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Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization

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We report a catalytic system that produces olefin block copolymers with alternating semicrystalline and amorphous segments, achieved by varying the ratio of α-olefin to ethylene in the two types of blocks. The system uses a chain shuttling agent to transfer growing chains between two distinct catalysts with different monomer selectivities in a single polymerization reactor. The block copolymers simultaneously have high melting temperatures and low glass transition temperatures, and therefore they maintain excellent elastomeric properties at high temperatures. Furthermore, the materials are effectively produced in economically favorable, continuous polymerization processes.

During the past 50 years, polyolefins have become, by far, the highest volume commercial class of synthetic polymers. Olefin polymerization catalysts have evolved during this time from heterogeneous mixtures (*1*) to well-defined soluble molecules (*2*), allowing chemists to understand and control the effects of catalyst structure on polymer composition and microstructure. These advancements in catalysis have enabled the production of polyolefins with an exquisite degree of control over stereochemistry (*3*) and macromolecular branch architecture (*4*), leading to new classes of polymers with useful combinations of physical properties. However, the economical preparation of olefin block copolymers (*5*) having both "hard" (semicrystalline or high glass transition temperature) and "soft" (amorphous and low glass transition temperature) segments remains one of the major challenges in the field of polymerization catalysis. Here we report a method for the preparation of linear ethylene-based block copolymers with such properties by using chain shuttling polymerization.

A few strategies for preparation of stereoblock polyolefins have been reported in the recent literature (*6–9*). Despite the high melting temperatures exhibited by isotactic or syndiotactic polypropylenes (PPs), the relatively high glass transition temperatures of these materials ($T_g \sim 0°C$) limit their utility in elastomeric applications. More recently, olefin-based block copolymers have been made using living coordination polymerization catalysts (*10*). These catalysts, like living anionic (*11*), cationic (*12*), or radical (*13–15*) polymerization processes, can be used to achieve precise structural control in block copolymer synthesis through sequential monomer addition strategies. However, living polymerization processes are uneconomical because they produce only one polymer chain per catalyst molecule and operate in a batch polymerization process. In addition, the low reaction temperatures typically required to achieve living behavior with these systems inhibit the synthesis of materials containing more than one semicrystalline block because of premature precipitation of the polymer.

To circumvent the problems associated with previous strategies for the preparation of polyolefin block copolymers, we pursued the synthesis of these materials via a technique that we call "chain shuttling polymerization" (*16*). We define chain shuttling as the passing of a growing polymer chain between catalyst sites, such that portions of a single polymer molecule are synthesized by at least two different catalysts. Likewise, a chain shuttling agent (CSA) is a component such as a metal alkyl complex that facilitates this transfer. This approach can thus be used to prepare block copolymers from a common monomer environment by using a mixture of catalysts of different selectivities, namely stereoselectivity or monomer selectivity. Under the right conditions, efficient chain shuttling produces a linear multiblock copolymer that features alternating hard and soft blocks.

One key to forming differentiated block copolymers via chain shuttling is finding a monomer or combination of monomers that, on the basis of their arrangement in the polymer chain, can give rise to both hard and soft materials. Stereoblock PPs do not have the low glass transition temperatures required for most elastomeric applications. On the other hand, ethylene-based polymers that incorporate varying fractions of α-olefin fit this criterion. Polyethylenes (PE) with low co-monomer content are semicrystalline (hard) materials with melting temperatures (T_m) approaching 135°C, whereas PEs with high levels of comonomer are amorphous (soft) materials with very low glass transition temperatures ($T_g <$ –40°C). We therefore focused on ethylene-based block copolymers with both hard and soft segments, with the hypothesis that the benefits of both the high T_m and low T_g would be retained. To this end, we required a mixed catalyst system capable of producing these different types of polymer in a common reaction environment. A further important requirement is that each of the catalysts undergoes chain shuttling with a common chain shuttling agent.

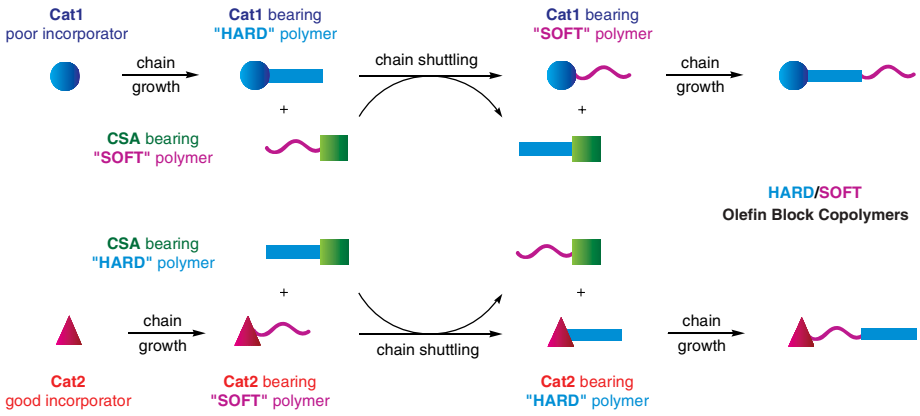

Fig. 1. Depiction of the likely chain shuttling mechanism in a single reactor, dual-catalyst approach. Cat1 (solid circles) and Cat2 (solid triangles) represent catalysts with high and low monomer selectivity, respectively, whereas the CSA (solid squares) facilitates the chain shuttling reaction. Cat1 produces a segment of hard polymer with low comonomer content. Shuttling occurs when this segment is exchanged with the CSA bearing a soft copolymer of higher comonomer content. Further chain growth at Cat1 then extends the soft copolymer chain with a hard segment, thus giving a block copolymer.

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This process (Fig. 1) requires one catalyst, Cat1, with high ethylene selectivity to form hard polymer chains. Meanwhile, a good incorporator of comonomer, Cat2, grows soft amorphous chains in the same reactor because of its dramatically different monomer selectivity. In the absence of chain shuttling, a polymer blend is produced with none of the advantageous properties of block copolymer architecture. In the presence of an effective CSA, however, polymer chains are swapped between catalysts before the chains terminate. To understand this swapping phenomenon, it is instructive to follow the lifetime of a representative polymer chain. The chain may begin growing on Cat1 as a hard polymer. The chain is then exchanged onto a CSA, where it is held for some period of time without growing. The dormant polymer chain may then return to another molecule of the same catalyst and lengthen the hard segment or it may shuttle to a molecule of Cat2, from which subsequent chain growth results in formation of a polymer chain with both soft and hard blocks. The process may be repeated any number of times during the lifetime of the chain before chain termination occurs via a usual mechanism such as hydrogenolysis. A statistical analysis of this chain shuttling phenomenon reveals multiblock copolymers with a most probable distribution of block lengths and number of blocks per chain. This microstructure is distinctly different from materials made with living polymerization techniques, which ideally have a Poisson distribution of block lengths and a precise number of blocks. Furthermore, the synthesis of these olefin block copolymers is not stoichiometrically limited by Cat1, Cat2, or CSA.

Furthermore, this approach enables precise control over polymer microstructure. Despite the differences in monomer selectivity between the two catalysts, fast rates of chain shuttling and judicious selection of process variables produce copolymers with homogeneous molecular weight and composition distributions. The overall composition, i.e., the hard-to-soft polymer ratio, can be easily controlled by the relative amount of the catalysts used. The comonomer content of the individual hard and soft blocks can be tailored by reactor feed or catalyst modifications. Finally, the average length of the blocks, which is a function of the relative rates of chain growth and shuttling, can be controlled simply by adjusting the ratio of concentrations of CSA and monomer ([CSA]/[C_2H_4]).

Selection of CSA and catalysts. It is well established in olefin polymerization that growing chains can be transferred from the catalyst to an added main-group metal in exchange for an alkyl group (i.e., chain transfer to metal) (*1*, *17*). This transfer is most often irreversible, leading to the termination of the growing chain and the initiation of a new polymer chain. However, the synthesis of block copolymers via chain shuttling requires this polymer chain transfer to be reversible. The main-group centers cannot act as a final repository for "dead" polymer chains; instead, they must serve as a reservoir of "live" chains that are intermittently reattached to catalyst centers for further growth. Chien (*7*) and Brintzinger (*8*) have independently claimed preparations of stereoblock PPs using reversible chain transfer between two catalyst centers with different stereoselectivities. However, polymer fractionation revealed that the samples were largely blends of isotactic and atactic PPs, with at most a small fraction of block copolymer. For single-catalyst systems, this process has been used to prepare long-chain metal alkyls (*18*–*22*) and has more recently been described as "catalyzed chain growth" (*23*, *24*). Gibson *et al.* have discussed the effects of catalyzed chain growth on molecular weight distribution, reporting that a Poisson distribution of molecular weights (M_w/M_n = 1, where M_w is the weight-average molecular weight and M_n is the number-average molecular weight) is expected under these conditions instead of the Schulz-Flory distribution (M_w/M_n = 2), observed when chain termination occurs (*24*). This behavior provides an easy means of probing the capabilities of a catalyst system for chain shuttling polymerization.

Given the multitude of olefin polymerization catalysts, it was daunting to identify a pair of catalysts with substantially different monomer selectivities that are also capable of chain shuttling. Furthermore, the chosen system also needs to operate at a high solution-reaction temperature ($T \geq 120°C$) to prevent undesired polymer precipitation. We therefore adopted a high-throughput method to expedite this discovery process. The technique uses a parallel screen of the effects of metal alkyl reagents on the molecular weight and molecular weight distributions of polyethylenes produced by catalyst/CSA combinations. These criteria provide a simple test for finding catalyst/CSA combinations suitable for use in our dual-catalyst system (Fig. 2).

To begin the selection process, we first selected representative examples from a broad variety of catalyst structure types known to have high polymerization rates. Two examples are shown in Fig. 2. Ethylene polymerizations were then carried out with these catalysts, in combi-

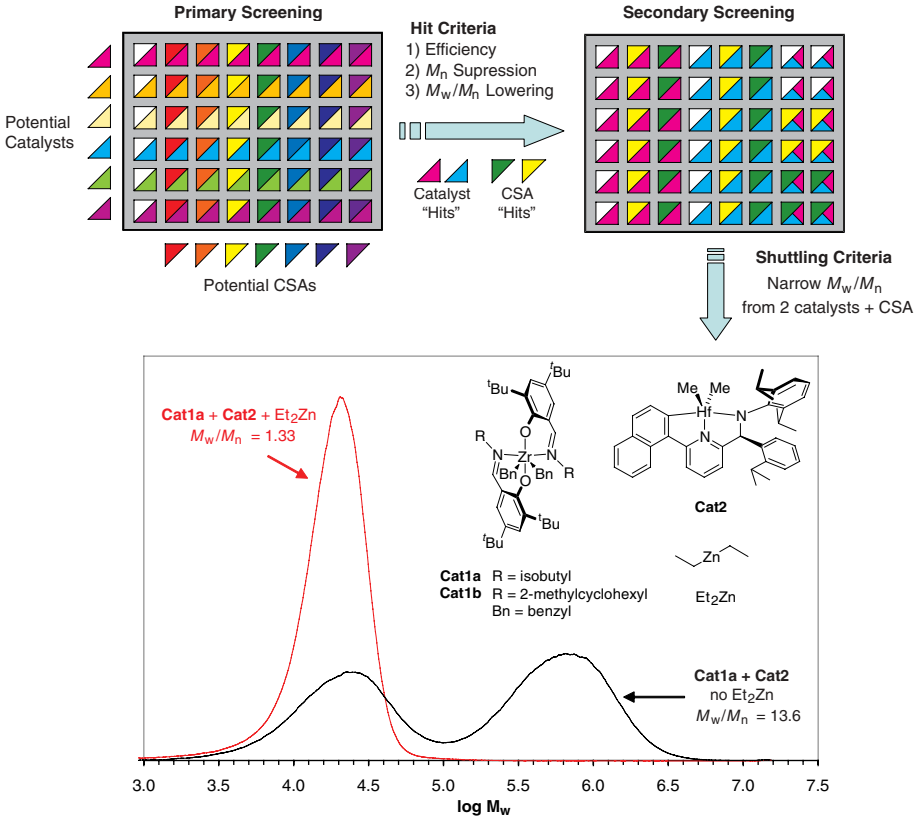

Fig. 2. High-throughput screening protocol and selected data from the chain shuttling screen. Polymerizations are conducted in a parallel grid of individual computer-controlled reactors with robotic addition of reagents and real-time monitoring, coupled with high-throughput characterization techniques. Primary screening involves a broad screen of several catalysts in combination with many potential shuttling agents. Combinations that result in good efficiency, lower molecular weight (M_n), and narrower molecular weight distribution (M_w/M_n), are considered hits. These hits are then subjected to a secondary screen, including individual catalyst and dual-catalyst/CSA combinations. Structures of **Cat1a**, **Cat1b**, **Cat2**, and the CSA are depicted. Shuttling for this trio is demonstrated by the coalescence of the bimodal molecular weight distribution by adding Et_2Zn to the dual-catalyst system.

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nation with a number of potential CSAs using high-throughput screening techniques (*25*). By using an array of robotically manipulated individual polymerization reactors combined with rapid polymer characterization methods, we conducted and evaluated more than 1600 individual polymerizations over a three-week period, a feat that would have taken several months using conventional techniques.

Catalyst efficiency, estimated by polymer yield, eliminated several of the potential CSAs due to their inhibition of polymerization. For those combinations that produced a sufficient amount of polymer for characterization, the molecular weight and molecular weight distribution of the polyethylene were then compared with a control polymer prepared with no added CSA (*26*). A reduction in M_n in combination with a narrowing of the molecular weight distribution (M_w/M_n) indicated a "hit" for chain shuttling behavior (*27*). A zirconium bis(phenoxyimine) catalyst (*28*), **Cat1a**, and a hafnium pyridylamide (*29*), **Cat2**, displayed significant differences in monomer selectivity and also showed characteristics of chain shuttling by using diethylzinc (Et_2Zn) as the CSA. Similar bis(phenoxyimine) catalysts have also been shown to exhibit characteristics of catalyzed chain growth (*30*). Also, whereas catalyzed chain growth on aluminum and magnesium has been well-documented, only recently has this phenomenon been claimed to occur on zinc (*23*, *24*, *30*).

After this dual-catalyst/CSA combination was identified, a secondary screening process was conducted to further validate the shuttling capability of these hits. This process involved evaluation of both individual catalyst/CSA combinations, as well as mixed catalyst experiments in the high-throughput reactor. Individual catalysts were screened to evaluate the effect of different catalyst/CSA ratios on M_n and M_w/M_n. Dual-catalyst experiments provided further confirmation of the shuttling behavior of this system. A mixture of **Cat1a** and **Cat2** produced a copolymer with a 1-octene content intermediate between those afforded by the individual catalysts, indicating that both catalysts were active in the polymerization. The copolymer had a high molecular weight (M_w = 446,000 g/mol) and a broad, bimodal molecular weight distribution (M_w/M_n = 13.6), indicating a large difference in propensities of the two catalysts for chain termination or transfer (Fig. 2). Introduction of Et_2Zn as the CSA resulted in the formation of copolymers with lower molecular weight and extremely narrow molecular weight distributions. The addition of 50 equivalents of Et_2Zn to the total catalyst metal in the mixed catalyst system gave a copolymer with M_w = 20,300 g/mol and M_w/M_n = 1.33. The resulting copolymer was again of intermediate comonomer composition, indicating that both catalysts were active. This observation of a very narrow molecular weight distribution copolymer produced by a mixture of catalysts with drastically different molecular weight capability and monomer selectivity indicates fast rates of chain shuttling with this dual-catalyst CSA system.

Although the initial dual-catalyst system met all the necessary requirements for production of olefin block copolymers, we decided to screen a small library of bis(phenoxyimine) catalysts in an attempt to increase the difference in monomer selectivities in our dual-catalyst system. A similar high-throughput screening approach allowed us to quickly evaluate these new catalysts for ethylene selectivity and chain shuttling characteristics. A simple replacement of the isobutyl substituent on the ligand of **Cat1a** with a 2-methylcyclohexyl moiety resulted in a catalyst, **Cat1b**, with higher molecular weight and ethylene selectivity and much stronger chain-shuttling response in the presence of Et_2Zn (*26*). We therefore decided to conduct dual-catalyst block copolymer synthesis with the combination of **Cat1b**, **Cat2**, and Et_2Zn.

Olefin block copolymers in a continuous process. The dual-catalyst process described above can be conducted in either a batch or in a continuous-polymerization reactor (*31*), but there are marked differences between the two. First, the catalyst onset and decay profiles are not an issue in a continuous process, because catalysts are continuously supplied and removed to give steady-state concentrations. In contrast, different catalyst deactivation rates in a batch system can lead to polymer inhomogeneities. For example, if Cat2 dies faster than Cat1, the total polymer may contain whole chains of hard polyethylene.

A second, more subtle difference is that shuttling occurs more efficiently in a continuous process. Typical CSAs begin as simple metal alkyl species such as Et_2Zn. The initial chain-transfer event with Et_2Zn involves exchange of an ethyl moiety for a polymer chain, which initiates growth of a new polymer chain but does not produce any polymer blockiness. Statistically, this event predominates over chain shuttling early in the course of the reaction. Only later in the reaction is the concentration of zinc-polymeryl species sufficient to enable true chain shuttling. In a continuous process, the reactor is populated with a steady-state concentration of these zinc-polymeryl species. Because the volume of the reactor is large compared with the volume of the continuous feed, the ratio of zinc-polymeryl species to fresh Et_2Zn is very high. Thus, polymeryl interchange predominates over ethyl-for-polymeryl exchange. In addition, the zinc alkyl compounds exhibit higher thermal stability than many catalysts. At high reactor temperatures, catalyst molecules often deactivate before exiting, but the zinc species continue to participate in chain shuttling throughout their entire residence time.

Operating an efficient chain shuttling system in a continuous process also affects the molecular weight distribution of the resulting copolymer. Extremely narrow molecular weight distributions can be achieved with fast chain shuttling between two different catalysts in a batch process. However, the same chemistry in a continuous process results in a Schulz-Flory molecular weight distribution simply because there is a distribution of residence times in a continuously-fed reactor (*32*). This feature is beneficial, because copolymers with broader distributions of molecular weights are typically easier to process.

To realize the full potential of chain-shuttling polymerization for making ethylene-based block copolymers, experiments were conducted with this dual-catalyst chain shuttling system in a continuous solution polymerization reactor. A series of ethylene-octene copolymers of similar melt index (i.e., molecular weight) were produced with a composition of ~30 weight percent (wt %) hard blocks and 70 wt % soft blocks. The level of Et_2Zn, reported in Table 1 as a $[Zn]/[C_2H_4]$ molar ratio, was

Table 1. Process details and properties of ethylene-octene block copolymers from the chain shuttling system in a continuous process.

Sample	Description	Catalyst package	$[Zn]/[C_2H_4]$* ($\times 10^3$)	Density (g/cm^3)	Efficiency (kgP/gM)	M_w† (g/mol)	M_w/M_n†	Chains per Zn‡	Chains per (Hf + Zr)‡	T_m§ (°C)	ΔH_f§ (J/g)
1	Soft PE	Cat2 + Et_2Zn	1.87	0.862	95.2	110,000	1.97	2.7	230	37	32
2	Hard PE	Cat1b + Et_2Zn	2.07	0.938	127	65,000	1.95	4.6	2,200	124	184
3	Blend	Cat1b + Cat2	–	0.890	258	137,300	13.8	–	3,600	125	90
4	Low CSA	Cat1b + Cat2 + Et_2Zn	0.56	0.883	261	129,000	3.22	12	820	124	68
5	Mid CSA	Cat1b + Cat2 + Et_2Zn	1.40	0.883	244	118,500	2.23	3.6	630	121	69
6	High CSA	Cat1b + Cat2 + Et_2Zn	2.39	0.879	118	104,600	1.97	1.9	260	120	60

*The $[Zn]/[C_2H_4]$ ratio is defined as the molar ratio of CSA to ethylene in the reactor. †Determined by GPC relative to polystyrene standards. ‡Chains per Zn was calculated by using the zinc feed and polymer production rates and the number-average molecular weight of the resulting copolymer corrected for comonomer content. Similarly, chains per (Hf + Zr) was estimated by using the total catalyst metal feed. §Melting point (T_m) and heat of fusion (ΔH_f) were determined by differential scanning calorimetry (DSC).

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systematically varied to study the effects of the ratio on polymer microstructure.

The set of experiments was begun with only **Cat2** to produce a copolymer with a density of 0.862 g/cm^3 by adjusting monomer feed rates and catalyst and cocatalyst flows (*26*). Molecular weight control was achieved with a mixture of Et_2Zn and hydrogen, which were adjusted to reach a M_w of 110,000 g/mol (sample 1). **Cat2** feed was then stopped, and **Cat1b** was introduced to the reactor under identical reactor conditions. The higher ethylene selectivity of this catalyst resulted in an increase in the measured polymer density to 0.936 g/cm^3. The large difference in comonomer content between these two copolymers, made under similar reaction conditions, demonstrates the substantial difference in the monomer selectivity of the two catalysts. The molecular weight of this hard comonomer–poor material was also much lower, indicative of faster chain termination (primarily by reaction with H_2) for this catalyst system. Et_2Zn feed was maintained, but some hydrogen was removed to give a polymer with M_w = 65,000 g/mol (sample 2).

These two baseline polymerizations provided an estimate of the catalyst ratio necessary to achieve the desired composition for the dual-catalyst product; an overall density of ~0.88 g/cm^3 was targeted to give the desired copolymer composed of 30% high-density material (*33*). As a control, a mixture of **Cat1b** and **Cat2** was added to the reactor under the same process conditions with no Et_2Zn, giving a reactor blend of the two component copolymers with an overall density of 0.89 g/cm^3. Hydrogen was added to give a polymer with M_w = 137,300 g/mol (sample 3), which was a simple blend of hard and soft PE made independently by the two catalysts. Et_2Zn was then added to induce chain shuttling between the two catalysts. Products were produced at three different levels of blockiness, controlled by the ratio of concentrations of Et_2Zn to ethylene ([Zn]/[C_2H_4]). Sample 6 was made with the highest Et_2Zn level possible, while still achieving the desired molecular weight.

Characterization of block copolymers. During this set of experiments, it was apparent by eye that this dual-catalyst chain shuttling system was producing desirable block copolymers at higher CSA levels. Physical blends of high-density and linear low-density PE are opaque because of the large high-density PE crystallites and the immiscibility of the two copolymers. However, the copolymers made at higher [Zn]/[C_2H_4] ratios are surprisingly transparent, despite having essentially identical octene content (Fig. 3). This difference is a clear indication that the copolymers produced with Et_2Zn have a very different microstructure than the physical blend of sample 3. We attribute the enhanced clarity to a decrease in crystallite size of the high-density blocks when the average block length is shorter.

From gel permeation chromatography (GPC), we found that the copolymer prepared without Et_2Zn was clearly bimodal, with M_w/M_n = 13.8 (Fig. 4). The GPC trace was deconvoluted into components of M_w ~ 240,000 and ~9600 g/mol, with the high–molecular weight, low-density copolymer making up 64 wt % of the overall material. This large molecular weight split reflects the differing propensities for hydrogen-induced termination between the two catalysts. The molecular weight distribution narrows as Et_2Zn is added, as expected for an efficient chain shuttling polymerization. At the highest Et_2Zn level, a most probable molecular weight distribution (M_w/M_n = 1.97) is obtained (sample 6). This narrow molecular weight distribution is normally associated with a single catalytic species and is indicative of the multiblock nature of the copolymer, because several shuttling events are required to generate such a homogeneous molecular weight distribution.

This molecular weight response clearly indicates that chain-shuttled ethylene-octene block copolymers, rather than blends, are formed upon introduction of Et_2Zn. The M_n can also be used in conjunction with the Et_2Zn feed and polymerization rate to calculate the number of chains produced per Zn molecule. The low Et_2Zn level of sample 4 results in the production of approximately 12 chains per Zn. However, the reaction is practically stoichiometric at higher Et_2Zn (no H_2), with the production of sample 6 resulting in 1.9 chains per Zn (or ~1 chain per Zn-alkyl moiety). This result indicates that almost every polymer chain exits the reactor bound to the CSA with very little chain termination, demonstrating the efficiency of the chain shuttling reaction.

Despite the stoichiometric nature of the reaction with the CSA, a similar calculation of the number of chains per catalyst molecule reveals that the polymerization is highly catalytic in the hafnium and zirconium species. Block copolymers produced with living polymerization techniques are inherently expensive, because the living nature of the polymerization makes it necessary to use one molecule of catalyst for each chain produced. In contrast, the chain shuttling methodology is capable of generating hundreds to thousands of olefin block copolymer chains per catalyst. For example, the synthesis of sample 6 resulted in the formation of ~260 chains per total catalyst. This feature allows these olefin block copolymers to be produced far more cheaply than materials available from living polymerization techniques.

Fig. 3. Image of compression-molded samples (thickness = 0.35 mm), illustrating the effect of chain shuttling on clarity. Sample 3 is a physical blend of high- and low-density polymer and is opaque. Adding Et_2Zn during polymerization results in a block copolymer microstructure with intimately mixed interchain hard and soft segments, resulting in the increased transparency of samples 4 to 6.

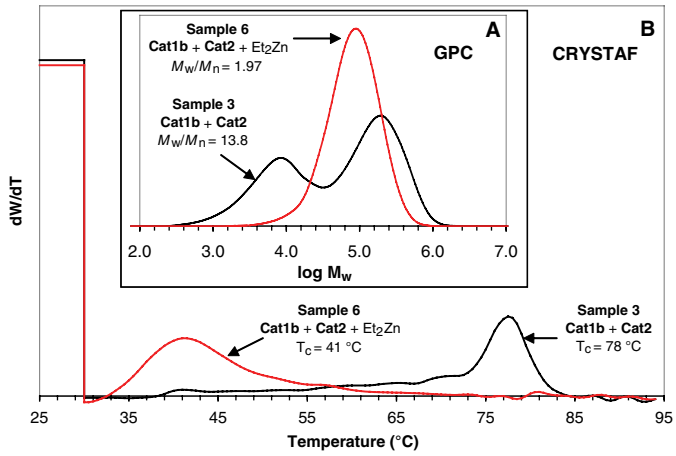

Fig. 4. Characterization of copolymers produced with the dual-catalyst chain shuttling system in a continuous process. Samples 3 (**Cat1b** + **Cat2**) and 6 (**Cat1b** + **Cat2** + CSA) are depicted. (**A**) GPC reveals a bimodal molecular weight distribution in the absence of CSA, whereas adding CSA homogenizes the copolymer to a most probable distribution (M_w/M_n = 2). (**B**) Crystallinity distributions as revealed by crystallization analysis fractionation (CRYSTAF). Sample 3, prepared in the absence of CSA, displays a bimodal composition distribution with a peak around 78°C from **Cat1b** and an amorphous soluble fraction from **Cat2**. Adding CSA gives a copolymer that crystallizes from solution at a much lower temperature, with no indication of highly crystalline material.

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The comonomer distributions of these new materials, as revealed by crystallization analysis fractionation (CRYSTAF), were also indicative of their homogeneous multiblock nature. As expected, the hard polymer from **Cat1b** crystallized from solution at ~80°C, whereas the soft copolymer from **Cat2** was completely soluble at the lowest temperature studied (30°C). Sample 3, prepared with both catalysts in the absence of a CSA, displayed behavior consistent with a physical blend of these two component copolymers (Fig. 4). The characteristic peak for the high density material at 80°C was completely absent for the dual-catalyst sample made at the highest Et_2Zn level (sample 6), and a new peak appeared at 41°C. A typical ethylene-octene random copolymer (RCP) with a density near 0.88 g/cm^3 was completely soluble in 1,2,4-trichlorobenzene at room temperature and eluted in the soluble fraction. A peak at 41°C would be expected for an RCP only if it were of considerably higher density (~0.90 g/cm^3). We attribute this unique crystallization behavior to the block copolymer microstructure, in which the amorphous domains disrupt the crystallization of the semicrystalline high-density segments.

The melting temperatures of these chain-shuttled copolymers were also indicative of their unusual microstructure. In polyethylene-based materials, comonomers such as butene and octene are introduced to disrupt crystallinity and to provide elasticity to the resulting polymer products. For common RCPs, both the melting point and modulus (hardness) are direct functions of the comonomer content (Fig. 5). It should be possible to break this longstanding product-property relationship by incorporating multiple regions of crystallizable and amorphous polymer segments in single polymer chains. This phenomenon is evident in the thermal characteristics of these copolymer samples. The hard polymer from **Cat1b** (sample 1) undergoes a sharp melting transition at 124°C, whereas the soft copolymer from **Cat2** (sample 2) displays a very weak melting peak at 37°C (Fig. 5). All of the chain-shuttled copolymers have melting peaks within a few degrees of the material produced by **Cat1b** alone (Fig. 5). As $[Zn]/[C_2H_4]$ is increased, the T_m decreases slightly, dropping to 120°C at the highest CSA level examined. We hypothesize that this decrease in T_m is related to the length of the hard blocks, which become shorter as more CSA is added (*34*). More importantly, these materials display excellent elastomeric properties at temperatures far higher than those of traditional RCPs of similar density, allowing these olefin block copolymers to be used in high-temperature applications.

Outlook. The economical production of olefin block copolymers has been a goal of academic researchers and polymer manufacturers alike. Tremendous progress toward this end has been achieved in recent years with the discovery of several designer catalysts capable of living olefin polymerization. However, the stoichiometric nature of the living process, coupled with related process limitations of low polymerization temperatures and slow batch processes, have prevented these approaches from achieving widespread application. The chain shuttling system described above overcomes these challenges, providing an economical means for production of polyolefins that display advantaged combinations of physical properties. The statistical multiblock architecture afforded by the chain shuttling process, with its distribution of block lengths and number of blocks per chain, is not easily accessible by any other means. The olefin block copolymers maintain excellent elastomeric properties at temperatures far higher than traditional ethylene-based elastomers (*35*), allowing them to be used in high-performance applications long inaccessible to polyolefins.

Although this technology introduces a solution to a long-standing challenge, it also poses several new questions. We anticipate future efforts will lead to further elucidation of the kinetic and mechanistic intricacies of chain-shuttling reactions, discoveries of catalysts with improved performance, and application of this technology to other polymer systems.

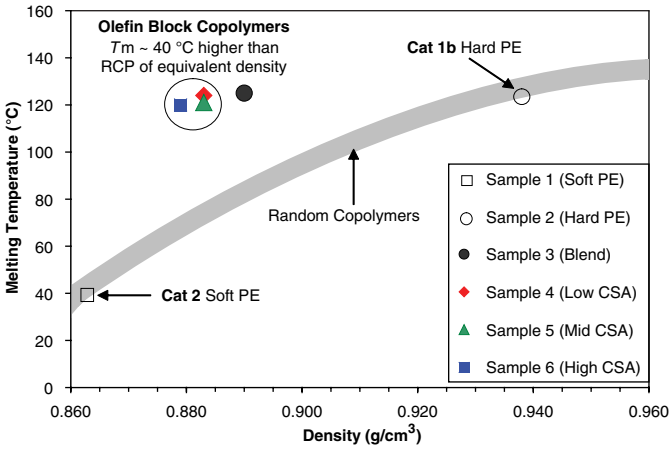

Fig. 5. Melting temperature of ethylene-octene copolymers as a function of density. Chain shuttled materials are compared to RCPs. A gray band representing ethylene-octene random copolymers and samples 1 (open squares), 2 (open circles), 3 (solid circles), 4 (solid diamonds), 5 (solid triangles), and 6 (solid squares) are displayed. Although the melting behavior of the copolymers from **Cat1b** and **Cat2** are similar to those of RCPs, the dual-catalyst chain-shuttled materials display melting temperatures >40°C higher than those of RCPs of equivalent density. The melting temperatures of the dual-catalyst samples decrease with increasing $[CSA]/[C_2H_4]$ ratio, indicative of shorter block lengths at higher CSA levels.

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REPORTS

Producing Ultrastrong Magnetic Fields in Neutron Star Mergers

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We report an extremely rapid mechanism for magnetic field amplification during the merger of a binary neutron star system. This has implications for the production of the short class of gamma-ray bursts, which recent observations suggest may originate in such mergers. In detailed magnetohydrodynamic simulations of the merger process, the fields are amplified by Kelvin-Helmholtz instabilities beyond magnetar field strength and may therefore represent the strongest magnetic fields in the universe. The amplification occurs in the shear layer that forms between the neutron stars and on a time scale of only 1 millisecond, that is, long before the remnant can collapse into a black hole.

The orbital decay of a neutron star binary system as a result of the emission of gravitational waves is one of the prime targets of gravitational wave detectors such as the Laser Interferometer Gravitational-Wave Observatory (*1*) or GEO600 (*2*). Moreover, the long-suspected connection of neutron star binaries to gamma-ray bursts (GRBs), the most luminous explosions in the universe, has received solid support from the first detections of afterglows from the short class of GRBs (*3*–*5*). Unlike their long-duration cousins (which are associated with the deaths of massive stars), short GRBs occur systematically at lower redshifts, in galaxies both with and without star formation, and are not accompanied by a supernova explosion. The millisecond variability observed in the light curves of short GRBs suggests that a compact object, either a neutron star or a stellar mass black hole, acts as the central engine.

The observed cosmological distances imply that large energies are involved; so, relativistic outflows with Lorentz factors of several hundreds are required to avoid the so-called "compactness problem" (*6*). To reach such extreme velocities, a large amount of energy has to be deposited per rest mass, for example, by the annihilation of neutrino-antineutrino pairs, $\bar{\nu}_i + \nu_i \rightarrow e + e^+$, or through magnetic mechanisms (*7*, *8*). Therefore, strong magnetic fields have been suggested as being important in producing GRBs (*9*–*13*), but the question of what field strengths can actually be reached in a merger remnant before it collapses to a black hole has so far remained unanswered. Recently, a very energetic giant flare from the magnetar SGR 1806-20 has been observed (*14*, *15*). If it had been farther away, but within 40 Mpc, its initial spike would—both on grounds of duration and spectrum—have been interpreted as a short gamma-ray burst. The lack of excess events from the direction of the Virgo cluster, however, suggests that only a small portion of previously observed short bursts could have been giant magnetar flares. Nevertheless, the similarity in physical properties may point to a common or similar mechanism behind both phenomena.

Although computer simulations of binary neutron star mergers have reached a good degree of realism (*16*–*19*), none has so far been able to take magnetic fields into account, primarily because of the numerical challenge posed by simulating even the hydrodynamics of the merger process. Here, we present global neutron star merger simulations that follow the evolution of the magnetic field. Our main result is that the existing neutron star magnetic fields (10^{12} G) become amplified by several orders of magnitude within the first millisecond after the merger, which is long before the collapse to a black hole can proceed. Our robust lower limit on the field that can be reached is 2×10^{15} G, but it is highly probable that much stronger fields are realized in nature.

Our simulations are three-dimensional computer simulations of two neutron stars that coalesce because of the emission of gravitational waves. The equations of hydrodynamics are solved with a Lagrangian particle scheme (smoothed particle hydrodynamics) [for a review see (*20*)] that is coupled to a temperature- and composition-dependent nuclear equation of state (*17*, *21*). We include the effects of cooling and the change in matter composition due to neutrino-producing weak interactions. Because the debris material covers the full range from completely opaque to completely transparent to neutrinos, we have to incorporate opacity effects. Thus, on an additional grid, we calculate for each fluid parcel the opacities for each neutrino species and take them into account in the emission process (*18*). The Newtonian self-gravity of the neutron star fluid is evaluated efficiently using a binary tree algorithm. In addition, we apply forces that emerge as a result of the emission of gravitational waves (*17*); these are the forces that drive the binary toward coalescence. The new physics employed in these simulations is the inclusion of magnetic fields. To ensure the robustness of our results, we apply two different methods: one using a recently developed algorithm for "smoothed particle magnetohydrodynamics" (*22*) and one using a method in which the magnetic field is calculated from the so-called "Euler potentials," α and β, that are advected with each fluid particle (*23*). The magnetic field is calculated from these potentials according to

$$\mathbf{B} = \nabla\alpha \times \nabla\beta \qquad (1)$$

This prescription has the advantage that the divergence constraint ("no monopoles condition") on the magnetic field is satisfied by construction. Apart from this difference, both methods yield similar results. The computational costs are dominated by the calculation of self-gravity; the costs for the magnetic fields, the equation of state, and the neutrino physics are negligible by comparison.

Our initial neutron stars are cold and have masses of 1.4 solar masses ($M_\odot$) each. The two stars are placed at an initial separation of 48 km with velocities corresponding to a circular orbit around their common center of mass. Because the inspiral dynamics only allows for a short time of tidal interaction, the neutron stars cannot be spun up substantially (*24*); therefore, we start

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