The Structure of Oligomeric Poly(isoprenyllithium)

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Received May 14, 1970

ABSTRACT: A study has been made of the ^1H nmr spectra of oligomeric poly(isoprenyllithium) ($\overline{DP}$ 1.2–3) prepared in benzene using *sec*- or *t*-butyllithium. In hydrocarbon solvents, *cis* and *trans* isomers can be distinguished but no measurable concentration of 3,4 structure can be found. There is a distinct preference (~66%) for one isomer in hydrocarbons at room temperature but the preference disappears on raising the temperature with all but the sample of lowest DP. This phenomenon is reversible. On transfer at low temperature to mixtures rich in THF, complete isomerization occurs at −40° to the form not preferred in benzene, which then remains stable at all temperatures between −80 and 0°. Evidence can also be obtained on rotation of the terminal methylene group. Although it has not been possible to identify positively which form is *cis* (or *trans*) the implications of the results to the phenomenon of stereospecific polymerization of isoprene by lithium alkyls are discussed.

It has been known for several years that polymerization of isoprene by lithium alkyls gives stereoregular polymers.[2a] In hydrocarbon solvents a highly *cis* 1,4 polymer is produced while a mainly 3,4 polymer is found in ether solvents, or even in the presence of small amounts of a highly basic ether such as THF.[2b] A number of attempts have been made to explain this stereoregulating action,[3–6] but it is difficult to assess the validity of such mechanisms in the absence of more specific information on the nature of the active centers. It is possible to obtain some information on these from proton resonance spectra. In a normal active polymer, the signals from the ultimate isoprene unit will be swamped by those of the many chain isoprene units so it is necessary to study a model poly(isoprenyllithium) of low DP. It has been shown recently[7] that an almost 1:1 addition compound of *sec*- or *t*-butyllithium with isoprene can be formed in benzene, and that its propagation characteristics are little different from poly(isoprenyllithium) of higher molecular weight. Such systems are therefore of interest for the study of stereospecific polymerization.

Experimental Section

Benzene[8] and isoprene[9] were purified as reported previously. Completely deuterated cyclohexane, methylcyclohexane, and tetrahydrofuran were obtained from Merck Sharpe and Dohme Ltd. The hydrocarbons were simply dried over calcium hydride before use; the tetrahydrofuran was first treated with metallic potassium. Early experiments were carried out with *sec*-butyllithium (Foote Mineral Co.) which was subjected to a short-path vacuum distillation before use. Later experiments were initiated with $t\text{-}C_4D_9Li$ prepared from $t\text{-}C_4D_9Cl$ and lithium suspension in a high-vacuum modification of the method of Kamiensky.[10] It also was subjected to a short-path vacuum sublimation before use.

Formation of "living" polymers of low molecular weight was carried out in benzene at 10° as described[7] for the preparation of oligomeric polyisoprenes except that the methanol termination step was omitted. The concentration was normally around 1 *M*. Nmr tubes were sealed onto a side arm to enable samples to be removed for study and provision was made for the removal of benzene by sublimation and resolution of the sample in cyclohexane or methylcyclohexane using standard break-seal techniques. With the latter solvent the sample could be later diluted with tetrahydrofuran at low temperature. Sample tubes were stored at −80° before use. All operations were carried out in a sealed vacuum apparatus.

Nmr spectra were measured on a Varian HR-100 spectrometer using a side-band technique to calibrate chemical shifts. The reference absorption was that of the benzene solvent or traces of benzene remaining on transfer to other solvents. In a few later experiments tetramethylsilane was included in the tubes and used as reference. It is not attacked by the lithium compounds.

Results

The characterization of an oligomeric poly(isoprenyllithium) in benzene was described in an earlier preliminary report.[11] The lithium-bearing monomer unit was shown to exist in *cis* and *trans* forms, for, in addition to weak signals from small amounts of nonlithium-bearing units, two signals in about 2:1 ratio were found for methine, methyl, and methylene groups. No evidence was found for a separate 3,4-type structure. Figure 1 shows comparison spectra of active and terminated products. Analysis of the terminated products[7] has shown that addition of butyllithium occurs almost exclusively in the direction

$$\underset{\delta}{RCH_2}\underset{\gamma}{CH}\underset{\beta}{C}(CH_3)\underset{\alpha}{CH_2}(Li)$$

The main signals will therefore be produced by this type of addition compound. There will be weak signals caused by a small amount of addition at the other end of the isoprene molecule, which was found to occur to

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(2) (a) F. W. Stavely, *et al.*, *Ind. Eng. Chem.*, **48**, 778 (1956); (b) H. Hsieh, D. J. Kelley, and A. V. Tobolsky, *J. Polym. Sci.*, **26**, 240 (1957); H. Hsieh and A. V. Tobolsky, *ibid.*, **25**, 245 (1957).

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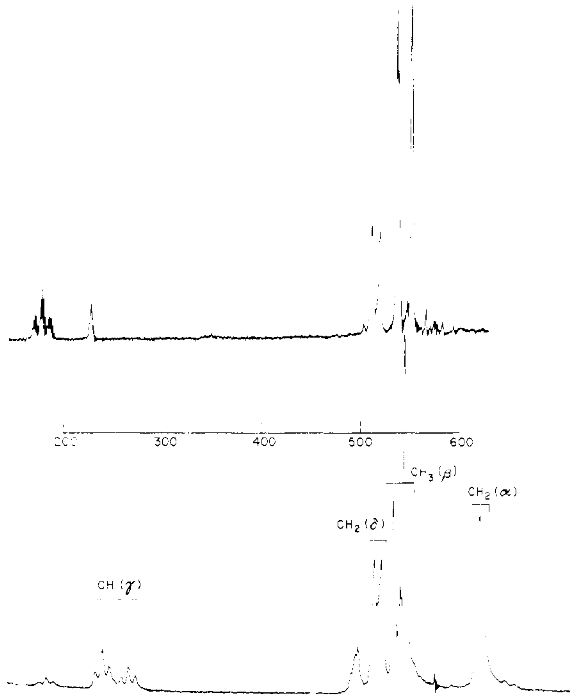

Figure 1. 100-MHz nmr spectra of C_4D_9Li adducts with isoprene (benzene T = 25°). Upper spectrum hydrolyzed 1:1 addition compound isolated by preparative gas chromatography. Lower curve, "living" lithium adduct ($\overline{DP}$ ~1.2). This spectrum shifted downfield ~20 Hz to normalize to the same position for "dead" -CH- signals. The small signal at lower field to the CH_2 (δ) peak comes from linking $-CH_2CH_2-$ groups in two isoprene unit chains. It appears also in hydrolyzed 1:2 addition products. The $-CH_2$ (α) signal is not resolved into its components at this temperature (*cf.* Figure 2, ref 11). Scale in hertz upfield from benzene.

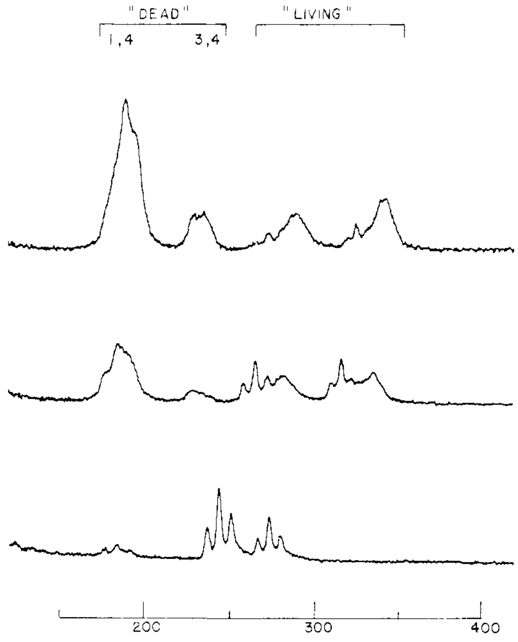

Figure 2. Olefinic region of three "living" oligomers in benzene at 60°: upper curve $\overline{DP}$ ≈2.7; middle curve, $\overline{DP}$ ≈1.65; lower curve $\overline{DP}$ ~1.2. Scale in hertz upfield from benzene (100 MHz).

the extent of about 3%. The weak triplet just observable at ~117 Hz and the small extra signal at 600 Hz (Figure 1, ref 11) may be caused by this reversed addition product. The assignments given previously[11] and indicated on Figure 1 are similar to those in normal polyisoprenes except that the CH_2 (α) and CH (γ) signals are upfield in the "living" unit compared with normal "dead" units. The areas under the CH, CH_2, and CH_3 signals are in the ratio expected from this assignment when allowance is made for the presence of some two-unit polymer. Of the two methyl signals attributed to the terminal unit, that at higher field is the stronger. In high molecular weight polyisoprenes the high-field signal corresponds to methyl *trans* to the methine proton (*trans*-polyisoprene). It is not sure that this assignment would be the same in the lithium compound as the chemical shift between *cis* and *trans* forms is small and could be different in the two types of compound. Some preference might be expected for the more outstretched *trans* form in packing in aggregates but the structure of the polymer formed under these conditions suggests a largely *cis* configuration. Whatever the predominant configuration, this was found to be independent of temperature to 70°. On transfer to (deuterated) cyclohexane or methylcyclohexane the spectrum was found to be very similar, except for a small general upfield shift and a poorer resolution than in benzene.

In order to establish if the behavior of this primarily one-unit polymer was characteristic, a poly(isoprenyllithium) of DP 3 was produced under the same conditions in benzene. A similar nmr spectrum was observed, the signals from the nonterminal units were stronger and the triplet structure of the methine protons of the terminal units was broadened to single peaks but their ratio at room temperature was the same as in the earlier sample. On raising the temperature, however, the two terminal methine proton bands moved upfield and the intensity ratio changed also, becoming equal at 60°. The change was quite reversible. Evidently *cis–trans* isomerization occurs freely with a time scale of less than 20 min and the measured intensities are equilibrium values. More illustrative were the spectra of two samples prepared to have $\overline{DP}$ of ~1.65 and 2.7. The olefinic region of these samples is shown in Figure 2. The triplets associated with methine protons of RM_1Li are seen on the shoulders of broader bands which must correspond to methine protons of the terminal ("living") units of RM_2Li and RM_3Li. The triplets are only just noticeable in the specimen of $\overline{DP}$ 2.7. This effect is probably present to a smaller extent even in the spectrum of the polymer of DP ~1.2 (Figure 1, ref 11). The triplets appear assymetric due to broader weak signals under the high-field end connected with the small amount of two-unit chains. The chemical shifts of the methine protons must be slightly different in the one-unit polymer but become more closely the same in longer unit, producing in the latter case structureless bands by overlapping and by the general viscosity broadening effect found to occur even at low DP with "dead" polymers. Both triplets and broad bands move upfield between 0 and 70° and the low-field/high-field intensity ratio changes with temperature. In the α-methylene position (~600 Hz upfield from

TABLE I
PER CENT OF LOW-FIELD METHINE TRIPLET AS A FUNCTION OF TEMPERATURE (BENZENE)

Polymer	$\overline{DP}$	Per cent of triplet 25°	40°	60°	70°
1X	1.25	64	64	61	
2X	3.0	68	64	50	49
ZZB	1.65		63	47.5	45
ZZC	2.7	66	60	47	44
IVW[a]	1.3	65			
IIIW[a]	1.2	66.5			

[a] Initiated with *sec*-butyllithium, others with *t*-butyllithium.

TABLE II
CHEMICAL SHIFTS OF METHINE AND α-METHYLENE GROUPS[a]

Methine "Dead" unit	"Living" unit	α-Methylene	Solvent (temp, °C)
180.5	236	619	Benzene (25)
	263		
182	244	622	Benzene (60)
	276	612	
202	263	646	Methylcyclohexane (25)
	281		
203	292	634	MCH + 8% THF (−20)
	327		
225	357	632	MCH + 50% THF (−80)
	414	676	
223	359	622	MCH + 50% THF (−60)
	410	652	
223	363 ↓[c]	616 ↓	MCH + 50% THF (−40)
	407 ↑[b]	646 ↑	
220	363	621	THF (−60)
	410	669	
220	367 ↓	611 ↓	THF (−40)
	409 ↑	644 ↑	
218			THF (−20)
	411	642	
219			THF (0)
	403	631	

[a] Poly(isoprenyllithium), $\overline{DP}$ ~1.2: Hertz upfield from benzene at 100 MHz. [b] ↑, increases with time. [c] ↓, decreases with time.

benzene) the bands also have slightly different positions for one- and two-unit chains. These bands reflect also the isomerization changes on heating and drift slightly *downfield* with temperature. The invariant behavior with respect to temperature is thus a characteristic of systems only having predominantly RM_1Li units, either because these form tighter aggregates, or because of the perturbing influence of some residual RLi which must be present in this type of sample. RM_1Li units mixed with RM_2Li units show the same behavior as those of higher molecular weight. These changes of ratio and chemical shift are summarized in Tables I and II.

Isomerization can also be induced even in the sample of $\overline{DP}$ 1.2 by diluting the sample with tetrahydrofuran. A typical sample was transferred to methylcyclohexane. (This does not cause isomerization.) THF (8%) was added at −78° to give about a 1:1 ratio to the poly(isoprenyllithium). Only broadened spectra could be obtained at low temperatures but at −20° good resolution could be obtained. Both methine proton triplets were found to be upfield from their position in methylcyclohexane (Table II) and their intensity ratio had changed to ~1:1.

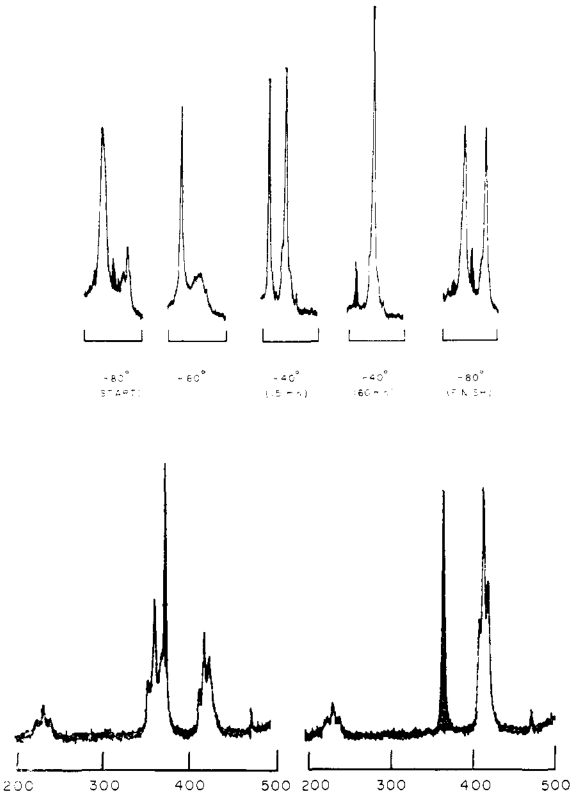

Figure 3. 100-MHz nmr spectra of α-CH_2 region (upper) and -CH- region (lower) of a poly(isoprenyllithium) oligomer ($\overline{DP}$ ~1.2) prepared in benzene and transferred to 50/50 THF-methylcyclohexane at low temperature. The shaded peaks are caused by residual undeuterated solvent. Temperature increased in stages from −80 to −40° and then returned to −80° (left to right). Scale in hertz upfield from residual benzene (600–700 Hz in upper figure); lower figure, −80° start (left) and −80° finish (right).

If the polymer ($\overline{DP}$ ~1.2) is transferred in a similar manner to a 50/50 v/v mixture of methylcyclohexane and THF more drastic changes occur. At −80° even, the spectra show good resolution. The methine triplets (Figure 3) are now even further upfield (~100 Hz) than in methylcyclohexane. In fact even in pure tetrahydrofuran their chemical shift is substantially the same (Table II). A limit has been reached which may correspond to complete disaggregation of the lithium compound. Little isomerization has occurred in the transfer process, the low-field methine triplet being still stronger. The terminal methylene region is complex and only interpretable by experiments in which the temperature is raised. On raising the temperature to −60° (Figure 3) the terminal methylene protons give rise to a broad band and a sharp signal. At −40° the former sharpens, leaving two fine lines in this region, one of which (low field) slowly disappears while the other increases in intensity. After about 1 hr only the one at higher field remains. At the same time in the methine region the low-field triplet disappears at the expense of that at a higher field. *cis–trans*

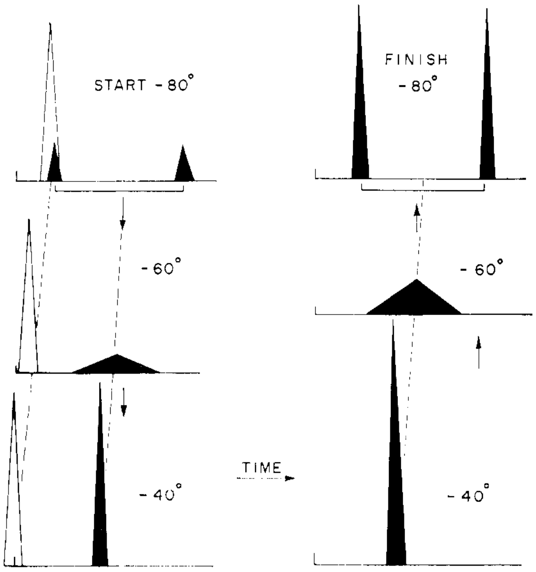

Figure 4. Schematic representation of changes in the α-methylene region. Conditions as in Figure 3.

isomerization is clearly occurring. Thus at $-40°$ the two sharp signals in the terminal methylene region must be associated with rapidly rotating $-CH_2$ groups in both *cis* and *trans* forms. At $-60°$ in one of these forms rotation is slow, giving an exchange-broadened wide band. Thus originally at $-80°$ we should have seen two equal bands from nonequivalent protons in the isomer which has a slow rotation speed on the nmr time scale and a single band from the other isomer where methylene rotation is still rapid. These overlap to produce the observed spectrum. This diagnosis can be confirmed by taking the completely isomerized sample at $-40°$ and recooling it to $-80°$; since only one isomer remains, the spectrum should be simpler. At $-60°$ the remaining sharp signal broadens and at $-80°$ splits to a doublet of separation 38.5 Hz, indicating progressive slowing of methylene rotation. A schematic diagram of the temperature-induced changes in the terminal methylene region is shown in Figure 4.

Table III

Structure of Polyisoprenes of High Molecular Weight as a Function of Temperature of Preparation in Benzene

	Temp, °C			
	20	40	60	80
cis	71	66	64	62
trans	23	27	27	30
3,4	6	7	8	8

Discussion

The observation that *cis* and *trans* forms of poly(isoprenyllithium) exist in equilibrium, the position of which depends on solvent and temperature, suggests some connection with stereospecificity in lithium-type polymerizations. It should be noted, however, that in hydrocarbon solvents, the nmr spectra are of necessity those of the associated species in which the majority of the molecules are known to exist. If monomer addition occurs directly with aggregated poly(isoprenyllithium) as sometimes suggested[12] and should the preferred configuration of the chain end there be *cis*, then there would be a close connection between stable configuration of the lithium compound and polymer microstructure in hydrocarbon solvents. We have previously suggested[13] that reaction only occurs with the monomeric dissociation product of these aggregates, and in this case we cannot be sure that the preferred configuration is the same in the dissociated state. This dissociative mechanism depends, however, on a very rapid association–dissociation equilibrium, where the reassociation step is much faster than the monomer addition step and the extent of dissociation is very low. Individual monomeric poly(isoprenyllithium) molecules would therefore have a very short lifetime and more than one monomer addition per dissociation step would be very unlikely. Under these conditions the probability of *cis/trans* isomerization before monomer addition might also be low and thus microstructure in hydrocarbons determined essentially by configurational preference in the aggregates.

There remains the possibility that the preferred configuration of the lithium compound is *trans* in the aggregated state in hydrocarbons. This would present problems in the interpretation of stereospecificity in polymerization unless our argument above is incorrect and the unassociated forms were able to isomerize before reaction. At the moment we cannot suggest a convincing method of identification of the two isomers. Glaze,[14] who recently reported data on the addition product of *sec*-butyllithium and butadiene, has suggested a 1:3 *cis/trans* ratio in this case. The hydrolysis product was predominantly *trans*-5-methyl-2-heptene. No such method is available for isoprene as hydrolysis produces the symmetrical end group $=C(CH_3)_2$. Hydrolysis with D_2O rather than H_2O to produce $=C(CH_2D)CH_3$ end groups shows that it is the signal at lower field of the two methyl signals which lowers in intensity due to preferential incorporation of deuterium. Nmr investigations of compounds of the type $RCH{=}C(CH_3)_2$,[15,16] however, fail to identify positively whether it is the *cis*-like or *trans*-like methyl which absorbs at lower field.

Some indication if the *cis* assignment for the larger fraction of the lithium compound in hydrocarbons is plausible can be made by checking the effect of temperature on the microstructure of normal polyisoprenes in benzene. The *cis* content in high polymers should decrease at higher temperature if it follows the change in preferred configuration in the "living" oligomers. Experiments to illustrate this point are given in Table III. At room temperature ~70% of the polymer has

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cis-1,4 structure,[17] slightly higher than the percentage of the preferred configuration in the oligomers. The *cis*-1,4 structure decreases as the temperature is raised but not quite so rapidly as does the *cis*/*trans* ratio in the oligomer (for $\overline{\mathrm{DP}} \sim 3$ which probably approximates best conditions in normal polymerization). The trend is the same and differences quantitatively would have to be explained by some differences in reactivity between *cis* and *trans* forms.

In THF rich mixtures the nmr spectrum is certainly that of unassociated poly(isoprenyllithium) molecules. The experiments show that rotation at −40° about the terminal C–C bond is rapid on the nmr time scale (at even lower temperatures for one of the isomers). Rotation about the penultimate C–C bond occurs slowly (time scale in minutes) at −40° and with any reasonable activation energy should be considerably faster at room temperature (see Figure 5). Hindered rotation about both bonds, with more double bond character in the penultimate C–C bond, is indicated. This checks with the fact that the methine proton signals are about 2 ppm upfield from their normal position in an olefin, suggesting considerable charge on the γ-carbon atom in THF. The most charge clearly is still on the terminal methylene group, whose signal moves only slightly between benzene and THF. Presumably some compensation has occurred involving differences in environment between aggregate and solvated forms for it would be expected to move downfield if charge were being distributed to the γ carbon. In THF, the system resembles the allyl anion[18] where a freely rotating anion was found to exist above −80°. Rotation is not as free as in this anion nor is the charge symmetrically placed between α and γ carbons but rather follows the rule that negative charge is preferred on primary carbon atoms. A similar effect can be noted in the pentadienyl anion.[19] Lowering the temperature freezes out rotation about the bonds, and does not separate 3,4 and 1,4 structures as might be expected if the system contained rapidly equilibrating covalent structures. There is no evidence for a change in basic nature of the species between benzene and THF but rather a gradation in properties. Hindered rotation is possible in both solvents about terminal and penultimate C–C bonds (at least for DP >1). This would suggest that the delocalized allylic form, albeit with more charge on the terminal carbon in benzene, is the best description under all conditions.

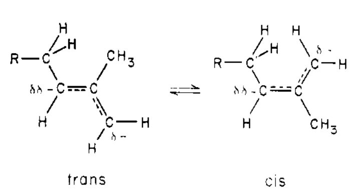

Figure 5. Relationship between the stereoisomers of the active chain end.

Both in benzene and THF, 3,4 structure is present in the polymer, in the former case to a minor extent and in the latter case becoming the major structure. The experiments on oligomer structure[7] showed that in hydrocarbon solvents, the percentage of 3,4 product depends somewhat on the reactant. This was confirmed by examining the structures of the products from methylcyclohexane–THF mixtures (50/50) after termination with methanol. Both the 1:1 and 1:2 *t*-BuLi–isoprene adducts were isolated by preparative gas chromatography. Both gave only 25–30% 3,4 structure in the terminal unit, independent of reaction temperature and whether or not the lithium compound had been allowed to isomerize from its benzene stable form. This is considerably higher than for termination in benzene but in a normal polymerization in this solvent mixture, the structure would have been overwhelmingly 3,4. This type of experiment is confirmatory evidence that no unique 3,4-poly(isoprenyllithium) exists but that reaction to form 3,4 products is determined in the reaction step influenced of course by electron density at the γ-carbon but with considerable latitute depending on the nature of the attacking reagent.

(17) The *cis*/*trans* ratios observed are appreciably lower than are often reported. Much of the earlier data was obtained by infrared methods which do not give accurate values for this ratio. The present values at a room temperature is even lower than our earlier reported nmr value (~80% *cis*)[9]. The tabulated values are more accurate and reflect improvements in instrumentation which allow better resolution of *cis* and *trans* methyl signals.

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