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$LiCB_{11}(CH_3)_{12}$-Catalyzed Radical Polymerization of Isobutylene: Highly Branched Polyisobutylene and an Isobutylene−Ethyl Acrylate Copolymer

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We have previously described[1] a $LiCB_{11}(CH_3)_{12}$-catalyzed polymerization of terminal alkenes in poorly ligating solvents at ambient pressure and temperature in the presence of a radical initiator and suggested a radical polymerization mechanism. This was provocative, since rapid chain transfer caused by allylic hydrogen abstraction is known to prevent the radical polymerization of terminal alkenes other than ethylene.[2] The least likely simple alkene to undergo radical polymerization is isobutylene (**1**), and it has therefore been our first candidate for a more detailed examination. Linear polyisobutylene (***l*-PIB**, $[-CH_2C(CH_3)_2-]_n$), the common homopolymer of **1**, is prepared commercially by cationic polymerization of **1** at low temperatures with a suitable Lewis acid.[3]

Under $LiCB_{11}(CH_3)_{12}$ catalysis and initiation under nonoxidizing conditions, radical polymerization of **1** takes place and produces a polyisobutylene with a degree of polymerization up to ~500 (GPC with polystyrene standards). Typical reactions were performed in 0.5 mL of a stirred dry 1,2-dichloroethane or toluene solution containing 50 mg of $(CH_3)_3C-N{=}N-C(CH_3)_3$ and 50 mg of dried $LiCB_{11}(CH_3)_{12}$[4] under 1 atm of excess **1** (dried with a molecular sieve), at 80 °C in the dark or at ambient temperature with 254 nm irradiation, until the initiator was consumed. The polymer was isolated in a 17−130 mg yield by extraction into hexane at 40 °C. The catalyst was recovered in an ~80% yield and could be recycled indefinitely.

As ordinarily prepared by removal of the sulfolane solvent at 180 °C/0.2 Torr overnight, the catalyst contains a few percent of residual sulfolane. We now find that this is necessary for catalytic activity, presumably because it reduces ion aggregation. The optimal concentration of sulfolane in the reaction mixture is ~0.6% by weight. Higher concentrations gradually suppress the catalysis, presumably by cation complexation. The solvent-free catalyst can also be activated with a small amount of ethyl acetate, and even a large amount does not inhibit the polymerization. Ion aggregation and the complexes formed with the various additives are currently under investigation.

Four aspects of the results are striking.

(i) The polyisobutylene formed from $CH_2{=}C(CH_3)_2$ (**1**), $CD_2{=}C(CH_3)_2$ (**1-*d*$_2$**), $CH_2{=}C(CD_3)_2$ (**1-*d*$_6$**), or $^{13}CH_2{=}C(CH_3)_2$ (**1-^{13}c**) is a previously unknown isomer (***b*-PIB**). Unlike ***l*-PIB**, it yields a negative peak on a GPC trace obtained in THF with a refractive index detector. It has a decomposition temperature of 220 °C (cf. ***l*-PIB**, 330 °C), an indistinct glass transition at 15 °C (cf. ***l*-PIB**, −28 to −30 °C), and very complicated NMR spectra, in which the known peaks of ***l*-PIB** are absent (Figures 1 and 2).

(ii) The 1-D and 2-D ^1H, ^2H, and ^{13}C NMR spectra of ***b*-PIB** formed in this fashion from **1**, **1-*d*$_2$**, **1-*d*$_6$** and **1-^{13}c** are only compatible with a highly branched structure, in which a backbone contains no or very few $-[CH_2-C(CH_3)_2]-$ units familiar from ***l*-PIB**, and consist primarily of $-[CHR-]_n-$ units, in which R is a short linear segment, $-C(CH_3)_2[CH_2C(CH_3)_2]_mH$. In both poly-**1** and poly-**1-*d*$_6$**, methyl groups of the terminal isobutyls represent ~20% of the total integrated intensity of all methyl groups, hence the maximum average value of *m* is 4. In poly-**1-*d*$_6$**, the intensity of CD and CD_2 signals is at most 5% of that of CD_3 signals. At least three different kinds of CH groups are clearly present in the spectrum of poly-**1-^{13}c** ($^1J_{CH}$ = 126−130 Hz). ^1H gCOSY and HSQC NMR permitted a ready identification of isobutyl branch ends and of one of the terminal groups as $-CH_2-C(CH_3){=}CH_2$, but provided no indication of the presence of any CH_2CH_2 moieties. A schematic representation of the structure is provided in Chart 1. A more complete characterization is being attempted, using fractionation, higher field NMR, and additional isotopically labeled monomers.

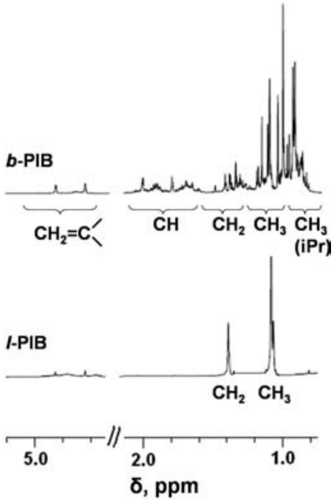

Figure 1. ^1H NMR (400 MHz) of ***l*-PIB** and ***b*-PIB**.

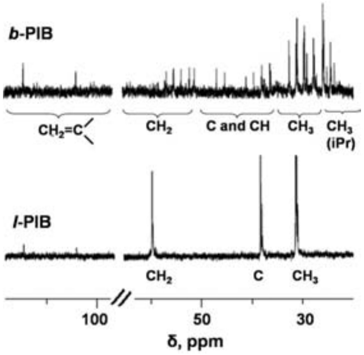

Figure 2. ^{13}C NMR (100 MHz) of ***l*-PIB** and ***b*-PIB**.

(iii) The results are compatible with a radical polymerization of a $\mathbf{1}/Li^+CB_{11}(CH_3)_{12}^-$ complex (**2**), observed by ^1H gDOSY NMR, triggered by the addition of an initiator-derived radical. In the absence of an initiator, or when a radical trap (TEMPO, C_{60}) is added, polymerization does not occur. The addition of *t*-BuOLi

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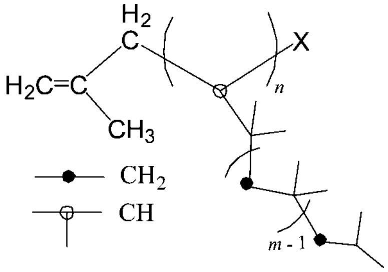
Chart 1. Schematic Representation of the Structure of ***b*-PIB**[a]



[a] Random presence of some very short linear segments in the backbone cannot be excluded. X originates in the initiator.

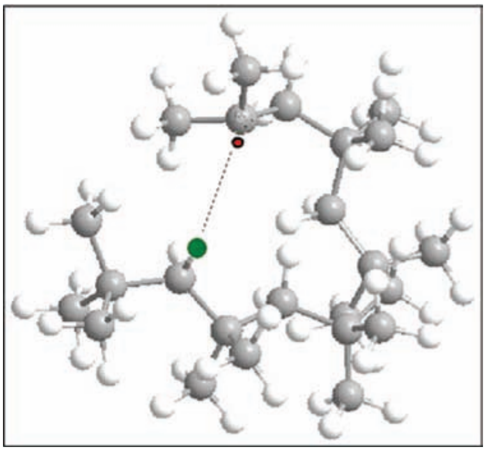


Figure 3. An MM2 optimized **PIB** conformation conducive to hydrogen abstraction via an 11-membered transition state.

slows down but does not prevent ***b*-PIB** formation, presumably by complexing some of the free Li^+ cation as t-$BuOLi_2^+$ $CB_{11}(CH_3)_{12}^-$. There is no polymerization in the absence of $LiCB_{11}(CH_3)_{12}$, even if all the initiator is decomposed by irradiation, nor when 12-crown-4 is added or the reaction attempted in THF solvent.

To rationalize the postulated acceleration of the radical chain propagation step upon conversion of **1** into **2**, which permits it to compete successfully with allylic abstraction, we invoke an analogy to the formal conversion of **1** into a methacrylate, which also enables radical polymerization. Acceleration by complexation has been predicted by quantum chemical calculations of the activation energy for methyl radical addition to the C_2H_4/Li^+ complex in the gas phase,[5] and catalysis of the radical polymerization of acrylonitrile with Li^+ has been long known.[6]

To account for the branched structure, we propose a backbiting CH_2 hydrogen atom transfer after several additions of a unit of **1**. The NMR results suggest little hydrogen abstraction from the sterically more accessible CH_3 groups. According to MM2 optimized geometries and energies, the 11-membered hydrogen transfer transition state is the smallest that can be easily accommodated (Figure 3). The transfer produces a quasi-equilibrium between a secondary radical and a tertiary one. We propose that the propagation step is slow relative to this transfer. The tertiary radical dominates in the steady state and is clearly seen along with the initiating t-butyl radical in an EPR spectrum taken under continuous irradiation.[7] The secondary radical, not observed in EPR, is apparently sufficiently more reactive to dictate the propagation path most of the time.

The vinylidene end group has the structure expected if a hydrogen abstraction from the chain end is somewhat competitive with the addition of **1** after the backbiting step. We plan to examine the polymerization kinetics next.

(iv) In keeping with the proposed radical mechanism, **1** reacts with ethyl acrylate (EA) to form a copolymer in a separable mixture with some ***b*-PIB**. In these experiments, 0.1 mL of freshly distilled ethyl acrylate was added to the reaction mixture at the outset. On the basis of NMR, the copolymer typically contained 50% IB by weight and is distinct from the alternating EA/**1** copolymer reported by Mashita at al.[8] Its detailed structure is under examination. Molecular weights were $2 \times 10^4-10^6$, depending on reaction conditions, with yields ranging from 130 to 350 mg. The presence of both components in the same chain was verified by ^1H gDOSY NMR and HPLC/GPC analysis.

The use of a radical initiator with oxidizing properties, such as O_2 or $CB_{11}(CH_3)_{12}^{\bullet}$ at 25 °C and (t-Bu-O)$_2$ at 70−80 °C, complicates the homopolymerization considerably and produces a separable mixture of ***b*-PIB** with ***l*-PIB** carrying a carborate chain end, via what we believe to be concurrent radical and cationic mechanisms. The formation of either can be suppressed with suitable additives. In the presence of ethyl acrylate, three separable polymers are formed under some conditions: ***b*-PIB**, a copolymer, and ***l*-PIB**. Details will be described elsewhere.

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Supporting Information Available: Experimental procedures, properties of ***b*-PIB**, NMR determination of ***b*-PIB** structure, polymerization and copolymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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