Ketene Functionalized Polyethylene: Control of Cross-Link Density and Material Properties

Frank A. Leibfarth,[†,‡,||] Yanika Schneider,[†,‡,||] Nathaniel A. Lynd,[‡] Alison Schultz,[‡] Bongjin Moon,[§] Edward J. Kramer,[‡] Guillermo C. Bazan,*,[†,‡] and Craig J. Hawker*,[†,‡]

Department of Chemistry & Biochemistry, University of California, Santa Barbara, California 93106, Department of Materials, Mitsubsihi Chemical, Center for Advanced Materials and Materials Research Laboratory, University of California, Santa Barbara, California 93106, and Department of Chemistry, Sogang University, Seoul, 121-742, Korea

Received July 8, 2010; E-mail: bazan@chem.ucsb.edu; hawker@mrl.ucsb.edu

Abstract: The functionalization and cross-linking of polyethylene is synthetically challenging, commonly relying on highly optimized radical based postpolymerization strategies. To address these difficulties, a norbornene monomer containing Meldrum's acid is shown to be effectively copolymerized with polyethylene using a nickel α-iminocarbaxamidato complex, providing high-melting, semicrystalline polymers with a tunable incorporation of the functional comonomer. Upon heating the copolymer to common polyethylene processing temperatures, the thermolysis of Meldrum's acid to ketene provides the desired reactive group. This simple and versatile methodology does not require small molecule radical sources or catalysts, and the dimerization of the *in situ* generated ketenes is shown to provide tunable cross-linking densities in polyethylene. Subsequent rheological and tensile experiments illustrate the ability to tune cross-linked polyethylene properties by comonomer incorporation and elucidate valuable structure/property relationships in these materials. This study illustrates the power of well-defined and synthetically accessible functional groups in polyolefin synthesis and functionalization.

The ability to reactively process and/or postmodify polyolefins is a major challenge in synthetic polymer chemistry.[1] The continuing interest in overcoming this challenge is driven by the wide range of applications afforded by cross-linked or functionalized derivatives of polyolefins. For example, the introduction of cross-links into polyethylene (PE) is prominently exploited in the design of high voltage cable insulation, biomedical joint replacement parts, and hot-water piping.[2,3] In addition, the grafting of polymer or small molecules onto PE provides access to new materials with improved physical and mechanical properties, such as increased affinity for polar surfaces/interfaces, efficient compatibilizing agents for commodity plastic blends, etc.[4] Synthetic hurdles to the controlled introduction of cross-links and functionality remain, however, due to the low reactivity of the C–H bonds along the polyolefin backbone coupled with the sensitivity of typical olefin polymerization catalysts to reactive functional groups.

The most commonly used strategy for controlling postpolymerization modification of polyolefins is a multicomponent, processing-driven approach which relies on inducing main-chain radicals through high energy irradiation[5] or reactive processing in the presence of peroxides,[6] followed by uncontrolled radical–radical coupling or addition reactions.[1] While commercially successful, this

Scheme 1. Synthesis of Meldrum's Acid Functionalized Norbornene (**3**) and Subsequent Copolymerization with Ethylene Employing the Nickel α-Iminocarbaxamidato Complex **4**
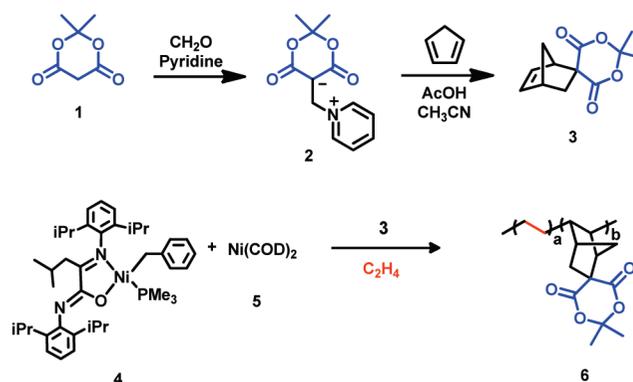
strategy leads to poorly defined polymeric structures and requires highly optimized conditions, extra processing steps/additives, and significant energy input. In contrast, development of a synthesis-driven, molecular approach involving the controlled introduction of reactive functional groups into the backbone of PE and other commodity polyolefins would allow for precise tailoring of polymer reactivity and final physical properties. The ultimate goal is the development of modular, well-defined, and synthetically accessible building blocks that provide for robust and efficient cross-linking and/or functionalization of polyolefins.

The key to this strategy is the incorporation of a stable building block into the polyolefin backbone that not only is compatible with the polymerization chemistry but also allows for the subsequent quantitative generation of reactive functional groups. Recently, we demonstrated the utility of Meldrum's acid based building blocks as a thermolytic precursor to dialkyl ketenes in vinyl polymer synthesis and functionalization.[7] The chemistry of ketenes, specifically their ability to provide cross-linking *via* dimerization and functionalization *via* nucleophilic addition, suggests that this versatile chemistry can provide access to reactive sites on a variety of polymer backbones. Formation of the ketene intermediates involves thermal treatment of 5,5-dialkyl-2,2-dimethyl-1,3-dioxa-4,6-dione (or 5,5-dialkyl Meldrum's acid),[8] which forms dialkyl ketene derivatives after loss of acetone and carbon dioxide[9] at temperatures compatible with the thermal stability and low reactivity of polyolefin backbones. Herein, we show that this strategy is particularly useful in commodity polyolefin systems, as thermolytic generation of reactive moieties takes place without the use of small-molecule radical sources or sensitive catalysts, and it is well-suited to the thermal treatment required for PE melt processing.

Traditionally, the introduction of functional groups is difficult for polyolefin systems, as polar groups deactivate conventional

Table 1. Physical and Molecular Properties of Copolymers[a]

Entry	$P_{C_2H_4}{}^c$	$[3]_0{}^d$	A^e	$M_n{}^f$	PDI	mol % 3^g	$T_m{}^h$	$X_c{}^i$
PE1	50	0.000	560	124	1.5	0.00	125	0.44
PE2	100	0.000	240	110	1.4	0.00	128	0.45
PEC1	50	0.002	280	79	2.1	0.09	125	0.39
PEC2	50	0.005	100	54	2.3	0.46	123	0.29
PEC3	50	0.008	15	15	2.7	0.70	115	0.26
PEC4[b]	50	0.008	75	61	2.2	0.30	121	0.31
PEC5	100	0.008	130	106	1.9	0.32	125	0.38
PEC6	100	0.011	30	87	1.9	0.56	123	0.24
PEC7	150	0.015	30	25	2.6	0.79	121	0.31
PEC8[b]	150	0.015	50	79	2.4	0.44	123	0.44
PEC9	175	0.015	70	57	2.4	0.45	124	0.32
PEC10	200	0.015	50	93	1.7	0.50	123	0.37

[a] Reaction time of 15 minutes unless noted. [b] 30 min reaction time. [c] Pressure of ethylene (psi). [d] Concentration of **3** in M. [e] Activity (kg/mol·h). [f] M_n (kg/mol) determined by GPC with polystyrene standards. [g] mol % of **3** determined by ^1H NMR spectroscopy. [h] Melting point (°C) determined by DSC. [i] Degree of crystallinity (%) determined by DSC.

olefin polymerization catalysts. In response, late transition metal catalysts have been developed which can incorporate polar comonomers into polyolefins.[10] Specifically, nickel α-iminocarbaxamidato complexes have been shown to be adept at copolymerizing ethylene and functionalized norbornenes with low to moderate levels of incorporation.[11,12] Thus, we anticipated that the same catalyst could also incorporate a Meldrum's acid functionalized norbornene, 2′,2′-dimethyl-spiro [bicyclo[2.2.1]-hept-5-ene-2,5′-[1,3]dioxane]-4′,6′-dione, **3**.[4] The monomer, **3**, was prepared *via* a low temperature Diels–Alder cycloaddition from the methylene Meldrum's acid precursor **2**[13] and cyclopentadiene, as described previously.[4] Copolymerization of ethylene with the functionalized norbornene, **3**, using [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)isobutanamidato] Ni(η^1-CH$_2$Ph) (PMe$_3$), **4**, activated with bis(1,5-cyclooctadiene) nickel, **5**, was then investigated (Scheme 1). In these reactions, ethylene was continuously fed to a solution of **4** and **5** (0.24 and 0.6 mM, respectively) in the presence of **3** at 20 °C to generate the copolymers described in Table 1. The concentration of **3**, ethylene pressure, and reaction time were systematically varied in order to determine the optimal reaction conditions to generate ethylene-*co*-norbornyl Meldrum's acid (PE-*co*-MelA, **6**), with the incorporation of **3** determined by ^1H NMR (Supporting Information). Although the incorporation of **3** can be increased by increasing the initial concentration of **3** in the reaction mixture, as illustrated in PEC3, this also has the detrimental effect of decreasing polymerization activity and molecular weight and increasing the polydispersity (PDI). Conversely, increasing ethylene pressure and reaction time results in an increase in number average molecular weight (M_n) and a decrease in PDI.

This synthetic study illustrates the subtle balance that is required to obtain copolymers with both high comonomer content and high M_n. The optimal copolymers (PEC5, PEC6, and PEC10), with respect to high M_n, moderate Meldrum's acid incorporation, and minimal disruption of melting point and crystallinity, were achieved with higher pressures of ethylene and a concentration of **3** of 0.01 to 0.015 M. These conditions yield polymers with molecular weights at or above 90 kg/mol, PDIs below 2, and incorporations of **3** around 0.5 mol %, resulting in approximately 15–20 Meldrum's acid units per polymer chain. It is also significant to note that the PE-*co*-MelA copolymers preserve the beneficial properties of the parent PE material, specifically a high melting point and degree of crystallinity, while inheriting the functionality provided by thermolytically generated ketenes.

Having successfully incorporated the reactive Meldrum's acid units into PE through the use of a nickel-based catalyst, it was

Scheme 2. Cross-Linking of PE-co-MelA, **6**, through the Dimerization of Thermally Generated Ketenes
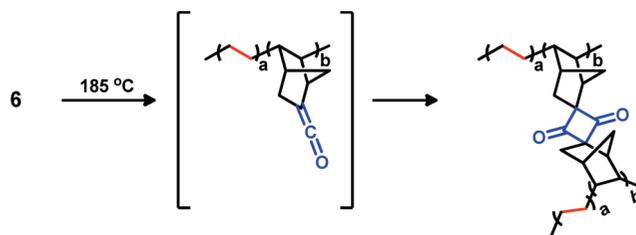
important to understand the thermolysis behavior of the norbornane building block. Employing a small molecule analogue (see Supporting Information) of the functional polymer backbone unit, full thermolysis to the desired ketene was observed after heating for 30 min at 185 °C. This temperature profile is compatible with polyethylene systems, as standard processing temperatures are in the range of 180–220 °C.[1] Accordingly, the gel content of the cross-linked polyethylene was determined by heating pellets of **6** (derived from samples PEC2–10) at 185 °C for 1 h followed by rigorous extraction of the cross-linked materials with refluxing chlorobenzene and subsequent drying (Scheme 2, Figure S2). The gel content, a representative measure of the cross-linking efficiency of the PE-*co*-MelA polymers, was shown to scale with the concentration of Meldrum's acid units along the backbone. Significantly, it was found that above one Meldrum's acid unit per 300 ethylene repeat units (i.e., 10 units for a PE chain of $M_n = 100\,000$ a.m.u.), the cross-linking efficiency is over 90%. Such cross-linking efficiency is in stark contrast to conventional radical-induced cross-linking, where 15 mol % of a small molecule radical source, relative to PE, and extensive processing are needed to produce cross-linked polyethylene with a gel content above 90%.[14]

This new strategy, where tuning comonomer incorporation allows for accurate control of the cross-linking density for polyethylene, holds considerable potential in developing fundamental structure/property relationships of cross-linked polyolefin materials. To demonstrate this point, a rheological study which tracked the storage and loss moduli (G' and G'') in a series of materials was performed to monitor the viscoelastic response of the polymers as a function of cross-linking (Figure 1). The consequence of cross-linking becomes apparent above the melting point of the materials (150 °C). As expected for cross-linked materials, the storage modulus is significantly higher than that of the un-cross-linked PE and increases with comonomer incorporation (Figure 1).[15] For example,
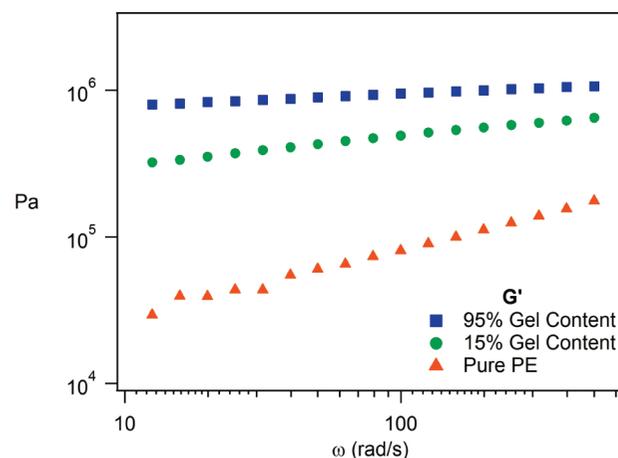
Figure 1. Rheology data collected at 150 °C comparing the storage modulus (G') of samples cross-linked through the dimerization of ketenes to that of native polyethylene.
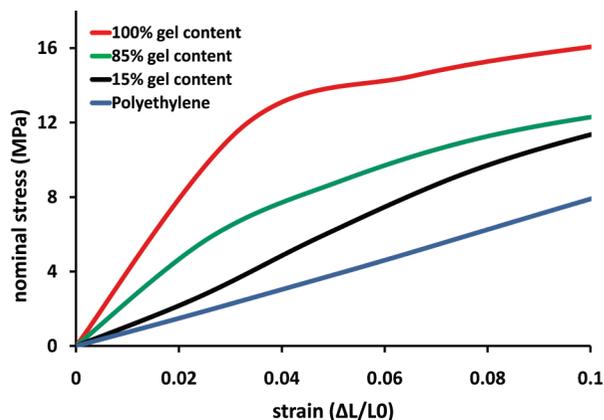
Figure 2. Elastic region of the stress−strain curve for samples of polyethylene cross-linked through ketene dimerization−strain at break is 920%, 440%, and 170% for the samples with 15%, 85%, and 100% gel contents, respectively.

the G' of a cross-linked sample of PE-*co*-MelA with 95% gel content is at least an order of magnitude larger than that for a PE sample of similar molecular weight in all frequencies sampled. Furthermore, the G' increases with cross-linking density, as the material with a gel content of 15% has a G' in between that of native PE and the more highly cross-linked sample. The relationship of G' to G'' gives further evidence of cross-linking and the material's improved properties at elevated temperatures (Supporting Information, Figure S5). In both cross-linked samples, G' remains almost an order of magnitude higher than G'' at 150 °C in all frequencies sampled. The native PE sample in the same conditions, however, appears very close to its crossover point, where G' becomes smaller than G'' and the material is able to flow. Significantly, the same resistance to flow evidenced here is one of the many properties of cross-linked PE that makes it valuable in thermally demanding applications such as high-voltage cable insulation and hot-water piping.[16] This rheological structure/property study not only provides further evidence of cross-linking but also demonstrates that the final properties of these cross-linked PE materials can be tuned by controlling the comonomer content.

To gain further insight into our ability to control the mechanical behavior of cross-linked PE, the tensile properties of the materials were examined through stress−strain tests. As shown in Figure 2, the change in properties after cross-linking is quite dramatic, especially considering the low density of cross-links in these materials. As we shift from native PE to a material with 100% gel content,[17] we observe a nearly 2-fold increase in Young's modulus, from 150 to 292 MPa, and a drastic decrease in elongation at break, from 1500 to 170%. Furthermore, the samples with gel contents of 15% and 85% show intermediate values of Youngs' moduli and elongation at break. Although Young's modulus should increase and is known to do so in samples cross-linked through irradiation,[3] the magnitude of the increase in Young's modulus for our materials is surprising and lacks significant literature precedence. The tensile data presented demonstrate the ability to tailor the physical properties of cross-linked polyethylene systems through polymer synthesis.

The decrease in ductility of polymers seen in the tensile testing is a common result of cross-linking,[3,15] but such behavior in PE-*co*-MelA shows that the chemical cross-links dominate the physical properties even at ambient temperatures. Past work attempting to deduce such structure/property relationships in cross-linked polyolefin systems has been convoluted by the many side reactions inherent in the commercially employed radical-based cross-linking

process.[3,18] The main chain radicals generated in these processes can undergo the desired recombination reactions, but they also disproportionate and fragment the PE chain, creating unsaturations and decreasing the molecular mass of the PE material during cross-linking. The consequence of such complex reaction pathways makes any structure/property relationship difficult to ascertain and requires highly optimized conditions to generate commercially valuable materials. Therefore, these results demonstrate the simplicity that a thermally activated and efficient cross-linking strategy can have for the generation of cross-linked polyolefin materials.[19]

In conclusion, the copolymerization of ethylene with a norbornene monomer containing a reactive Meldrum's acid unit, **3**, using a nickel α-iminocarbaxamidato complex, **4**, provides high molecular weight copolymers with levels of crystallinity and melting temperatures similar to those of native PE. By employing standard thermal conditions used for PE melt processing, highly efficient cross-linking is observed in these systems through the generation of reactive ketene groups. The ability to tune the incorporation of Meldrum's acid in the polymer backbone provides synthetic control of cross-linking density and subsequent rheological and tensile properties. In addition, the ability to postmodify a PE backbone while employing no catalysts or extra reagents is very different from the traditional multistep processes and offers a range of advantages.[20] The modular approach inherent in this strategy also provides the potential to understand the fundamental relationship between polyolefin synthesis, cross-linking, and final polymer properties in a wide range of commercially relevant polyolefin materials.

Supporting Information Available: Experimental procedures for monomer synthesis and polymer processing. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267–275.
(2) Atkinson, J. R.; Cicek, R. Z. *Biomaterials* **1983**, *4*, 267–670.
(3) Chodak, I. *Prog. Polym. Sci.* **1995**, *20*, 1165–1199.
(4) Datta, S.; Lohse, D. J. *Polymeric Compatibilizers: Uses and Benefits in Polymer Blends*; Carl Hanser Verlag: Munich, 1996.
(5) (a) Rijke, A. M.; Mandelkern, L. *Macromolecules* **1971**, *4*, 594–599. (b) Dole, M. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1981**, *15*, 1403–1409.
(6) (a) Matsuo, M.; Sawatari, C. *Macromolecules* **1986**, *19*, 2028–2035. (b) Matsuo, M.; Sawatari, C. *Macromolecules* **1987**, *20*, 1745–1747.
(7) Leibfarth, F. A.; Kang, M.; Ham, M.; Kim, J.; Campos, L. M.; Gupta, N.; Moon, B.; Hawker, C. J. *Nat. Chem.* **2010**, *2*, 207–212.
(8) Meldrum, A. N. *J. Am. Chem. Soc.* **1908**, *93*, 598–601.
(9) (a) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373–2384. (b) Hyatt, J. A.; Raynolds, P. W. *Org. React.* **1994**, *45*, 159–646.
(10) (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479–1493. (b) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30–92. (c) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244. (d) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267–268. (e) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899. (f) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460–462.
(11) Boardman, B. M.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1597–1606.
(12) (a) Schneider, Y.; Azoulay, J. D.; Coffin, R. C.; Bazan, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 10464–10465. (b) Schneider, Y.; Lynd, N. A.; Kramer, E. J.; Bazan, G. C. *Macromolecules* **2009**, *42*, 8763–8768.
(13) Zia-Ebrahimi, M.; Huffman, G. W. *Synthesis* **1996**, 215–218.

(14) Anbarasan, R.; Babot, O.; Maillard, B. *J. Appl. Polym. Sci.* **2004**, *93*, 75–81.
(15) Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd ed.; Taylor & Francis Group: FL, 2007.
(16) Munier, C. *J. Mater. Sci.* **2002**, *37*, 4159–4163.
(17) The sample deemed to have 100% gel content was prepared by rigorous extraction with refluxing chlorobenzene of a material with 95% gel content.
(18) Lazár, M.; Rado, R.; Rychlý, J. *Adv. Polym. Sci.* **1990**, *95*, 149–197.
(19) Khonakdar, H. A.; Morshedian, J.; Wagenknecht, U.; Jafari, S. H. *Polymer* **2003**, *44*, 4301–4309.
(20) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1143–1170. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203. (c) Schellekens, M.; Klumperman, B. *J. Macromol. Sci., Polym. Rev.* **2000**, *40* (2), 167–192. (d) Lin, W.; Shao, Z.; Dong, J.; Chung, T. C. M. *Macromolecules* **2009**, *42*, 3750–3754. (e) Stehling, U. M.; Malmstrom, E. E.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **1998**, *31*, 4396–4398.