Lithium Alkyl Initiated Polymerization of Isoprene. Effect of Cis/Trans Isomerization of Organolithium Compounds on Polymer Microstructure

D. J. Worsfold and S. Bywater*

Chemistry Division, National Research Council of Canada,
Ottawa, Ontario K1A 0R9, Canada. *Received November 15, 1977*

ABSTRACT: The microstructure of polyisoprene produced by *sec*-butyllithium initiation in a hydrocarbon solvent has been investigated as a function of initial monomer and initiator concentrations. The trans-1,4 content was found to increase as the initiator concentration increased and as the monomer concentration decreased. It is suggested that the trans content increases because cis-active centers produced by monomer addition can isomerize to trans-centers when monomer addition is slow. To check this hypothesis the isomerization rates of model compounds of DP = 1 and 2 have been measured. It is found that such a mechanism in conjunction with a higher rate of addition of monomer to cis-centers can account for the observed changes in microstructure.

The stereospecific polymerization of isoprene in hydrocarbon solvents by lithium-based initiators to give a polymer having a largely cis-1,4 structure[1] still presents some unexplained features. The commonly suggested mechanism involves [2-4] the formation of a Diels–Alder type six-membered ring activation complex between *cis*-isoprene and the carbon–lithium bond. On this basis it is not clear why butadiene generally forms a polymer containing a much more mixed cis/trans ratio.[5] In addition, the discovery[6,7] that the active centers themselves exist in both cis and trans forms with the trans predominating in hydrocarbon solvents[8,9] raises other problems. The simple mechanism implicity assumes that no isomerization of the end occurs between monomer addition steps whereas it was shown[7] that this can indeed occur but at a rate which is unknown.

If some isomerization of cis to trans centers does occur, its importance in determination of microstructure will depend on the rate of monomer addition. Sinn[10] has in fact suggested that isomerization could be a deciding factor in the observed[2,10,11] increase in trans content in the polymer as the initiator concentration is raised. Under these conditions the microstructure of a terminal unit is only decided on monomer addition. Modification of the simple scheme involving a cis-stereospecific addition process could then be made in the following way. Both cis and trans active centers produce a new cis center on monomer addition but perhaps at different rates. The original cis center would become a cis unit in the chain and a trans unit an internal trans unit, i.e.,

$$\begin{array}{c} \sim\text{cis}^* + \text{M} \xrightarrow{k_p^{\text{cis}}} \sim\text{cis, cis}^* \\ k_1 \downarrow\uparrow k_{-1} \\ \sim\text{trans}^* + \text{M} \xrightarrow{k_p^{\text{trans}}} \sim\text{trans, cis}^* \end{array}$$

The microstructure of polyisoprene will in fact be particularly sensitive to the probability of isomerization because of the rather peculiar kinetic behavior observed in these systems. The rate of monomer addition is known to be proportional to the fourth root of the total active center concentration. An increase by a factor of 10^4 will only cause the rate to increase tenfold but there will still be 10^4 times more chains, which although they may be dormant from time to time on average will individually add monomer 10^3 times more slowly at the higher initiator concentration. This would not be the case if the propagation rate were simply first order; the average lifetime of a particular active center between monomer additions would be independent of initiator concentration.

In order to determine the validity of such a mechanism, more experiments have been carried out on polymer microstructure as functions of monomer and initiator concentrations. In addition, isomerization rates of the model compound 2,5,5-trimethyl-2-hexenyllithium have been determined together with its rates of monomer addition as a function of its configuration. Rates for the two-unit polymer have also been estimated.

Experimental Section

Polyisoprenes were prepared in cyclohexane using *sec*-butyllithium as initiator under conditions reported earlier.[12] Conversions were restricted to 10% to avoid undue changes in the [M]/[c*] ratio during the reaction ([M] is the monomer concentration and [c*] the concentration of active centers ≡ concentration of initiator). Microstructures were determined using 10% solutions in benzene on a Varian HA-100 instrument.

2,5,5-Trimethyl-2-hexenyllithium (I, Table I) was prepared by reacting the corresponding bis(allyl)mercury compound[13] with finely divided lithium. The lithium was obtained from a commercial lithium suspension in mineral oil (Lithium Corp.) by washing with a heptane solution of *n*-butyllithium followed by repeated cycling of the solvent by distillation through a sintered filter in an all-glass vacuum apparatus. The reaction time with the mercury compound was 4 min at 0 °C after which the solution was filtered, cooled, and shared between several tubes provided with break seals. The configuration of the mercury compound was ~65% cis as was that of the lithium compound immediately formed. The stable configuration of the latter is however 65% trans in hydrocarbon solvents. Isomerization was followed by immersing the tubes in a bath at the appropriate temperature after which individual break seals were broken at set times to admit trimethylsilyl chloride. It is known[14] that the configuration is retained in this reaction and thus the cis/trans ratio can be determined by simple gas-chromatographic techniques on the silyl compounds. This was confirmed by NMR measurements. A 3920B Perkin-Elmer gas chromatograph equipped with capillary columns was used.

Identification of the configuration of the model compound of DP = 2 (2,6,9,9-tetramethyl-2,6-decadienyllithium, II) poses more problems as four principal products of the silyl compound are found, cis_i–cis_e, cis_i–trans_e, trans_i–cis_e, and trans_i–trans_e, corresponding to different configurations of internal (i) and terminal (e) isoprene units. The silyl derivative was prepared by reacting *tert*-butyllithium with 2 mol of isoprene followed by reaction with trimethylsilyl chloride. The product was distilled on a spinning band column and fractions were cross-checked by Gas chromatography and NMR. The $-\text{CH}_2\text{Si}-$ signals occur at higher field and can be used to identify the cis/trans ratio in the terminal unit. At lower field there are three signals from the methyl groups. These could be assigned by comparison with known structures and NMR spectra of the parent hydrocarbons. The signals for internal and terminal *trans*-methyl groups appear to coincide. A comparison of NMR spectra and gas chromatograms of the fractions enabled the four principal gas chromatograph peaks to be assigned.

Two types of experiments were carried out involving the reaction of I with isoprene. In both it became apparent that the addition of trimethylsilyl chloride accelerated the rate of monomer addition. The excess isoprene was for this reason flash distilled at the required time before the addition of the silicon compound. The resultant rapid evaporation cooled the mixture sufficiently to stop further reaction. In the first type of experiment a large excess of isoprene was allowed to react with I for set times. After removal of the isoprene followed by reaction with trimethylsilyl chloride, the cis and trans contents

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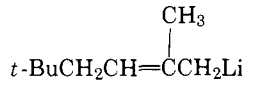
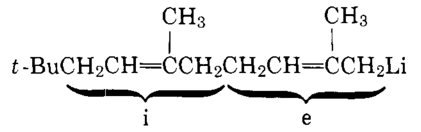
Table I



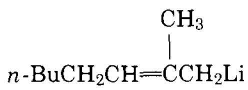
$$t\text{-BuCH}_2\text{CH}{=}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{CH}_2\text{Li}$$

I



$$t\text{-BuCH}_2\text{CH}{=}\underbrace{\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{CH}_2}_{i}\underbrace{\text{CH}_2\text{CH}{=}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{CH}_2\text{Li}}_{e}$$

II



$$n\text{-BuCH}_2\text{CH}{=}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{CH}_2\text{Li}$$

III

of residual I could be determined, as well as the composition and amount of II and quantity of higher derivatives. In the second type, I was allowed to react for 30 s with isoprene at 0 °C before flash distillation. The cool (−50 °C) mixture was rediluted with heptane and subdivided at this temperature into several vessels. These were warmed to the required reaction temperature, allowed to isomerize, and terminated with trimethylsilyl chloride at set times. In this type of experiment the isomerization rate of II could be determined.

In order to obtain information on the effect of end groups on the isomerization rate of model compounds of DP = 1, bis(2-methyl-2-octenyl)mercury was prepared. *n*-Butyllithium in hexane containing 1 equiv of hexamethylethylenediamine was reacted at 0 °C with an equivalent of isoprene. After 30 min, a 0.4 molar equivalent of $HgCl_2$ in THF was added. The excess lithium compound was removed by reaction with methanol and the reaction product was washed with water. Solvent was removed before subjecting the mercury compound to a short-path vacuum distillation at 85 °C. Unlike the compound prepared from *tert*-butyllithium, appreciable decomposition occurs on distillation for the product contains high-boiling material. Nevertheless it was converted to the lithium compound in the manner described above and attempts were made to measure its isomerization rate.

Results

Figure 1 shows the trans content of polyisoprenes prepared at different monomer/initiator ratios at 30 °C in cyclohexane. The results are plotted as a function of the logarithm of $[M]/[c^*]^{3/4}$ for reasons which will be apparent later. A more straightforward plot against $[M]/[c^*]$ would not have appreciably altered the form of the curve. Monomer concentrations varied between 6 and 0.06 M and initiator concentrations from 2 to 450 × 10^{-5} M. The decrease in trans content as $[c^*]$ decreases has been amply demonstrated.[2,10,11] The shaded points in Figure 1 refer to experiments with almost equal initiator concentrations but a 20-fold range of monomer concentrations. Trans content decreases as [M] increases. In fact the monomer/initiator ratio appears to be the important variable in microstructure determination. The 3,4 content is not very sensitive to $[M]/[c^*]$ and remains in the 5–6% range.

The isomerization of compound I was studied in heptane at 0 °C at three concentrations (Figure 2). Isomerization followed first-order kinetics both within each experiment and between experiments having different initial concentrations, with a rate constant of $2.8 \times 10^{-4}\ \text{s}^{-1}$. Repetition of these experiments at 15.5 °C yields a rate constant of $2.2 \times 10^{-3}\ \text{s}^{-1}$. Hence $k_{\text{iso}} = 1.9 \times 10^{13} \exp[-21000/RT]$ which would predict a rate constant $\sim 10^{-2}\ \text{s}^{-1}$ at +30 °C (as determined in this way k_{iso} is in fact $k_1 + k_{-1}$, hence $k_1 = {}^2\!/_3 k_{\text{iso}}$). A qualitative examination of the mechanism we suggest together with known propagation rates indicates that in the region where a drop in trans content occurs the *average* lifetime of an active center between monomer addition steps is ~1 s (Figure 3). Since the drop in trans content must occur in the range where monomer addition and isomerization rates are of comparable magnitude, the measured isomerization rate is too low to fit in with our mechanism.

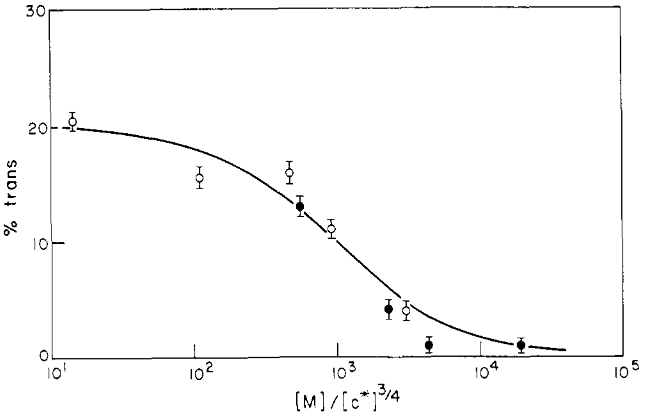


Figure 1. Microstructure of polyisoprenes produced in cyclohexane at 30 °C using *sec*-butyllithium as initiator. Conversion 10%.

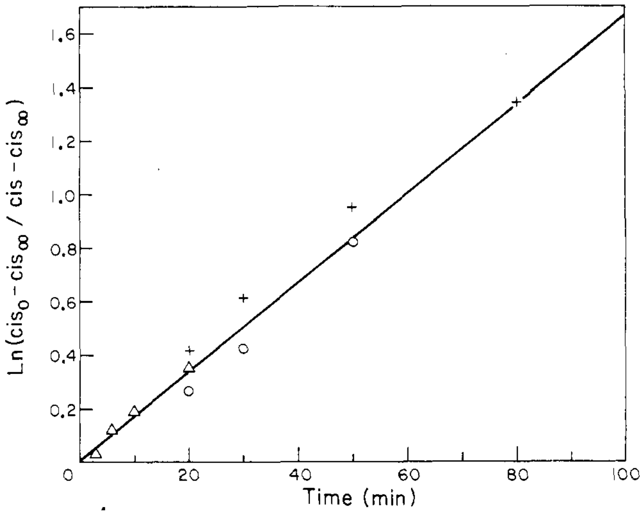


Figure 2. Isomerization of I in heptane at 0 °C. (+) [I] = 3 × 10^{-1} M; (△) [I] = 2 × 10^{-1} M; (○) [I] = 4 × 10^{-2} M.

Compound I differs from a growing poly(isoprenyl)lithium chain in that a *tert*-butyl group is present at the 4 position rather than another isoprene unit. An *n*-butyl group in its place would at least ensure equivalence in structure up to the 5 position. Bis(2-methyl-2-octenyl)mercury when treated with lithium at 0 °C was found to yield 2-methyl-2-octenyllithium (III) predominantly in the trans form within the time required to prepare it (6–7 min). As the mercury compound can be shown from its NMR spectrum to be predominantly in the cis form this indicates a half-lifetime of *cis*-III of less than 2 min as opposed to ~40 min for *cis*-I. This experiment confirms that the *tert*-butyl group of I has a large effect on isomerization rate.

The product of DP = 2 (II) should be typical of all longer chain lithium compounds of isoprene. End effects should be negligible since eight backbone carbons from lithium are identical. Unfortunately the parent mercury compound cannot be isolated so that it is necessary to study its properties as formed in situ by the addition of isoprene to I. Mixing a large excess of isoprene with I for a short time allows 5–10% conversion of I to II. (Second type experiment described above.) The II formed is still highly cis so its isomerization can be measured. The rate at 0 °C was too fast (half-lifetime ~1 min) to measure accurately but at −20 °C the change from $\text{cis}_i\text{–cis}_e$ to $\text{cis}_i\text{–trans}_e$ could be easily measured. An internal first-order process was found ($k_{\text{iso}} = 1.04 \times 10^{-3}\ \text{s}^{-1}$, Figure

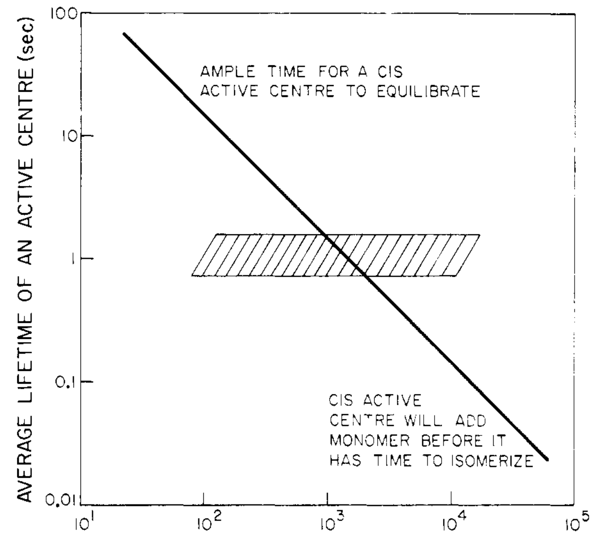


Figure 3. Average lifetime of an active center between monomer addition steps at 30 °C in heptane. Values calculated from Table 2, ref 16. The shaded zone corresponds to the region in which the trans content of the polymer falls in Figure 1.

4). The rate observed is consistent with the rough estimate obtained from III at 0 °C and the activation energy found for I. Again a considerable substituent effect of the *tert*-butyl group is indicated. It is also of interest that despite the rather cumbersome experimental procedure necessary, compound II initially had ~80% of the terminal unit in the cis form. Extrapolation to its time of formation suggests nearly if not all the active centers formed on isoprene addition are in the cis form immediately after formation. Unfortunately, no accurate rates could be measured above −20 °C due to the time loss involved in isoprene removal and reequilibration of temperature. The predicted isomerization rate at 30 °C can therefore only be estimated roughly. Two assumptions can be made. Either E or A is unchanged from its value for I. The first leads to a rate constant of 1 s^{-1} at 30 °C and the second to one of 0.5 s^{-1}. Clearly these are of the required order of magnitude for the suggested mechanism.

The rate of monomer addition to *cis*- and *trans*-I could also be measured (first type experiment). *cis*-I disappears rapidly (Figure 5) due to addition of monomer plus isomerization to *trans*-I. *trans*-I on the other hand at first increases slightly because its rate of formation from *cis*-I is initially greater than its rate of addition of monomer. After a short time, *cis*-I is depleted and falls to a level below the equilibrium value and *trans*-I begins to fall as its formation from *cis*-I falls below its monomer addition rate. Evidently *cis*-I adds monomer much faster than *trans*-I. If the calculated initial isomerization rate is subtracted from the initial rate of loss of *cis*-I and added to the (negative) initial rate of loss of *trans*-I, the rate of monomer addition to the *cis*-I units is found to be 14 times faster than to the *trans*-I units. When the different starting concentrations of the two types of centers are taken into account, this leads to a ratio (R) = k_p^{cis}/k_p^{trans} of 8.4. R can also be calculated from the composition of II formed initially from different concentrations of *cis*-I and *trans*-I on the assumption that the former always produces cis_i-II and the latter $trans_i$-II. The results are shown in Table II. The agreement with the ratio calculated from the rates of disappearance of the isomers of I is sufficiently good to confirm the hypothesis.

Discussion

The experiments on the model compounds of DP = 1 (I) and DP = 2 (II) have made possible the following conclusions.

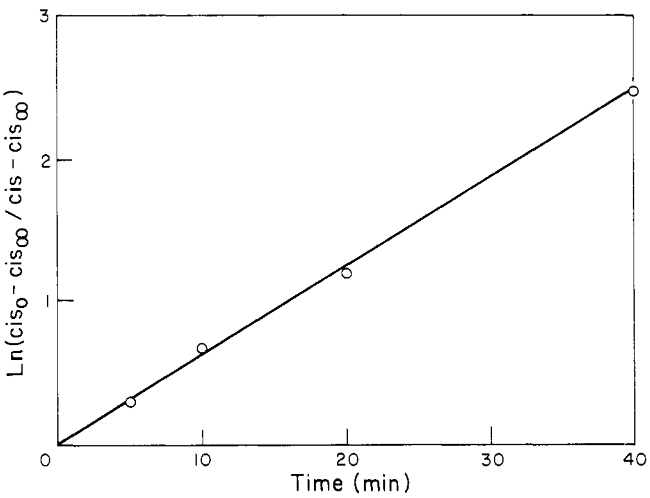


Figure 4. Isomerization of II in heptane at −20 °C.

(1) In the reaction I + isoprene → II, the initial product exists almost entirely with cis-active centers. (2) Within experimental accuracy *cis*-I produces II with an internal cis unit and *trans*-I produces II with an internal trans unit. (3) cis_i–cis_e-II and probably longer chain polymers can isomerize their terminal unit with a rate constant ~1 s^{-1} at 30 °C, i.e., at a rate sufficient to affect microstructure under certain polymerization conditions. These observations confirm the mechanism suggested in the introductory section.

In the Appendix is given a more quantitative description of the reaction mechanism. It leads to the following expression for the trans content of the polymer:

$$f_{trans} = \left[1 + \frac{R}{X}\left(\frac{1 + X\alpha_0}{1 - \alpha_0}\right)\right]^{-1} \tag{1}$$

Where $X = k_{iso}[c^*]/k_p^{trans}[c^*]^{1/4}[M]$ and α_0 is the equilibrium fraction of cis-active centers. The expression predicts two plateau regions with a transition zone. In the first, (low $[M]/[c^*]$) f_{trans} will be

$$(1 - \alpha_0)/(1 - \alpha_0 + \alpha_0 R) \tag{2}$$

when all active centers have ample time to equilibrate, and in the second, f_{trans} is zero (high $[M]/[c^*]$) when monomer addition is very rapid. All the constants required can be estimated with reasonable accuracy if not exactly. α_0 is known to be ⅓ in hydrocarbon solvents at all temperatures for I and even for longer chain polymers[7] at 30 °C or below although the ratio does change at higher temperatures. The isomerization constant k_{iso} will be taken as 0.75 s^{-1} midway between the estimates given earlier for II. k_p (cis and trans) and their ratio R can be easily determined for I but not for active polymer chains of higher DP. They are probably not markedly different from the values appropriate to I, for the following reason. In a typical experiment having [M] = 5 M and $[I_{cis}] = 5 \times 10^{-2}$ M, the rate of monomer addition was found to be 4.3×10^{-5} M s^{-1} at 0 °C. A normal polymerization reaction with $[c^*] = 1.5 \times 10^{-1}$ M and [M] = 5 M would lead to monomer addition at a rate of 7.2×10^{-5} M s^{-1} [15,16] at this temperature. At this low $[M]/[c^*]$ ratio, α must be close to its equilibrium value of ⅓ and the polymer under these conditions is known to have a trans content of ~20%. Thus the overall rate is caused principally by 5×10^{-2} M cis-active centers with a 20% contribution from the trans ends. It follows that the former units are adding monomer at a rate of 5.7×10^{-5} M s^{-1}, i.e., at a rate only 33% greater than *cis*-I units. The terminal *tert*-butyl group of I has a large effect on k_{iso} but a small effect on k_p. We will assume, therefore, that R determined on I is applicable at all DP's. Similar arguments lead to a $k_p^{cis}(30\ °C) = 2.4 \times$

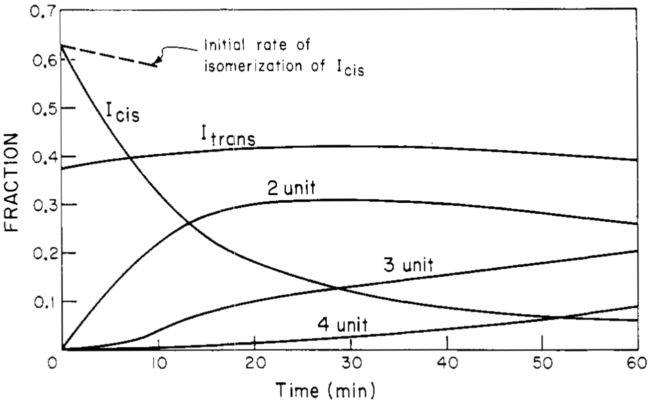


Figure 5. The reaction of I with isoprene in heptane at 0 °C: $[I_0] = 8 \times 10^{-2}$ M, [isoprene] = 5 M.

Table II

Initial fraction *trans*-I	Resultant fraction $trans_i$-II	R
0.40	0.066	9.4[a]
0.65	0.21	7.0[a]
0.38	0.067	8.5[a]
		8.4[b]
		8[c]

[a] $k_p^{cis}/k_p^{trans} = R$ calculated from composition of initial II.
[b] Calculated from initial rates of reaction of *cis*-I and *trans*-I.
[c] Calculated from the trans content of the polymer.

10^{-3} $M^{-1/4}$ s^{-1} for long-chain polymers. Substitution of the estimated values for α_0, R, k_p^{cis}, and k_{iso} in eq 1 leads to

$$f_{trans} = \left[5 + 4.9 \times 10^{-3} \frac{[M]}{[c^*]^{3/4}}\right]^{-1} \quad (3)$$

for polymerization in aliphatic hydrocarbon solvents at 30 °C. The line drawn in Figure 1 was calculated from this formula. While some difficulties exist as to the exact values of the constants for long polymer chains, it is clear that a mechanism involving preferential formation of cis-active centers on monomer addition, followed by some isomerization to trans forms when monomer addition is slow, adequately explains the variation in microstructure.

It will be noted that no mention has been made of the state of aggregation and its role in the polymerization process. The vast majority of the active centers are known to be aggregated in heptane so that the measured cis/trans populations really refer to the associated state which we have previously suggested merely acts as a reservoir supplying a very small equilibrium concentration active in polymerization. The observation of an internal first-order process for isomerization with a normal preexponential factor suggests that it occurs as a simple reorganization within the aggregates. If only dissociated species are active in monomer addition then their cis/trans ratio must be the same as in the aggregate state, maintained by a rapid exchange process. These requirements are in fact the same required to rationalize the quarter-order dependence on active center concentration.

A few microstructure determinations were made on polymers produced in benzene solution at 30 °C. At an [M]/[c*] ratio of 1.4×10^4 the polymer still contained 20% trans structures, falling to 14% at a ratio of 7×10^4. In cyclohexane the corresponding figures would be 9 and 1%, respectively. The limiting trans content at low [M]/[c*] is about 22% in benzene, within experimental error the same as in cyclohexane. This means that since α_0 is the same in the two solvents at 30 °C, the ratio R must also be similar (eq 2). On the other hand to maintain this plateau region to higher [M]/[c*] ratios, then k_{iso}/k_p must be significantly higher. As the propagation rates in benzene are twice as large as in heptane this means a considerable increase in isomerization rates in benzene. These observations are also of practical value. For the preparation of a series of polyisoprenes with a wide range of molecular weights but a constant microstructure, it is necessary to use benzene as solvent. Molecular weights in a range up to over 10^6 can be prepared in this solvent all having slightly greater than 20% trans and 5% 3,4 structure.

The present results may also explain why the trans contents of polybutadienes prepared under similar conditions in aliphatic hydrocarbons are so much higher than with polyisoprenes. Neopentylallyllithium has a similar α_0 value (0.25).[14] At low values of [M]/[c*] the trans content in the polymer is probably 50–60%.[15] This is consistent (eq 2) with a smaller value of R than for isoprene (~2). The trans content of the polymer does not decrease appreciably until quite high values of [M]/[c*]. This effect would be produced by increasing the isomerization/propagation ratio by a factor of about 10, or since the propagation rates are about three times lower than for isoprene by an absolute increase of isomerization rate about a factor of 3.

Finally, particularly for isoprene, because the cis form reacts so much faster than the trans, the apparent propagation constant will drift with M/c* ratio. The overall k_p is in fact given by $k_p^{cis}(1 + 7\alpha)/8$. In the determination of kinetic behavior in such a system, the range of $[M]/[c^*]^{3/4}$ used is smaller than used in the present investigation and about 10 to 10^3. Over this range the apparent k_p will change from $0.42k_p^{cis}$ to $0.59k_p^{cis}$, i.e., at constant M it will be 50% higher at lower initiator concentration. One quarter-order kinetics in initiator concentration leads to a drop in rate by a factor of ~4.5 in the same range. It is unlikely that this effect will be noticeable in normal kinetic experiments. The observation that R seems to be higher for isoprene than for butadiene suggests that the higher reactivity of the cis form in the former case is mostly steric in origin and connected with the presence of the β-methyl group. Some caution in interpretation of the results in this way is necessary, however, since the rate constants involved are complex quantities.

Appendix

If the new active centers formed on monomer addition are always cis then the rate of change of their concentration is given by the rate of addition of monomer to trans centers minus the net rate of isomerization, i.e.,

$$\frac{d\Sigma P_i^{\,cis}}{dt} = \left(-\frac{d[M]}{dt}\right)\left\{\frac{(1-\alpha)k_p^{trans}}{k_p}\right\} - k_{iso}[c^*](\alpha - \alpha_0) \quad (A1)$$

All k_p's defined here are actually complex constants involving a true rate constant and an aggregate dissociation constant. k_p is the measured overall rate constant, α is the fraction of cis active centers, and α_0 their equilibrium value.

Now

$$(-d[M]/dt) = k_p[c^*]^{1/4}[M] \quad (A2)$$

from experiment.[16]

Let us assume a steady state concentration of cis (and trans) centers is rapidly established during polymerization, i.e.,

$$d\Sigma P_i^{\,cis}/dt = 0 \quad (A3)$$

Combination of eq A1, A2, and A3 gives

$$k_p^{\mathrm{trans}}[c^*]^{1/4}(1-\alpha)[M] = k_{\mathrm{iso}}[c^*](\alpha-\alpha_0) \qquad (A4)$$

or

$$\alpha = (1 + X\alpha_0)/(1 + X) \qquad (A5)$$

where $X = k_{\mathrm{iso}}[c^*]/k_p^{\mathrm{trans}}[c^*]^{1/4}[M]$.

Now the fraction of trans units (f_{trans}) incorporated in the polymer will be given by the fraction of trans units adding monomer if trans centers alone incorporate their structure on monomer addition i.e.,

$$f_{\mathrm{trans}} = k_p^{\mathrm{trans}}(1-\alpha)/(k_p^{\mathrm{trans}}(1-\alpha) + k_p^{\mathrm{cis}}\alpha) \qquad (A6)$$

Let the ratio $k_p^{\mathrm{cis}}/k_p^{\mathrm{trans}} = R$, then

$$f_{\mathrm{trans}} = (1-\alpha)/(1 + \alpha(R-1)) \qquad (A7)$$

Substitution of eq A5 in A7 gives

$$f_{\mathrm{trans}} = \left[1 + \frac{R}{X}\left(\frac{1+X\alpha_0}{1-\alpha_0}\right)\right]^{-1} \qquad (A8)$$

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Magnesium-Assisted Stereospecific Oligomerization of Isoprene. Unique Chemical Behaviors of Magnesium–Isoprene Adducts, $[\mathrm{Mg(C_5H_8)}_m]_n$

Hajime Yasuda,* Yoshio Nakano, Kazuteru Natsukawa, and Hisaya Tani

Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan.

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ABSTRACT: The mechanism of the stepwise formation of oligomeric 3,4-polyisoprene with activated magnesium was studied. The oligomerization successively proceeded via the magnesium–isoprene 1:1 (**1**), 1:2 (**2**), 1:3 (**3**), and 1:4 (**4**) adducts. These adducts were isolated in a pure state and their macrocyclic structures were confirmed by the measurement of the molecular weight and by NMR spectroscopy. Based on the geometry of the isoprene moiety of adducts **1–4**, the process of initiation in the oligomerization was explained by the 4,3 addition of isoprene to the Mg–C_4 carbon bond of **1** and that of the propagation by the 4,3 addition of isoprene to the Mg–C_3 carbon bond. To understand the unique catalytic behavior of the magnesium–isoprene adducts, the initial stages in the polymerization of isoprene catalyzed by Grignard reagents and dialkyl- and dialkenylmagnesium compounds were also investigated.

The initial stages in the *n*-butyllithium[1–14] or π-allylmetal[15–19] catalyzed oligomerization of conjugated dienes have been extensively studied to clarify the structure of propagating chain ends,[2–8,17–19] association of the "living" oligomer,[9–11] and the effect of ligands on the microstructure of the polymer.[12–14] In contrast to these detailed studies concerning the 1,4 polymer, the corresponding study which deals with the 3,4 polymer has not been undertaken much,[20–22] because of the lack of suitable catalyst systems.

Recently, Ramsden[23] and Akutagawa[24] found that magnesium activated with alkyl halides and/or metal halides can react with various kinds of conjugated dienes to give unusual "magnesium-diene compounds". A new terpenoid synthesis using these systems has recently been reported.[25–29] The remarkably high reactivity of the activated magnesium and the quantitative yield of the linear diene dimers led us to attempt the oligomerization of dienes using this "enediylmetal"[27] system. In a previous paper,[30] we reported the stepwise formation of magnesium–butadiene 1:1, 1:2, 1:3, and 1:4 adducts. Higher oligomers having more than five butadiene units could not be obtained in this case, as the propagating chain ends isomerized to inactive chain ends by ring closure. By contrast, isoprene provided linear 3,4-oligomers in a stepwise manner with this enediylmetal catalyst system. This paper describes the structures and association behavior of the magnesium–isoprene 1:1 (**1**), 1:2 (**2**), 1:3 (**3**), and 1:4 (**4**) adducts which were formed in a stepwise manner in the initial stages in the polymerization and the succeeding process for the formation of 3,4-polyisoprene.

Results and Discussion

Isolation of the Magnesium–Isoprene 1:1, 1:2, and 1:3 Adducts. Isoprene is known to react with magnesium activated with minute quantities of iodine, alkyl halides,[23] and/or metal halides[24] to give the magnesium–isoprene 1:2 adduct. We found that the activated magnesium also functions as a catalyst for the oligomerization of isoprene and the chain growth of the oligomer is dependent on the initial g-atom/mol ratio of magnesium to isoprene. The reaction proceeded by the addition of organic halides to the mixture of magnesium and isoprene only at temperatures higher than 60 °C (method 1) but the resulting magnesium–isoprene adducts were always a mixture; i.e., the reaction of 0.1 molar equiv of isoprene with magnesium at 60 °C gave a mixture of $(\mathrm{MgC_5H_8})_n$ **1** and $(\mathrm{MgC_{10}H_{16}})_n$ **2** in 1:5 ratio. The 1:2 reaction of magnesium with isoprene gave **1**, **2** and $(\mathrm{MgC_{15}H_{24}})_n$ **3** in 1:6:3 ratio. The

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