,[27] while another reference gives r_1 of 85 and r_2 of 0.01 for ethylene–butene copolymerization at 80 °C with the same catalyst.[28] In general, r_1 values for Cp_2ZrCl_2 falls in the range 55–85 for copolymerization involving ethylene with butene or hexene in the temperature range 20–80 °C,[29] all pointing to the very low tendency of this catalyst to incorporate comonomers. In contrast, the r_1 and r_2 values for ($C_5Me_4SiMe_2NBu$)$TiCl_2$ catalyst system (a mono-Cp catalyst similar to the one utilized in this paper) are reported to be ~8 and 0.1, respectively, for the copolymerization of ethylene and octene at 140 °C.[22,27] If the ratios of r_2 to r_1 are used, one gets approximate r_2/r_1 values of $1.2\ 5 \times 10^{-2}$ for ($C_5Me_4SiMe_2NBu$)$TiCl_2$ and $1.2\ 5 \times 10^{-4}$ for Cp_2ZrCl_2, indicating an about 100-fold higher comonomer incorporation capability of the mono-Cp catalyst relative to Cp_2ZrCl_2. One could envision that, in a simultaneous polymerization process, as Cp_2ZrCl_2 catalyst is producing essentially low molecular weight, vinyl-terminated polyethylene macromonomers containing relatively low levels of comonomer, the ($C_5Me_4SiMe_2NC_{12}H_{23}$)$TiCl_2$ catalyst would be assembling the high molecular weight copolymer backbones while consuming some of the macromonomers. In the case of sequential polymerization, the final product would be a complex mixture primarily consisting of comb polymers, unreacted macromonomers, and ethylene–butene copolymer backbone containing no macromonomer. In the simultaneous polymerization case the mixture could be even more complicated, as there may be a possibility of forming cross-products involving various reactive fragments. The analysis of such mixtures poses an analytical challenge. However, control experiments and kinetic modeling may help guide their analysis.

3. Characterization of Long Chain Branched Polymers. Direct quantification of long chain branches by ^{13}C NMR is possible in some ethylene homopolymers and copolymers.[30] This technique, however, has its limitations when it comes to analyzing complex copolymers such as the ones described here. In particular, it would be a daunting task to analyze the unfractionated complex mixture from the simultaneous polymerization since the polymer would have a distribution of side chains ranging from butene all the way to high molecular weight macromonomers.

To spectroscopically assess the branching pattern in these branch–block copolymers, a distinguishing feature was introduced, into either the branch or the backbone. “Model” polymer compositions were made using a sequential process. One such polymer had ethylene–butene macromonomers assembled over a pure polyethylene backbone, the butene in the side chain acting as a tag. The ethylene–butene macromonomers were made using high comonomer incorporating catalysts such as ($C_5Me_4SiMe_2NC_{12}H_{23}$)$TiCl_2$ and *rac*-$(CH_3)_2Si(Ind)_2HfCl_2$ (Table 1). GPC-FTIR was used to obtain the branching distribution. Figure 2 shows the deconvolution of GPC data for such a polymer sample and the mole percent of butene detected using GPC-FTIR. The average butene content in the branched, high molecular weight material (consisting of homopolyethylene backbones incorporating E/B macromonomer) was 3.7 mol %, as opposed to that of the macromonomer product at 6.6 mol % butene. The branching level can be calculated from the following equation:

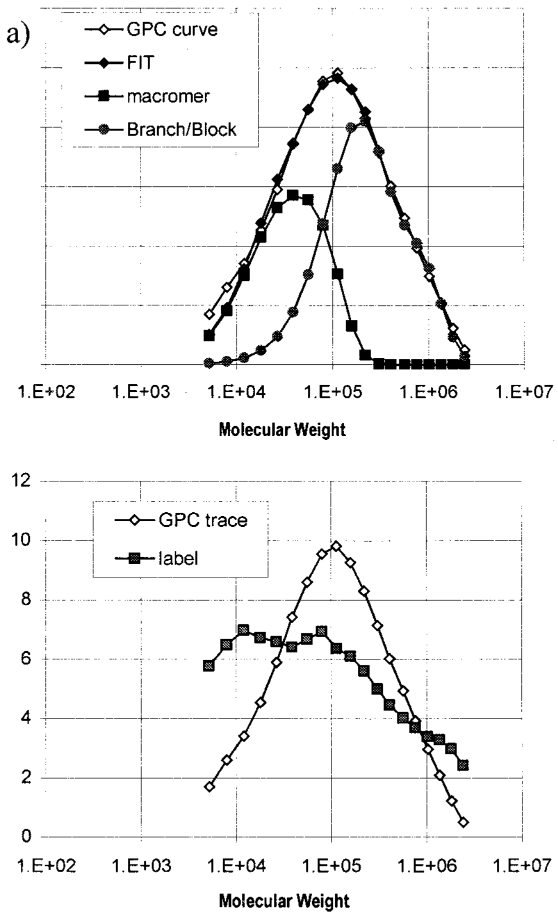


Figure 2. Characterization of long chain branches in a branch–block copolymer (PE-*g*-EB): (a) deconvolution of GPC data; (b) mole percent label (butene) by GPC-FTIR.

$$\text{wt \% branches} = \frac{\text{\% butene in high MW fractions}}{\text{\% butene in macromers}} \times 100\%$$

When combined with the FTIR data, it is possible to convert the butene intensity to a long chain branch distribution, corresponding to the number of branches along the molecular weight distribution, as shown in Figure 3. Figure 3a shows the average mole percent of butene labels (labfit) obtained from GPC-FTIR. This gives the average weight percent of macromonomers incorporated into branch–block copolymers at different molecular weights. Using the number-average molecular weight (M_n) of the macromonomer to specify the average molecular weight of branches, the number of branches per chain at a given molecular weight is

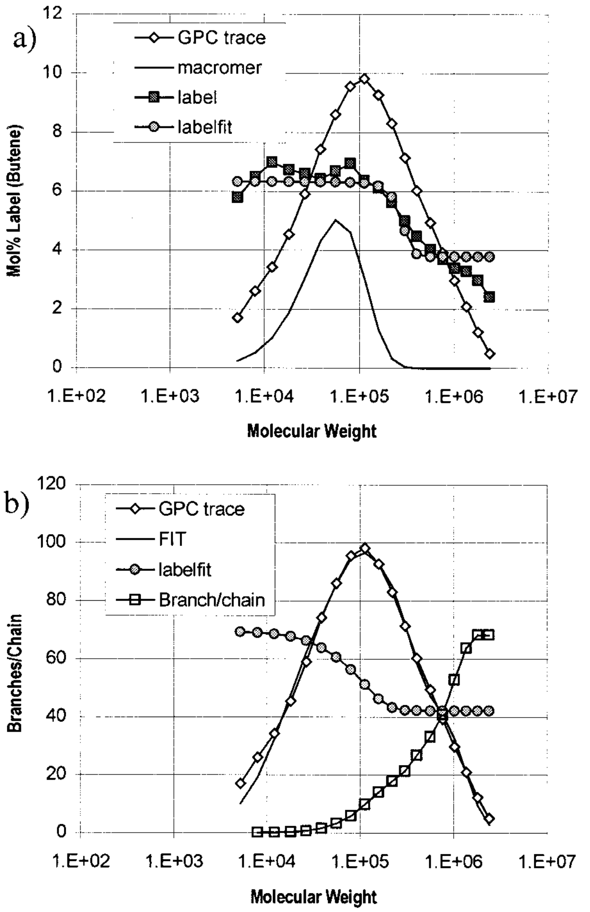


Figure 3. Analysis of long chain branching data from Figure 2: (a) fitting the measured mole percent label (butene) from GPC-FTIR; (b) computed average branch distribution.

calculated (eq 2) to obtain an LCB distribution, as shown in Figure 3b.

$$\text{av no. of branches/chain} = \frac{(\text{MW of branch polymer})(\text{wt fraction of macromer})}{(M_n \text{ of macromer})(1 - \text{wt fraction of macromer})} \qquad (2)$$

The use of the GPC-FTIR technique to determine the LCB distribution in branch−block copolymers is further illustrated in the following example. In this case, polyethylene macromonomers were incorporated into polypropylene backbones. Since the ethylene content as a function of molecular weight can be readily determined by FTIR, it is possible to quantify the incorporation of macromonomer and calculate the LCB distribution. Figure 4 shows the GPC-FTIR trace of a branch−block copolymer containing polyethylene branches and polypropylene backbones (BB5). The squares indicate the ethylene content measured by FTIR at different molecular weight along the GPC curve. Since the number-average molecular weight of the polyethylene macromonomer is 7500, the ethylene content detected at high molecular weights clearly indicates the incorporation of the macromonomer in the polypropylene backbones. More importantly, it is possible to calculate the statistical LCB distribution (also shown in Figure 4). Assuming that all macromonomers have an equal probability of incorporation (i.e., all macromonomers are randomly spaced along the polypropylene backbones), then the number of long chain branches at a given molecular weight may be calculated (eq 2).

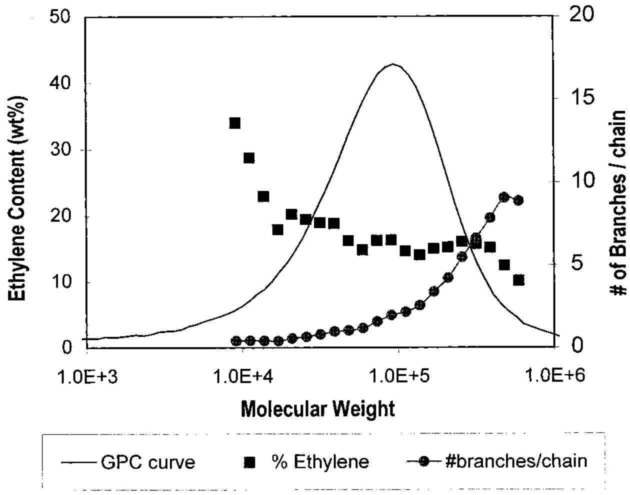


Figure 4. GPC-FTIR analysis of a branch−block copolymer (iPP-*g*-PE): one trace showing ethylene content as a function of molecular weight and the other the computed average branch distribution.

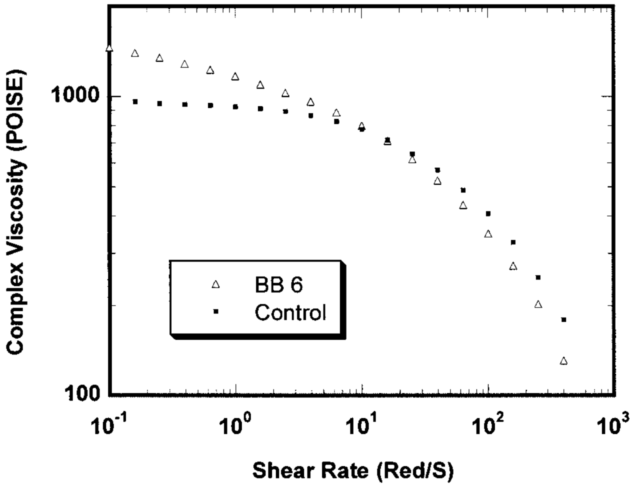


Figure 5. Shear rheology data of a branch−block copolymer (iPP-*g*-PE) compared to that of a homo-PP control made under similar conditions.

Shear rheology may also be used to detect long chain branching in branch−block copolymers. Figure 5 shows the plot of complex viscosity (η^*) vs shear rate for branch−block copolymer BB6. To evaluate the effect of LCB, rheology tests were also conducted on a control homopolymer made under similar conditions, and the data is plotted in the same figure for comparison. Clearly, the branch−block copolymer shows higher viscosity at low frequency and lower viscosity at high frequency compared to the homopolymer control. Such a shear thinning behavior is typical of long chain branched copolymers.

As these polymers are branch−block copolymers they may serve as model polymers in the study of elastomeric copolymers. It is important to note that, in both Figures 3 and 4, the branch level increases rapidly as the molecular weight increases. This suggests that highly branched block copolymer may be obtained using macromonomer incorporation, which in turn would have large impact on the physical, rheological, and mechanical properties of the polymer. Since similar macromonomers and polymerization conditions were used

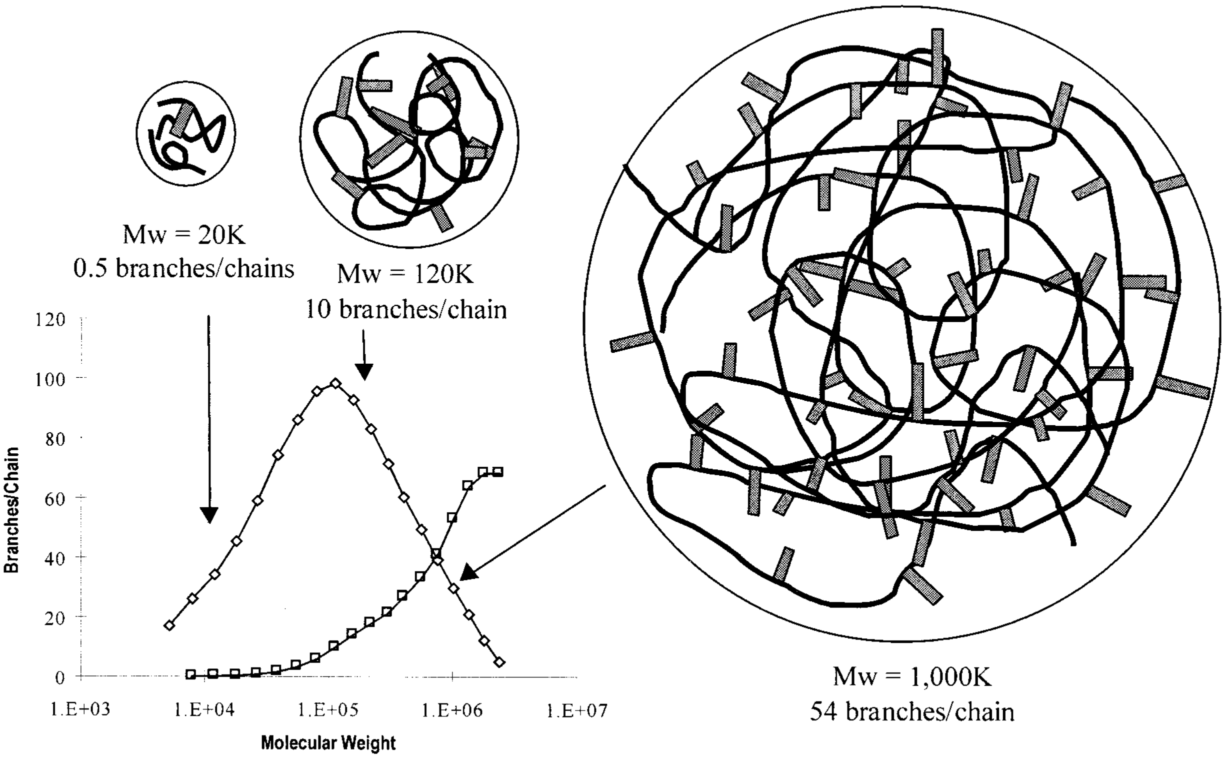


Figure 6. Schematic representation of branch–block structures at various molecular weight slices.

Table 3. Mechanical Properties of Branch–Block Copolymers[a]

	sample BB 1	sample BB 2	sample BB 3	sample BB 4
synthetic method	sequential	sequential	mixed metallocene	mixed metallocene
branch type	ethylene/butene copolymer	ethylene/norbornene copolymer	ethylene/butene copolymer	ethylene/butene copolymer
backbone type	ethylene/butene copolymer	ethylene/norbornene copolymer	ethylene/butene copolymer	ethylene/butene copolymer
sample density (g/cm^3)	0.887		0.895	0.887
peak melting temp (°C)	119[a]	116[a]		124[a]
tensile strength (RT) (psi)	2401	4011	2174	3054
elongation at break (RT) (%)	905	386	595	669
tensile strength (80 °C) (psi)	306	1544	1010	351
elongation at break (80 °C) (%)	489	583	606	505
recovery from 150% strain (%)	76	60	36	87

[a] The high melting point of ~120 °C is due to high crystallinity of macromonomers, both incorporated (branches) and unreacted. It does not correlate to the density of the branch–block copolymers as that in random copolymer. The lower measured density is attributed to the elastic backbones that have high butene contents (~20 mol %) and much lower crstallinity.

in the syntheses of elastomeric and "model" branch–block copolymers, we may assume the incorporation and the distribution of macromonomers in copolymer backbones would also be similar. Thus, the branch–block thermoplastic elastomers would have more or less similar LCB distribution as the model polymers. By virtue of the high number of crystalline blocks associated with the high molecular weight ends (e.g., the 960 000 molecular weight fraction shown in Figure 6), the system may acquire a network character in which long chain branches crystallize to form physical cross-links connected by noncrystalline backbone chains. The 960 000 molecular weight fraction has been computed to have, on the average, 54 branches/chain. Even as a minor component, such huge macromolecules may play a significant role in controlling material properties.

In the ideal case of random incorporation across the molecular weight distribution (nearly the case for the present system), the average number of branches per chain is proportional to the backbone molecular weight. A convenient representation of the random copolymer (Figure 6) shows the structure in terms of the average spacing (molecular weight) between macromonomer insertion points and the number-average molecular weight of the macromonomer blocks. In reality, the lengths of the macromonomer and the spacing (molecular weights) along the backbone between macromonomers are described by most-probable distributions. Also present in the final product are unincorporated macromonomer and unbranched noncrystallizable backbones, the effect of which on properties is as yet unknown. Control of these compositional and topological variables is expected to yield products with different mechanical and rheological properties. Further experimental and kinetic modeling effort is essential for building quantitative measures of LCB distribution in such systems.

4. Mechanical Properties. Using the synthetic strategies described above, it is possible to produce long chain branched samples with a wide range of physical properties. Key mechanical data of some samples are listed in Table 3. In particular, it is possible to produce samples with good elastic recovery that also exhibit relatively high melting temperatures and good tensile

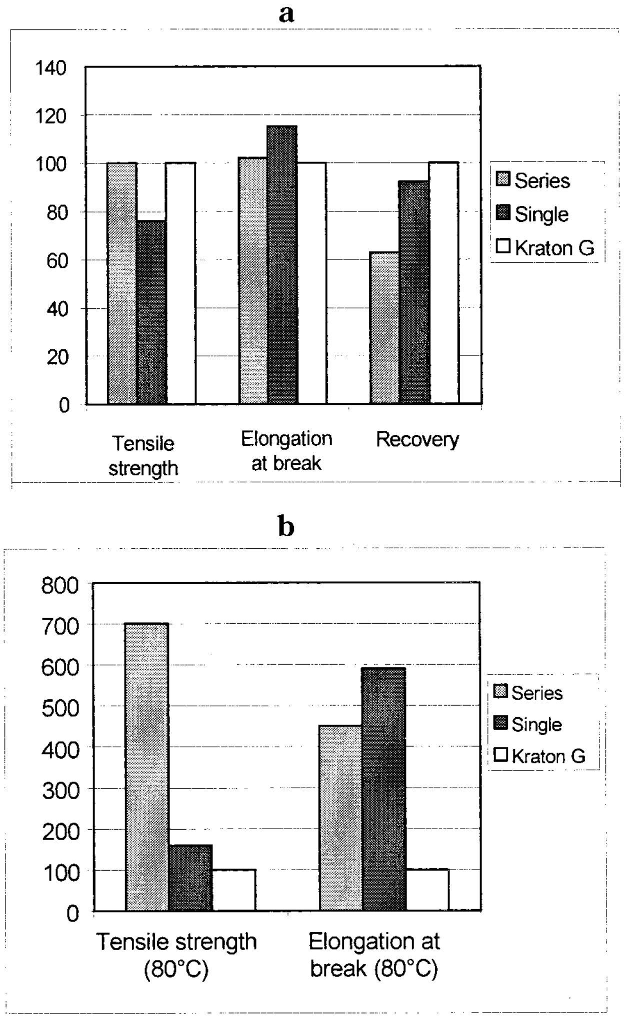


Figure 7. Room temperature (top) and high temperature (80 °C, bottom) performance of branch–block copolymer compared to Kraton G (series: polymer made with preformed macromonomers; single: polymer made with mixed metallocene catalysts).

strength. The best of the branch–block copolymers exhibit initial moduli, tensile strengths, and elastic recoveries that surpass those of commercial ethylene/butene random copolymers with similar densities and are comparable with Kraton G (Figure 7).

Unlike random copolymers, in which only the molecular weight characteristics and comonomer ratio can be varied, it is conceivable that one can tune the physical and mechanical properties of long chain branch–block copolymers by adjusting molecular parameters. Such molecular parameters include relative size and proportion of branch and backbone segments, their comonomer contents, and the number of branches per chain. With such an array of controllable parameters, it may be possible to create polyolefin materials with a wide range of physical properties, in which it is possible to decouple properties that are normally closely correlated (such as heat of fusion and elasticity.

5. Morphology. Transmission electron micrographs illustrating some of the morphologies resulting from these syntheses are shown in Figure 8. In Figure 8a the product of a sequential synthesis (BB1), containing 47% ethylene–butene macromonomer, is shown to form a fine dispersion of noncrystalline (dark) particles, within a partially crystalline matrix. Typical particle sizes range from approximately 0.25 to 0.5 μm. In contrast,

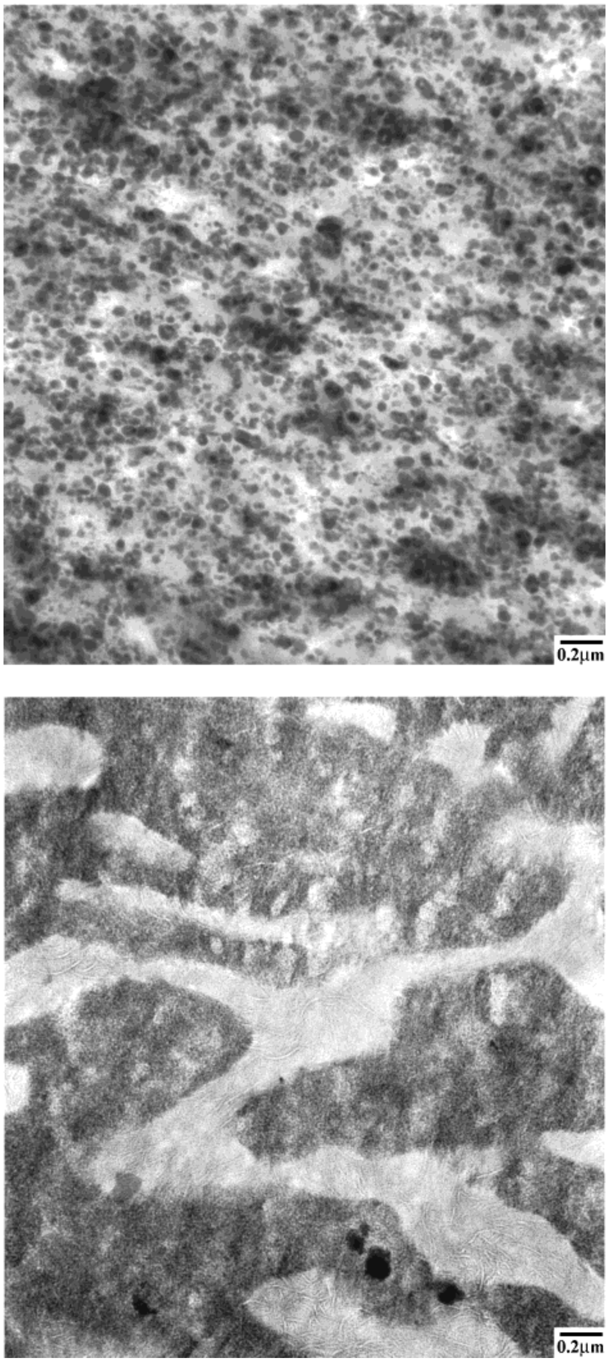


Figure 8. Transmission electron micrographs: (a, top) BB1 and (b, bottom) BB4.

the electron micrograph of the product of a simultaneous synthesis (BB4) reveals a co-continuous domain structure comprising semicrystalline and noncrystalline components. The phase boundaries between the components in BB4 are much less distinct than in BB1. Many lamellae, which originate in the semicrystalline regions, can be seen to penetrate the noncrystalline regions to a distance of approximately 100 Å. The more homogeneous morphology seen in BB4 gives rise to improved elastic recovery when compared to BB1.

Conclusions

Long chain branch–block copolymers from mixed metallocenes offer novel pathways to polyolefin-based thermoplastic elastomers. The mechanical properties of the resulting materials can be controlled by systematically varying polymer design in terms of branch and backbone composition, and length and branching concentration. In addition to elastic properties, the rheological characteristics of long chain branch–block copolymers are likely to be superior to their linear counterparts. In particular, it is expected that melt strength and processability will be improved.

With appropriate manipulation of the control variables it should be possible to prepare many classes of thermoplastic polymers, other than elastomers. The incorporation of macromonomers into polymeric backbones has the potential for creating hard elastic materials, impact-resistant copolymers, and various materials that could be useful as compatibilizers in immiscible blends. Work is currently in progress to probe the synthetic limits of this strategy and to examine the properties of thermoplastics produced.

Acknowledgment. The authors thank Material Characterization Lab staff for polymer characterization, especially G. M. Brown for TEM and A. Faldi and T. Sun for GPC-FTIR analysis. The permission to publish this work granted by ExxonMobil Chemical Company is also greatly appreciated.

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MA001087B