# Gradient Methylidene-Ethylidene Copolymer via C1 Polymerization: an Ersatz Gradient Ethylene-Propylene Copolymer

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Ⓢ Supporting Information

ABSTRACT: We report the first synthesis of a gradient methylidene-ethylidene copolymer via a living C1 polymerization. The copolymer has a similar chemical structure as the corresponding ethylene-propylene copolymer. To achieve this goal a new and convenient source of the ethylide monomer, diethylsulfoxonium ethylide, was developed for the introduction of the methyl branch in the polymer backbone. The gradient copolymer contains a gradual change of instantaneous methyl branch content from 0% on one end of the polymer chain to 63% on the other end. Thermal analysis revealed that the gradient copolymers have a narrow glass transition temperature range with values intermediate between those of linear polyethylene and atactic polypropylene.

Ersatz Gradient Ethylene-Propylene Copolymer
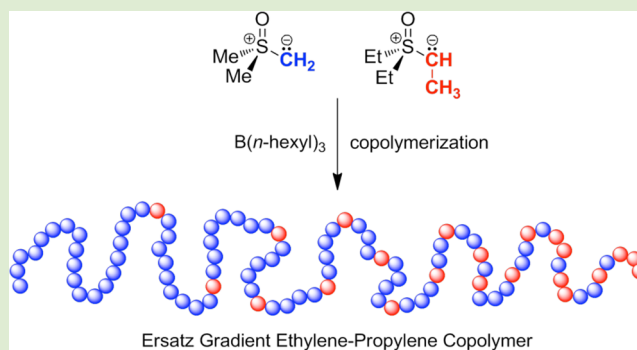
Carbon backbone polymers, especially polyethylene (PE) and polypropylene (PP), are ubiquitous in contemporary society, serving as components for paints, lubricants, printing inks, packaging materials and surface coatings. Ethylene-propylene block copolymers are used as the compatibilizer for PE/PP blends. These blends have improved tensile and impact strength and expand the potential applications of these abundant, inexpensive materials.[1,2] In contrast to conventional random and block copolymers, gradient copolymers are materials where the instantaneous composition varies continuously from one end of the polymer chain to the other. Theoretical calculations indicate that gradient copolymers can undergo microphase separation with a blurred interface region between chemically different components.[3] These gradient copolymers are expected to have unique thermal properties,[4] particularly a broad glass transition temperature (T_g) range in situations where the corresponding homopolymers have very different T_gs.[5] Experimental studies provided examples of materials containing incompatible comonomers with a very broad T_g range.[6]

In order to achieve a homogeneous gradient copolymer, all polymer chains must be initiated simultaneously and survive until the end of polymerization. This requires a living polymerization. Well-defined gradient copolymers have been synthesized from controlled/living polymerizations such as NMP (nitroxide mediated polymerization),[7] ATRP (atom transfer radical polymerization),[8,9] and RAFT (reversible addition–fragmentation chain transfer radical polymerization).[10] Many gradient copolymers are produced from functionalized olefin monomers, for example, poly(styrene-*grad*-butadiene)[11] and poly(styrene-*grad*-butyl acrylate).[8] Very few gradient copolymers based on nonfunctionalized hydrocarbon monomers have been reported. For example, ethylene-

norbornene gradient copolymers were obtained via Pd-diimine-catalyzed copolymerization.[12] A somewhat related simple triblock ethylene-propylene copolymer, PE-*b*-poly(ethylene-*co*-propylene)-*b*-PP, was first reported via living olefin polymerization with a fluorine-containing titanium catalyst bearing phenoxy-imine ligands.[13] Well-defined ethylene-propylene gradient copolymers, the simplest gradient hydrocarbon polymers, have not been reported and their properties have yet to be studied.

The living C1 polymerization allows for the production of linear hydrocarbon polymers with controlled molecular weight, polydispersity, and well-defined topology. We have previously reported a sp³–sp³ carbon–carbon bond forming polyhomologation reaction which produces a carbon backbone polymer by sequential insertion of C1 building blocks.[14] The mechanism involves initial formation of a zwitterionic "ate" complex **3** between an organoborane initiator **1** and ylide monomer **2** (Scheme 1). After a rate determining intramolecular 1,2-migration, a new sp³–sp³ carbon–carbon bond is formed, and an active trialkylborane catalytic site **4** is regenerated. Repetition of this process produces a star polymethylene organoborane **5**, which upon oxidation of the carbon–boron bond results in α-hydroxypolymethylene **6**. Here we report the synthesis of a gradient methylidene-ethylidene copolymer via the living C1 polymerization.
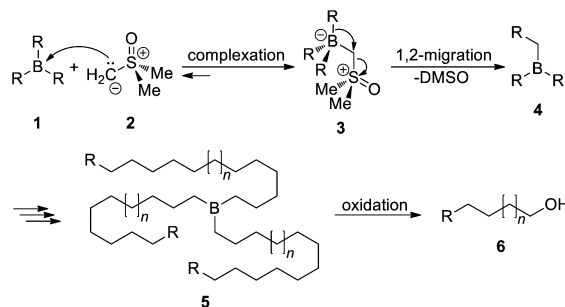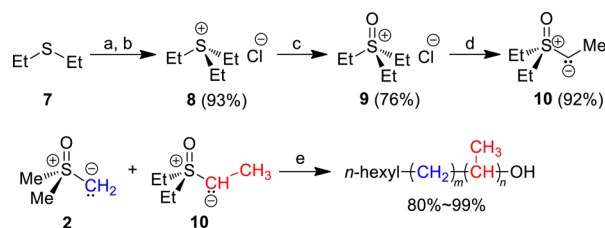
The synthesis of gradient methylidene-ethylidene copolymers using the polyhomologation reaction requires development of a convenient source of the ethylide monomer. We had
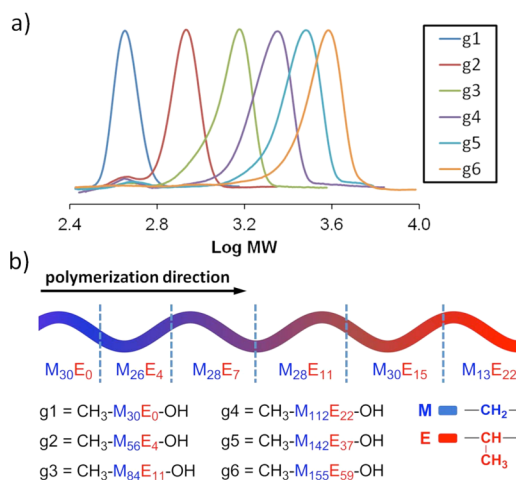
Scheme 1. Mechanism of the Polyhomologation Reaction

Scheme 2. Synthesis of Diethylsulfoxonium Ethylide 10 and Copolymerization of the Methylide 2 and Ethylide 10[a]

[a]Reagents and conditions: (a) iodoethane, 0.5 equiv I_2, 70 °C, overnight; (b) n-Bu$_3$BnNCl, H$_2$O/CH$_2$Cl$_2$, rt, overnight; (c) mCPBA, NaOH aq, 50 °C, 0.5 h; (d) LDA, 0 °C, 10 min; (e) B(n-hexyl)$_3$, THF/toluene, 75 °C; then trimethylamine N-oxide dihydrate, 75 °C.

Figure 1. (a) GPC traces of the gradient copolymers g1 to g6 sampled during the copolymerization. The small low MW peak in polymer g2−g5 belongs to a small amount of g1 with active chain terminated by trace O_2 introduced during sampling periods. It can be easily removed in the final polymer g6. (b) Experimentally determined methylidene-ethylidene compositions in the gradient copolymer. The colored ribbon represents the final gradient copolymer color scaled using the experimentally determined M/E units in each segment (e.g., $M_{30}E_0$, $M_{26}E_4$, etc.). g1 = CH$_3$−$M_{30}E_0$−OH to g6 = CH$_3$−$M_{155}E_{59}$−OH represents the cumulative number of M/E units for the copolymers isolated at each stage of polymer growth. g6 = CH$_3$−$M_{155}E_{59}$−OH is the final composition of the gradient copolymer.

previously demonstrated that (dimethylamino)-phenyloxosulfonium ylides can be employed to synthesize substituted carbon backbones.[15] The synthesis of this ylide, however, is tedious and involves potentially hazardous steps. Here we report a new secondary ylide, diethylsulfoxonium ethylide, which functions as an ethylidene monomer. The ylide inserts a methyl branch in the polymer backbone via C1 polymerization. Its synthesis starts from diethyl sulfide 7 (Scheme 2). Following alkylation with iodoethane and an anion exchange, sulfide 7 was converted to triethylsulfonium chloride 8. Oxidation of 8 with m-chloroperoxybenzoic acid (mCPBA) under basic conditions gave the ylide precursor Et$_3$SOCl 9.[16] Deprotonation of 9 using lithium diisopropylamide (LDA) at 0 °C results in near quantitative conversion to the ethylide 10. The identity of ylide 10 was confirmed by its use as a cyclopropanation reagent with (E)-chalcone in an overall yield of 91%.[17]

To evaluate its utility as a secondary ylide monomer for the polyhomologation reaction, batch copolymerizations of ylide 10 with the methylide 2 were studied. The polymerization starts with a pool of premixed monomers 2 and 10, followed by

injection of the organoborane initiator, tri(n-hexyl)borane, at 75 °C (Scheme 2). After oxidation and hydrolysis, an α-hydroxyl terminated hydrocarbon polymer was obtained in high yield. The ^{1}H NMR spectrum exhibited two diagnostic regions at 0.7—1.1 ppm (CH$_3$) and 1.1—2.0 ppm (CH$_2$ + CH). The obtained copolymer had a similar chemical structure of an ethylene-propylene random copolymer. Poly(methylidene-co-ethylidene) copolymers were obtained with monomer incorporation molar ratios [CH$_2$]/[CHCH$_3$] ranging from 8.0 to 2.0 (Supporting Information, Table S1). All copolymers have a narrow polydispersity in the range of 1.02−1.17 with the monomer composition close to the feed ratio.

There have been no previous reports of gradient ethylene-propylene copolymers. To achieve a structural equivalent as poly(methylidene-$grad$-ethylidene), we examined a semibatch copolymerization of methylide 2 and ethylide 10 monomers. The polymerization is initiated by injection of tri(n-hexyl)-borane to a pool of ethylide 10. Then methylide 2 was continuously added in a controlled manner via a syringe pump. However, all attempts resulted in polymers with a multimodal MW distribution. The chain propagation between ethylide 10

Table 1. Monitoring the Formation of Gradient Copolymers with the Chemical Composition of Poly(ethylene-$grad$-propylene)

| sample	number of segments	$(M/E)_{feed}^a$	$(M/E)_{cum}^a$	Et$_{cum}$%[b]	M_n^c (g/mol)	M_w^c (g/mol)	PDI[c]	T_g^d (°C)	T_m^d (°C)	cryst.[d] (%)
g1	1	100:0	100:0	0	451	458	1.02	[e]	82,71[17]	70
g2	2	93.8:6.2	92.0:8.0	8.0	784	837	1.07	[e]	65	41
g3	3	88.2:11.8	87.5:12.5	12.5	1314	1400	1.07	−35	58	32
g4	4	83.0:17.0	82.9:17.1	17.1	1912	2103	1.10	−37	50	22
g5	5	78.3:21.7	78.9:21.1	21.1	2613	2933	1.12	−38	46	15
g6	6	72.1:27.9	72.0:28.0	28.0	3081	3483	1.13	−32	45	10

[a]$(M/E)_{feed}$ is the cumulative molar feed ratio of monomers 2/10. $(M/E)_{cum}$ is the cumulative monomer incorporation ratio in the polymer calculated from ^{1}H NMR in toluene-d_8 at 363 K. [b]Et$_{cum}$% represents the cumulative ethylidene content in the copolymer determined as Et$_{cum}$% = 1/[1 + $(M/E)_{cum}$] × 100%. [c]Determined using GPC analysis. [d]Determined using DSC analysis. [e]Not observed in the range of −80 to 140 °C.
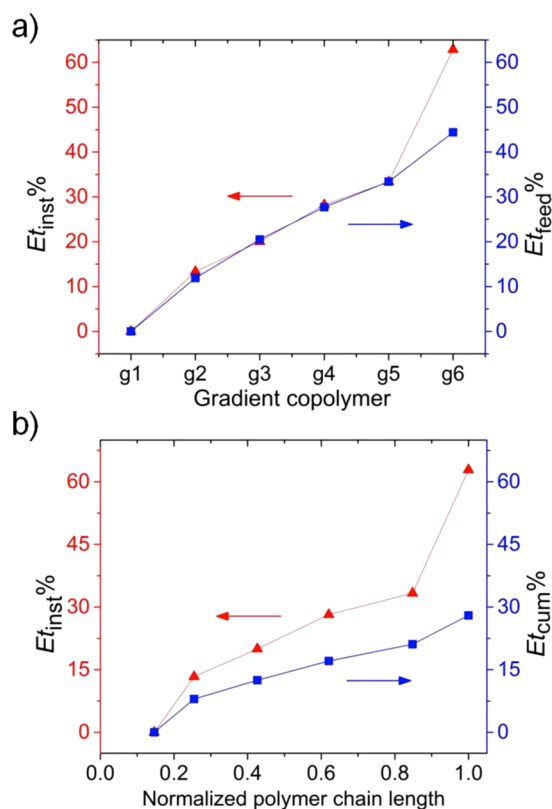
Figure 2. (a) Comparison between the instantaneous ethylidene content in the copolymer and the ethylide ratio in each monomer feed.[17] (b) The instantaneous and cumulative ethylidene contents as a function of the polymer chain length. The normalized chain length is calculated from M_n of each sample (g1−g6) divided by M_n of g6.

Figure 3. Stacked DSC traces of (a) random and (b) gradient methylidene-ethylidene copolymers expanded in the temperature range of −75 to 25 °C.

and tri(n-hexyl)borane lead to formation of organoboranes containing 2−3 2° carbons adjacent to the boron center rendering them less (or non) reactive compared to boron species with 0 or only one adjacent 2° carbon. The sterically congested boron centers result in kinetically distinct propagating species and a broadened or bimodal MW distribution.

Ylides are used as monomers for the polyhomologation reaction and their rate of incorporation is quite fast. This presents a challenge to monitor the monomer consumption during chain growth. As a practical matter to verify the compositional gradient during the course of polymerization, gradient copolymers were synthesized by sequential addition of monomer mixtures to the polymerization reaction. This allowed sampling the composition of the growing polymer chain at various stages of growth. The final gradient copolymer was synthesized from six incremental additions of the methylide and ethylide monomers starting with a segment of linear polymethylene and ending up with a segment rich in methyl branches. Each increment of added monomers contained a greater proportion of ethylide **10** than the previous one. The polymerization progress was monitored by removing, quenching and oxidizing an aliquot of the reaction prior to addition of the next increment of monomers. The MW distribution of the isolated polymers, measured by GPC, remained narrow and shifted to higher MW as the polymerization proceeded (Figure 1a). The cumulative ethylidene content increased with an increase of ethylide **10** in the monomer feed (Table 1). Progress of gradient polymerizations is traditionally tracked by monitoring monomer consumptions with in situ ^{1}H NMR. The
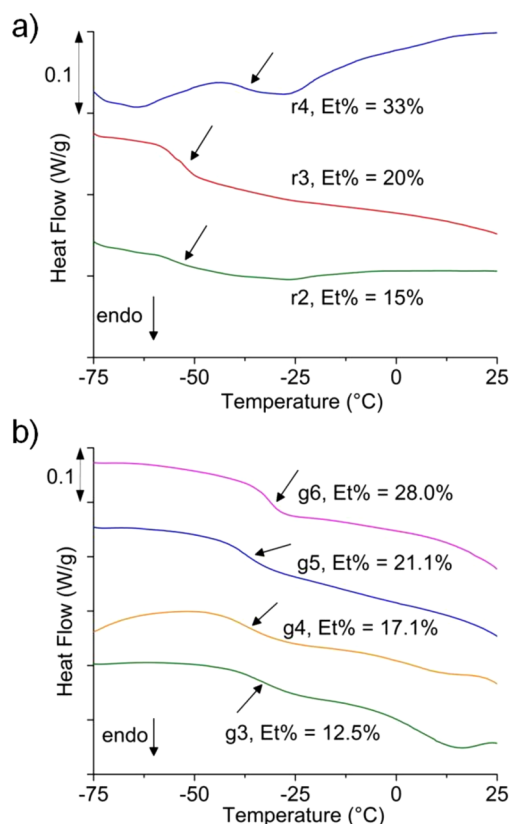
practical challenges of measuring the monomer conversion by this method necessitate estimation of the polymer compositions in order to calculate the instantaneous monomer content. This was accomplished by determining the average number of monomer units in the polymer at different polymerization stages. The instantaneous monomer content was then calculated based on the polymer compositions at the beginning and the end of each segment.

We assigned the number of both methylidene and ethylidene units for all polymers sampled during the course of the copolymerization (Figure 1b and Table S4). Both the calculated polymer MW and monomer incorporation ratio based on these numbers are very close to the experimental values (Table S4). The instantaneous ethylidene content calculated with this method is also very close to the experimental ethylide ratio in the monomer feed at each stage (Figure 2a) and increases progressively as the polymerization reaction proceeded (Figure 2b). The high ethylidene content (over 60%) in the last segment of the polymer indicates that it contains a significant number of ethylidene dyads −CH(CH$_3$)−CH(CH$_3$)− and, in the extreme, triads −CH(CH$_3$)−CH(CH$_3$)−CH(CH$_3$)−. These substructures have a higher ethylidene content than polypropylene and cannot be obtained by C2 polymerization of propylene. The living C1 polymerization therefore is able to continuously tune the content of methyl branches along the polymer chain over a wider range than what can be achieved by ethylene-propylene copolymerization.

Thermal analyses of all polymer samples revealed that the polymer crystallinity decreased with increasing methyl branch

content (Tables 1 and S1 and Figure S5). The T_g of random copolymers r2–r4 increases from −56 to −38 °C as the ethylidene content increased (Table S1 and Figure 3a). The gradient copolymers g3–g6 have similar T_g in the range of −32 to −38 °C (Table 1 and Figure 3b), in between the values of linear PE ($T_g = -78 \pm 10$ °C)[18] and atactic PP with similar MW ($T_g = -24$ °C, $M_n = 3800$).[19] A broad T_g range, as proposed for some gradient copolymers, was not observed in these materials due to the chemical similarity between the comonomers.

In conclusion, we have developed a convenient protocol to prepare diethylsulfoxonium ethylide. This ethylide is used in the polyhomologation reaction for the controlled synthesis of poly(methylidene-co-ethylidene) copolymers. Moreover, the structurally unique hydrocarbon polymer, gradient methylidene-ethylidene copolymer, an ersatz gradient ethylene-propylene copolymer, can be realized via the living C1 polymerization permitting investigation of the physical and thermal properties of this material. This methodology can be used for the synthesis of multisegment hydrocarbon copolymers with control of monomer content and allows for the insertion of functionality at any location on the linear polyethylene chain.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Materials, instrumentation, detailed experimental conditions, and supplemental figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00218.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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