Materials Properties Derived from INSITE Metallocene Catalysts

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Novel metallocene catalysts for the synthesis of ethylene/α-olefin copolymers are reviewed here. The technology used—single-site constrained geometry catalyst technology—is demonstrated to be useful for the preparation of a wide array of copolymers with unique materials properties, such as a high melt fracture resistance, as illustrated in the Figure.

1. General Aspects and Challenges of Catalysis

Over the past decade, the development of Dow’s INSITE (trademark of The Dow Chemical Co.) metallocene catalysts has led to the launch of many new polyolefin product lines that had been previously unattainable from conventional Ziegler–Natta catalysis.[1] From a structure–activity perspective, the catalyst ligand structures are readily tailored synthetically from both an electronic and steric point of view. This alteration motif has led to the development and screening of several hundred ansa-cyclopentadienyl amido group IV metal constrained-geometry catalysts (CGCs), which have been evaluated for the preparation of a wide array of ethylene/α-olefin copolymers possessing unique materials properties.[2]

The catalyst precursor or procatalyst (see Scheme 1) contains a group IV metal, preferably titanium, which can be activated either as the TiIV dialkyl or TiII diene complex.[3] The procatalyst is inactive for olefin polymerization and may be activated through the use of modified methylalumoxane (MMAO) and electron-deficient boranes such as tris-perfluorophenylborane (FAB). Alternatively, the procatalyst may be activated through the use of preformed, non-coordinating counterions, which are appropriately ion-paired with protonated ammonium or trityl salts. The nature of the catalytically active species derived from TiIV analogues under polymerization conditions has recently been reviewed.[4] It is clear from our studies that variation of the Lewis acid components of the catalyst package can affect parameters such as efficiency, comonomer incorporation, $M_w$, polydispersity, and more importantly, polymer microstructure and stereoregularity. These parameters are far more dramatically affected by the structural variation of the base ligand structure through different synthetic approaches.[5]

Dow has focussed on catalyst structures that have outstanding efficiency or turnover number (typically in excess of 5–7 × 10^6 kg polymer/kg metal) at high temperature (140–180 °C) as well as a high propensity for incorporating α-olefin comonomer throughout the polyethylene backbone. The quest for high catalyst activity at higher temperature is economically driven since higher temperature activity relates to faster polymerization kinetics and higher throughput of product in existing plant facilities. Dow has recently developed a series of heteroatom-containing catalyst systems that show outstanding performance at higher temperatures with excellent efficiency and $M_w$.[6]

At these high temperatures the active catalysts are not “living” (i.e., one polymer chain per catalyst metal site) and as polymerization proceeds via monomer insertion into the metal–carbon bond of the growing polymer chain, a termination event may occur via β-hydride elimination of the chain.[7] This event produces an α-olefinic macromer and a metal hydride catalyst species, the latter being capable of producing a new...
polymer chain via the same monomer initiation/propagation process. An important consequence of this repetitive process is that numerous polymer chains, typically $3-5 \times 10^3$ per metal center, are generated from a single catalyst site. Another sought after feature of these systems is their ability to re-incorporate the \(\alpha\)-olefinic macromer into another propagating polymer chain, much like a short chain \(\alpha\)-olefin. This phenomenon leads to long-chain branching (LCB) in the polymer microstructure, rendering the polymer highly processable under melt-flow operations such as extrusion. The unique materials properties imparted by LCB to the polymer structure will be subsequently enumerated.

Heterogeneous catalysts for Ziegler–Natta polymerizations have in general suffered from the inability to incorporate substantial amounts of \(\alpha\)-olefin under high-temperature, solution conditions. A second and more demanding challenge involves the synthesis of catalyst structures that will not only provide good \(\alpha\)-olefin reactivity, but will allow the incorporation of diene monomers (e.g., butadiene, isoprene, ethylidene norbornene) or styrene (S) into the polymer backbone. Diene monomers are frequently strong poisons for the activated metallocene species, but are important for the production of ethylene propylene diene monomer (EPDM) rubbers and new lines of extended thermoplastic olefins (TPOs). We have successfully identified several catalysts based upon indenyl structures that are capable of producing these materials in a high-temperature, solution process. We have likewise developed catalysts capable of incorporating variable amounts of aromatic olefins such as S into the ethylene (E) backbone (ethylene styrene inter polymers, ESIs), giving rise to a new family of materials.[8]

The ultimate and largely unmet challenge in E/\(\alpha\)-olefin
copolymerization involves the discovery of industrially feasible catalysts for the incorporation of heteroatom-functionalized or so-called polar comonomers into the polymer backbone.[9] These would include commercial monomers such as acrylate esters, acrylonitrile, vinyl acetate, and vinyl chloride to name a few. The ability to copolymerize these monomers with E or propylene could enable the production of low-cost TPOs that could rival engineering thermoplastics and condensation polymers in terms of materials performance at a fraction of the cost. Clearly many group IV single-site catalysts (SSCs), including our portfolio, do not yet meet this rigorous catalytic challenge. A final note on stereoregular polymers is in order relative to CGCs. These catalysts for the most part lack C2 or pseudo-C2 symmetry and do not provide predominately isotactic polypropylene via a site-control mechanism.[10] The most cost-efficient systems for the production of the latter may still remain in the realm of Ziegler–Natta heterogeneous catalysis.[11]

In addition to the first generation of INSITE catalysts, a new array of Dow CGCs have evolved for many of these expanded challenges. In summary, this portfolio of catalysts has afforded the ability to incorporate more α-olefin, produce greater LCB, incorporate dienes and aromatic olefins into an E polymer backbone, and provide higher plant productivity at higher temperature. The materials properties of these unique polymers derived from novel catalysts will be described in this review.

2. Ethylene Polymers and Copolymers

E polymers and copolymers are the most widely used polymers in the world today. World consumption of these polymers reached 49 million metric tons in 1999 with a compounding growth rate of approximately 6% annually. Applications for these polymers include food-packaging film and containers, waste-disposal bags, can liners, industrial packaging film and containers, toys, appliances, and many others in the forms of foam, film, molded parts, etc.

E polymers and copolymers are produced by homo-polymerization of E or co-polymerization of E with an α-olefin comonomer. The polymer can be produced by a radical polymerization process using a free-radical initiator in a high pressure reactor (15 000–30 000 psig), or by a transition-metal-catalyzed, coordination-insertion polymerization process at a moderate pressure (usually less than 500 psig).

High-pressure radical polymerization produces E homopolymer with many long branches of undetermined length and short branches, mostly two or four carbons along the polymer backbone. The long branches have a significant effect upon the melt properties, and the short branches affect the solid-state properties (crystallinity, modulus, etc.). This class of polymer is called low-density polyethylene (LDPE).

Polymers produced using Ziegler–Natta-type transition-metal catalysts are linear and contain no long branches. Homopolymerization of E via this process yields a linear polymer, which can be crystallized into a high-crystallinity, high-density polymer, called high-density polyethylene (HDPE). Copolymerization of E and α-olefin comonomer using the Ziegler–Natta catalyst yields linear polymer with short branches (from the α-olefin comonomer) along the polymer backbone. This class of polymer is called linear low-density polyethylene (LLDPE) because the short branches in the polymer backbone partially inhibit the crystallization of the polymer and result in a lower density, lower crystallinity polymer. At similar molecular weight, LLDPE generally is tougher than both LDPE and HDPE because of a higher content of tie molecules. This fundamental will be discussed later in this section.

Recent developments in SSC technology, including metallocene catalysts and constrained-geometry catalysts developed by Dow, have enabled the polyolefin industry to develop and commercialize many new families of homogeneous E/α-olefin copolymers with enhanced properties. The previous section in this article discussed the various types of SSCs used by the industry. This section will focus on the solid-state structure and properties of the homogeneous polyethylene copolymers produced by SSC technology.

2.1. Molecular Structure of Polyethylene Copolymers Made by Single-Site Catalyst Technology

Dow’s single-site constrained geometry catalyst technology is capable of producing polyolefin copolymers with well-defined molecular structure. The unique molecular structure for the polyethylene copolymers made by this technology is discussed below.

2.1.1. Comonomer Distribution

Because of the significant effect of the α-olefin comonomer on the properties of the polymer, it is critical to understand and to measure the comonomer distribution in the polymer backbone. Intermolecular comonomer distributions can be measured by the temperature rising elution fraction (TREF) technique.[12] As illustrated in Figure 1, the comonomer distri-

![Fig. 1. Comonomer distribution of E/octene copolymers measured by TREF.](https://example.com/fig1.png)
bution for a homogeneous E/octene copolymer prepared by the CGC is much narrower than that of a conventional LLDPE, which is a mixture of different kinds of polymer molecules that have different levels of \( \alpha \)-olefin comonomer incorporated in the polymer backbone.

The narrow TREF curve for the homogeneous copolymer signifies that the number of comonomer units per unit chain length between the homogeneous copolymer molecules is very similar, while the number for heterogeneous molecules is not. However, although the intermolecular comonomer distribution for the homogeneous polymer is very narrow, this does not mean that the intramolecular comonomer distribution is uniform. The narrow intermolecular comonomer distribution for the homogeneous polymer arises from the single-site nature of the CGC. The uniformity of the intramolecular comonomer distribution, however, is dictated by the reactivity ratio of the monomer and the comonomer \((r_1/r_2)\) to the catalyst. From the polymer property point of view, intramolecular comonomer distribution in homogeneous copolymers made by SSC technology can have a significant effect on the solid-state structure and properties of the polymer (e.g., thermal properties, dynamic mechanical properties, etc.).

To address the issue of the effect of intramolecular comonomer distribution on polymer properties of a homogeneous polymer, the structural characteristics for CGC E/octene copolymers were modeled using Monte-Carlo simulation.\(^\text{[13]}\) Figure 2 illustrates the intramolecular comonomer distribution for three CGC copolymers, from 0.87 g/cm\(^3\) to 0.92 g/cm\(^3\) density, in terms of E block length between comonomers. Between the short branches, and the distribution is also narrower. This well-defined unique comonomer distribution has a significant effect on many polymer properties, such as crystal morphology, tie chain formation, modulus, optical properties, etc., and is one of the key molecular architecture tools for designing new polyethylene products such as elastomers, plasticomers, and enhanced polyethylenes\(^\text{[14-19]}\).

2.1.2. Molecular Weight Distribution

Homogeneous E/\( \alpha \)-olefin copolymers prepared by SSC technology exhibit a narrow composition distribution. Copolymers prepared by conventional Ziegler–Natta catalysts have a molecular weight distribution (MWD) usually larger than three while the MWD of homogeneous polyolefins made by SSC technology is usually less than 2.5. MWD, or polydispersity, is the ratio \(M_w/M_n\), where \(M_w\) is the weight average molecular weight and \(M_n\) is the number average molecular weight. Figure 3 compares GPC traces of a conventional, heterogeneous E/octene copolymer vs. a homogeneous copolymer.

![Fig. 2. Model prediction for intramolecular comonomer distribution of Dow’s E/octene copolymers made by CGC catalyst: E block length distribution between comonomers.](image)

![Fig. 3. GPC molecular weight distribution comparison of two E/octene copolymers having a density of 0.920 g/cm\(^3\).](image)

Polymers with a narrow MWD in general have increased toughness and less “solvent extractables”. On the other hand, the narrow MWD of a linear homogeneous copolymer also results in poor melt processability (low melt strength, high extruded back pressure, high energy consumption during extrusion, etc.).

2.1.3. Long-Chain Branching

Homogeneous E homopolymers and E/\( \alpha \)-olefin copolymers made by CGC technology have one more unique molecular structural feature not generally found in other metallocene technology polymers. This unique molecular structural feature is LCB. Homopolymers and copolymers made by CGC technology at certain process conditions contain a certain amount of LCB. To summarize this, the molecular structure of three E/\( \alpha \)-olefin copolymers—conventional LLDPE made by Ziegler–Natta catalyst, homogeneous copolymers made by other metallocene technology catalysts (MTCs), and substantially linear homogeneous copolymers made by CGCs, are illustrat-
Polymers with LCB made by CGC technology have many unique rheological properties. A few of the most significant features for the CGC technology polymer are its melt fracture resistance and the control of shear-thinning behavior as illustrated in Figures 5 and 6, respectively. The unique molecular structure and rheological properties of these polymers allow one to design new polyethylene products with excellent processability for applications such as blown film, cast film, injection molding, blow molding, thermoforming, etc.

2.2. New Polyethylene Products Based on Computer-Based Model Molecular Design

Single-site and metallocene catalyst technology resulted in the production of polyolefin copolymers with well-defined molecular structure as previously discussed. INSITE technology, based on the constrained-geometry catalyst chemistry coupled with Dow’s flexible process technology, will further expand the capability and flexibility of molecular architecture by allowing more flexibility in molecular designs, such as comonomer choices, LCB structure, and morphology control in the polymer. Because of the increase in the design flexibility, it is essential for the product designer to take advantage of modern computer technology to increase the efficiency of polymer design. Based on this philosophy, Dow developed and currently utilizes a computer-based product design software system. The system consists of product design software driven by performance requirements and is based on the logic described in Figure 7. In addition, it utilizes advanced on-line control systems to monitor and control basic polymer structure variables such as rheology, density, \( M_n \) and MWD during the manufacturing process. This has resulted in enhanced polymer property control and allows Dow to manufacture INSITE technology polymers consistently and efficiently.

The most critical element to enhance the success of the product design exercise is to acquire precise performance requirements for the applications defined by the customers. Once the performance requirements are defined, the computer-based materials science models can be used to relate polymer structure to performance requirements, and the kinetic and process models can be applied to optimize the manufacturing process to produce the defined polymer structure. Examples of materials science models that relate performance attributes to molecular structure are listed in Table 1. Using the computer-driven, model-based product design approach, Dow has successfully demonstrated significant improvement in speed to market. This has resulted in both improved values for Dow and its customers by meeting performance requirements quickly and efficiently. Since 1993, Dow has successfully launched many new polyethylene-based product families, including AFFINITY polyolefin plastomers, AFFINITY polyolefin adhesive, ELITE enhanced polyethylene, INDEX interpolymers (all trademarks...
of The Dow Chemical Company), ENGAGE polyolefin elastomers, and NORDEL IP EPDM (trademarks of DuPont Dow Elastomers, L.L.C.).

3. Interpolymers of Ethylene and Styrene

The preparation of ES copolymers by different methods has been reported but the produced copolymers typically contained low levels (<4 mol.-%) of comonomer S incorporation, or were heterogeneous in nature. Developments in single-site, constrained-geometry, addition-polymerization catalysts [22] described above have enabled the effective production of copolymers having high levels of S incorporation. As a result of the catalyst selection and process conditions used, the particular copolymers of current interest are atactic, and contain typically up to about 50 mol.-% (~80 wt.-%) S content. They have been described as “pseudo-random”, since successive head-to-tail S chain insertions have been shown to be absent, even at high levels of S incorporation. [22] The term “ethylene/styrene interpolymer” (ESI) is used herein to describe the specific ES copolymers produced via INSITE technology. For convenience, all subsequent comonomer contents are expressed in weight percentages, unless otherwise stated. Where used, the code ES## refers to an interpolymer having ## wt.-% copolymerized S monomer content.

The introduction of aromatic groups into the polyethylene chain structure results in significant changes to the viscoelastic behavior, mechanical properties, and compatibility of ES copolymers with a wide range of other materials compared, for example, to aliphatic olefin copolymers such as E/1-octene (EO). This overview includes information from a publication on the structure, properties, and applications of ESI,[23] updated with more recent developments. Interrelated elements of this technology, namely structure–property relationships and materials engineering, are discussed below, and potential application areas are introduced.

3.1. Structure–Property Relationships for Ethylene/Styrene Interpolymers

The general background to ESI structure–property relationships includes density, thermal transitions, viscoelastic behavior, and mechanical properties. [24,25]

3.1.1. Thermal Transitions/Viscoelastic Behavior

Crystallization and melting temperatures ($T_c$, $T_m$) and crystallinity decrease with increasing copolymer S content. Crystallizability of E chain sequences is suppressed and ultimately inhibited by the incorporation of increasing S comonomer content into the crystallizing chains. Transition from the semicrystalline state to an essentially amorphous solid-state structure occurs at about 45 % S incorporation. This is manifested in differential scanning calorimetry (DSC) data as a change in the form of the melting endotherm. At low S contents (<40 %) the copolymers generally exhibit a well-defined melting process. At higher S content there is no discernible melting endotherm, and the materials are essentially amorphous.

Figure 8 shows that ESIs generally exhibit glass-transition temperatures ($T_g$) in the range −20 °C to +35 °C. In the range of 15 to 50 % S content, the single number $T_g$ (ESI) are essentially independent of S content. Of further note in Figure 8 is the so-called $\gamma$-transition. This has been associated with local chain motions in polyethylene; [26] such chain motions are believed to contribute to the toughness found at low, subambient temperatures in ESIs.

From dynamic mechanical spectroscopy (DMS) studies of semicrystalline ESI, the loss peak evident in the temperature range −50 °C to +50 °C shows increasing breadth of the relaxation process as the copolymer S content decreases. [25,27] The relaxation processes associated with this loss peak are complex in nature. There is an increasing contribution of the so-called $\alpha$-relaxation for polymers of high crystallinity. This is attributed in part to the constraining effect of crystalline domains present that restrict molecular mobility in the amorphous domains. Developing an understanding of the viscoelastic properties and time/temperature/rate dependency of properties has been a key element of the materials science of these interpolymers.

The linear viscoelastic behavior of ESIs has been studied by DMS techniques. In particular, the effect of composition was investigated in the range from 43 to 76 % copolymer S. Master
curves of dynamic moduli extending from glassy to terminal zones were obtained by combining torsion rectangular measurements in the glass-transition region, with parallel-plate rheometry in the melt. Analysis of data showed that all these copolymers exhibited time-temperature superposition and that the temperature dependence of the properties for the amorphous copolymers studied could be described by a single pair of Williams–Landel–Ferry (WLF) coefficients in the range $T_g < T < T_g + 100 \, ^\circ C$.

Further aspects of the viscoelastic behavior of ESIs that have been reported to date include linear and nonlinear stress relaxation behavior of amorphous ESL[28] and the creep behavior of amorphous ESL in the glass-transition region.[29] In another aspect of viscoelastic behavior, Chen et al.[30] reported large strain/stress relaxation and strain recovery of ESLs at temperatures above $T_g$, and found that the observed behavior could be rationalized in terms of various network models.

3.1.2. Mechanical Properties

The tensile stress/strain behavior (23 $^\circ C$, 5.7 min$^{-1}$) for ESLs studied has shown that the copolymers show strain at rupture in excess of 200 % and uniform deformation behavior. The large-scale deformation behavior and recovery behavior of semicrystalline ESIs and EO copolymers has been studied by Chang et al. as a function of temperature, comonomer content, and crystallinity.[31,32] Clearly a major factor that is different between the two classes of copolymers is the respective location of the $T_g$ and the influence of chain mobility on the mechanical response observed.

The materials in the mid-S region (40 to 65 % S copolymer) are characterized by low modulus, and they show some elastomeric characteristics. Information on the deformation and recovery behavior of selected ESIs was reported by Mudrich et al.[33] with an ES45 copolymer of particular note in terms of strain recovery after deformation. The effects of S become dominant in the high-S region where the modulus and yield stress increase. ESIs having a $T_g$ above ambient temperature show some characteristics of glassy materials. ESIs, including high S (70 % and greater S) copolymers, show interesting shape/reshape functionality.

Compared to amorphous ESIs, the mechanical properties of semicrystalline ESIs show much less sensitivity to molecular weight, which is associated with the load-bearing capability of the crystalline regions networked together with tie molecules.

Good low-temperature toughness of ESL has been evident from impact testing and low-temperature tensile testing. As discussed above, DMS provides some evidence that there are sub-$T_g$ chain motions that may contribute to energy dissipation and toughness. In addition, Chen et al. provided estimates of the entanglement molecular weights for ESL.[29] The low $M_e$ values found suggest high entanglement density in the amorphous polymers, which is considered to contribute to the ability of the polymers to shear yield at temperatures below $T_g$ rather than undergo brittle fracture.

3.1.3. Melt Rheology and Processability

The melt rheology and associated information from solid-state DMS, melt strength, and pressure–volume–temperature (PVT) testing of ESIs have been reported by Karjala et al.[34,35] The polymers were shown to have good thermal stability at processing temperatures, viscosities that are a strong function of copolymer S content in addition to molecular weight, excellent processability, particularly regarding shear-thinning characteristics at high shear rates, and good melt strength. Melt rheological master curves could be generated through data-modeling procedures, including time-temperature superposition. In addition to providing fundamental structure–property understanding, melt rheology has further found utility in the design of polymer blends based on ESL.[36]

As a general comment, melt processability of interpolymers is favorable towards most fabrication techniques. These characteristics have allowed the fabrication of ESL articles by a wide range of standard melt-processing techniques, including injection molding, film fabrication, blow molding, and melt extrusion. The potential for ESL to be utilized in calendering operations has been described by Karjala et al.[37] Selected ESLs were found to demonstrate the requisite rheological properties and thermal stability to be successfully calendered, and this was supported by commercial-scale validation.

3.2. Interpolymer Materials Engineering

3.2.1. Chemistry/Comonomer

INSITE technology also enables the copolymerization of E and S with additional monomers,[38] such as dienes, higher α-olefins, and norbornene. Possibilities are further evident from the work of Sernetz and Mühlaupt, who have reported terpolymerization with propylene, 1-octene, and norbornene[39] as additional monomers.

Regarding the ESIs, the higher reactivity offered by the phenyl group leads to some additional possibilities for secondary chemistry, such as sulfonation, not readily available for saturated olefin-based polymers.

3.2.2. Blends and Compatibility

The S content and chain microstructure of ESL are potential contributors to the observed compatibility between ESL and other materials, including oils, low-molecular-weight materials such as plasticizers and tackifiers, processing aids, bitumens, and high-molecular-weight polymers.

Blending two or more interpolymers of the same comonomer type but different comonomer content has been studied.[40,41] The critical composition difference above which
phase separation will occur for ESI/ESI blends as a function of molecular weight and solubility parameter has been determined and correlated to theoretical observations. It was found that the critical comonomer difference in S content at which phase separation occurs is about 8 wt.-% S for ES copolymers with molecular weight around 105. Such ESI/ESI blends can thus be designed to be immiscible in nature, and offer the opportunity to engineer materials with broadened Tg loss processes and enhancements in relaxation behavior, mechanical properties, and melt rheology/processability.

Extending the above rational regarding miscibility to blends of ESI with styrenic polymers, it is evident that ESIs having less than 80 % S content will be immiscible with polystyrene (PS), unless the molecular weights of the respective polymers are very low. Initial studies on ESI blends with PS show that significant toughening of brittle atactic PS can be achieved with selected ESIs, in large part due to good compatibility between these polymers. The olefin nature of ESI helps provide compatibility with olefin polymers and copolymers, including polyethylene, E/α-olefin copolymers, and polypropylene homopolymers and copolymers.

As reported by Diehl et al.[42] interpolymers are further compatible with a wide range of polymers, including S block copolymers, polyvinyl chloride-based polymers, polyphenylene ethers, and olefin polymers such as E/acrylic acid copolymer, E/vinyl acetate copolymer, and chlorinated polyethylene. Due to their unique molecular structure, specific ESIs have been demonstrated as effective blend compatibilizers for PS/polyethylene blends.[43]

3.2.3. Filler Composites

ESIs offer good filler acceptance.[44,45] The resulting composite materials have shown very good mechanical properties, even for what is considered to be high loadings of fillers. Many combinations of filler types and ESIs of different copolymer S content show exceptional tensile elongations at rupture. Alumina trihydrate (ATH) filler loading levels can be adjusted to achieve the desired flame-retardancy performance, whilst retaining good mechanical properties. Impact testing of ESI/filler systems has further shown that these composites have good toughness. The mechanical properties, and particularly failure performance, indicate that good interfacial bonding exists between ESI and fillers. Fillers can be used to increase the upper service temperature of ESI. Filled ESIs show rheological characteristics suggesting that the compositions can be easily fabricated into final parts. Filled ESI composites are expected to find broad utility in applications, for example, wire and cable,[46] injection-molded articles, film and sheet structures, profile extrusions, and flooring systems.

4. Summary

ESIs are a new class of polymers, and show characteristics distinct from polyethylenes or PS. Materials offering a wide spectrum of properties can be tailored by molecular architecture offering unique performance attributes. The effective production of these novel copolymers has been enabled by INSITE technology. INDEX interpolymers were formally launched by Dow in December 1998, and this technology includes ESIs. A product development plant to produce interpolymers (Sarnia, Ontario, Canada) had a successful start-up in September 1999. This plant has a nameplate production capacity of around 22,500 metric tons (50 million pounds) per year.

A range of technologies for materials engineering includes terpolymerization, blending, and the use of fillers. Although intermaterial substitutions in existing applications are potential application areas for ESIs, the novel combination of materials attributes suggests new application areas will emerge. Of particular note to date are developments using ESI-based materials in foam applications. Novel foam structures offer attractive properties and characteristics including softness, aesthetics, and drape for a wide range of non-crosslinked and crosslinked foam applications. Other product technologies of interest are injection-molded structural foams, as foamed layers in multilayer structures and as foamed blends of interpolymers with styrenic and olefinic polymers.[47] Interpolymers also have potential for film and sheet applications. Materials attributes such as processability, mechanical properties, and heat scalability are the basis for utility in elastic films, deadfold film and sheet, in laminated structures, and in thermosettable film and sheet. The current range of potential markets/applications for ESI that have been identified also include bitumen modification, packaging, injection- and blow-molded articles, adhesives, toys, wire and cable, automotive, building, and construction. The temperature/frequency ranges for the Tg process of ESI, combined with other attributes such as excellent filler acceptance, indicate its utility in a range of energy-management applications, including flooring and sound/vibration damping systems.

These interpolymers of E and S are part of an exciting new generic class of materials, offering unique opportunities for innovative developments in basic polymer chemistry and materials science, materials engineering, and application technology. Partnerships with research groups at Case Western Reserve University and Virginia Polytechnic Institute and State University have contributed significantly to our understanding of structure–property relationships. Fundamental to the research and development process has been the development and validation of models describing structure–property relationships.

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For an example of an olefin polymerization that proceeds via a living mechanism at room temperature, see: J. D. Scollard, D. H. McConville, PCT Int. Appl. WO 1999/06 727, 1999.


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