The Cross-Association of Polyisoprenyllithium with Ethyllithium

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ABSTRACT: The cross-association of ethyllithium with polyisoprenyllithium has been studied by means of concentrated solution viscosity measurements, which can yield accurate and reproducible values of the relative molecular weights of the polymeric species. On this basis, the following association equilibrium can be written for this system: $(RM_jLi)_2 + (EtLi)_6 \rightleftharpoons 2RM_jLi\cdot(EtLi)_3$. The proposed equilibrium is consistent with the known states of association of both the polyisoprenyllithium and the ethyllithium, and yields a constant value for the equilibrium constant of 6.5, indicating preferential cross-association.

A most important aspect of the association phenomena in organolithium polymerizations in hydrocarbon solvents is the possibility of cross-association between the propagating polymer–lithium species and any residual alkyllithium initiator, since this can lead to complex kinetics in both the initiation and propagation reactions. The viscosity method[2,3] previously described can be conveniently used to elucidate the nature of the cross-complex of polyisoprenyllithium and ethyllithium. Earlier work[4] had shown, in a qualitative way, that such a cross-association must occur between polyisoprenyllithium and *n*-butyllithium. More recent qualitative results indicate a similar interaction between *sec*-butyllithium and polyisoprenyllithium[5] as well as between *t*-butyllithium and polyisoprenyllithium.[6]

Experimental Section

The purification of solvent and monomers,[7] the preparation of ethyllithium,[8] and the purification of *sec*-butyllithium[9] are presented elsewhere. As before, all experimental manipulations were accomplished on a high-vacuum system or in closed, evacuated flasks. The general techniques used have been described previously.[2,7]

Cross-Association Measurements. The viscometer described in a previous papers was modified as shown in Figure 1. Ampoules A contained either ethyllithium in *n*-hexane, low molecular weight polyisoprenyllithium in *n*-hexane, or polystyryllithium in benzene. Ampoule B contained methanol, ampoule C contained the initiator, and ampoule D contained the purge solution for rinsing the reactor. The viscometer was attached to the vacuum line at outlet E and then, following purging, at outlet F. The basic techniques involved in performing the viscometry measurements are described elsewhere[2,3] as is the method of preparing the low molecular weight polymer–lithium species. The low molecular weight polymer–lithium species were made with either *sec*-butyllithium or ethyllithium initiator. The stoichiometric molecular weight (based on the ratio of monomer to initiator) of the isoprenyllithium chain was 5×10^3 whereas the value for the styryllithium chain was 4×10^3.

During purging and other manipulations, it was necessary to immobilize the hammers (sections of nail covered with glass) with a magnet to prevent premature rupture of the various break-seals. Handling was made easier by eliminating all but one hammer in the section shown in Figure 1. Medium-wall tubing (10 mm o.d.) was used to connect the lithium alkyl and seed ampoules to this section, instead of the usual constrictions. The medium-wall tubing could be sealed off almost as easily as the constrictions and had the added advantage of allowing a hammer to pass through it.

If a polymer chain associates with a lithium alkyl instead of another polymer chain, this cross-associated chain will have only about half the molecular weight of the chains participating in polymer–polymer association. Thus, the average "molecular weight" of the polymer species present will be decreased. This results in a shorter flow time for the polymer solution and consequently a lower calculated value for N. From this decrease in N, the number of associated species containing only one polymer chain can then be calculated. If a series of additions of ethyllithium are made, one can calculate the equilibrium constant for the cross-association equilibrium.

The volume fraction of polymer, however, also affects the viscosity of the polymer solution. Thus, in order to make the relative viscosity measurements needed to determine the association number, the volume fraction of polymer must be held constant. This was easily accomplished in the polymer association runs since the only addition of liquid to the polymer solution was less than 0.1 ml of methanol for termination. However, in the cross-association runs, a significant volume of liquid was introduced with each addition of lithium alkyl. Thus, in order to keep the volume fraction of polymer constant, a volume of solvent equivalent to the volume of lithium alkyl solution added was removed from the polymer solution. This was accomplished by distilling the proper amount of solvent back into the volumetric ampoule before it was sealed off from the rest of the viscometer.

The formation of the cross-associated complex between polyisoprenyllithium and ethyllithium occurs quite rapidly. This was confirmed by the observation that on mixing ethyllithium with polyisoprenyllithium solutions, a drop in the solution viscosity was observed within the time required for mixing and measurement of the flow time (*ca.* 10 min). No further change was observed over 72 hr. Similar results have been reported[6,7] for *sec*- and *t*-butyllithium.

Results

Test of the Validity of the Calculation of Association Equilibria. Prior to an examination of the cross-

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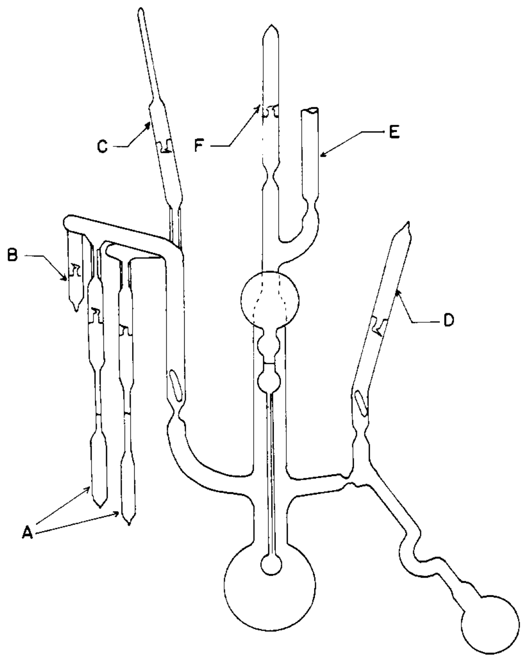

Figure 1. Vacuum viscometer.

association between ethyllithium and polyisoprenyllithium, the validity of the association equilibrium was tested as follows. To fully polymerized solutions of polyisoprenyllithium or polystyryllithium there were added varying amounts of solutions of previously prepared oligoisoprenyl- or oligostyryllithium, followed by the usual measurement of the N value by viscometry, before and after termination. It was then noted whether these N values led to the expected equilibrium expression[2,3]

$$(\mathrm{RM_jLi})_2 + (\mathrm{RM_oLi})_2 \overset{K}{\rightleftharpoons} 2(\mathrm{RM_jLi \cdot RM_oLi})$$

where $\mathrm{RM_jLi}$ denotes either polyisoprenyl- or polystyryllithium and $\mathrm{RM_oLi}$ denotes the corresponding oligomerlithium. These data ase shown in Table I. The concentrations of monomer in these polymerizations ranged from 1.5 to 2.3 *M*.

It can be seen that a consistent value of K, close to the predicted value of 1 (see Appendix A), was obtained.

For the hypothetical cases, where other states of association were assigned to the respective polymer–lithium species, the values of K were found to vary. These inconsistencies were found for all higher orders of association (N = 3–6) as well as for the case where one of the two polymer–lithium species was assumed to be unassociated.

TABLE I
POLYMER–LITHIUM ASSOCIATION AT 30°

$[\mathrm{RM_jLi}] \times 10^3$	$[\mathrm{RM_oLi}] \times 10^3$	N	K
	Polyisoprenyllithium in *n*-Hexane		
1.1	6.8	1.34	0.85
1.0	4.6	1.40	0.90
2.5	5.3	1.53	1.1
	Polystyryllithium in Benzene		
2.0	2.0	1.67	0.97
2.0	4.0	1.52	1.1

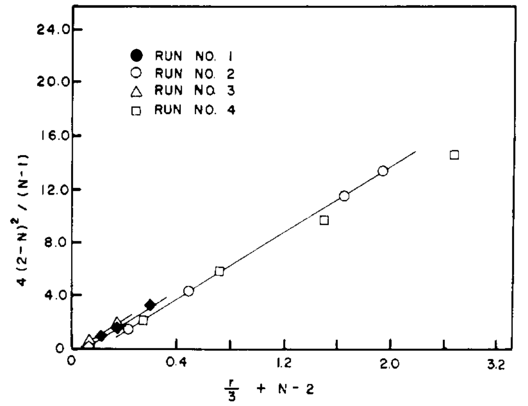

Figure 2. Plot according to eq 3.

Treatment of Ethyllithium–Polyisoprenyllithium Cross-Association Data. In order to determine which equation describes the cross-association equilibrium, it is convenient to define this equilibrium as

$$(\mathrm{RM_jLi})_2 + (2v/y)(\mathrm{EtLi})_y \overset{K}{\rightleftharpoons} 2\mathrm{RM_jLi \cdot (EtLi)}_v \quad (1)$$

where $(\mathrm{EtLi})_y$ represents associated ethyllithium.

When this equation is evaluated in terms of the experimentally measurable quantities, *i.e.*, the amount of ethyllithium added ($[\mathrm{EtLi}]_0$), the amount of polyisoprenyllithium present ($[\mathrm{RM_jLi}]_0$), and the association number (N), the following relation is obtained (see Appendix B).

$$K\{(1/y)[\mathrm{EtLi}]_0 - (v/y)(2 - N)[\mathrm{RM_jLi}]_0\}^{2v/y} = 2(2 - N)^2[\mathrm{RM_jLi}]_0/(N - 1) \quad (2)$$

In order to solve this equation for the best values of v and y, it may be more conveniently expressed in its logarithmic form. This isolates the term due to K so that only the experimental terms remain. Hence, a

$$\log K + (2v/y) \log \{(1/y)[\mathrm{EtLi}]_0 - (v/y)(2 - N) \times [\mathrm{RLi}]_0\} = \log \{2(2 - N)^2[\mathrm{RM_jLi}]_0/(N - 1)\} \quad (3)$$

plot of $\log \{2(2 - N)^2[\mathrm{RM_jLi}]_0/(N - 1)\}$ *vs.* $\log \{(1/y) \cdot [\mathrm{EtLi}]_0 - (v/y)(2 - N)[\mathrm{RM_jLi}]_0\}$ should yield a straight line of slope $2v/y$, and an intercept $\log K$ (Figure 2).

Once the most probable values of v and y are determined, the general equation (2) can be solved for each of the systems individually. This solution with rearrangement (see Appendix C) yields the following equations for the most likely values of v and y

for $y = 6$, $v = 3$

$$K = \frac{4(2 - N)^2/(N - 1)}{[(r/3) + N - 2]} \quad (4)$$

where $r = [\mathrm{EtLi}]_0/[\mathrm{RM_jLi}]_0$.

for $y = 6$, $v = 4$

$$K = \frac{3.434(2 - N)^2/(N - 1)[\mathrm{RM_jLi}]_0^{1/3}}{[(r/4) + N - 2]^{4/3}} \quad (5)$$

for $y = 4$, $v = 3$

$$K = \frac{3.079(2 - N)^2/(N - 1)[\mathrm{RM_jLi}]_0^{1/2}}{[(r/3) + N - 2]^{3/2}} \quad (6)$$

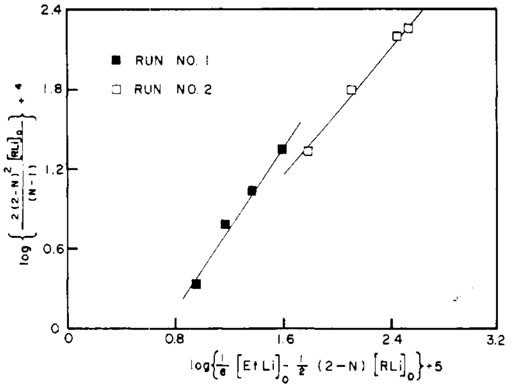

Figure 3. Plot of cross-association data at 40°, according to eq 4.

Thus, the systems can be checked individually to see if constant K values are obtained.

Implicit in the above derivations is the assumption that all of the single (unassociated) chains are due to cross-association. However, at low r values this will not be the case, since the single chains from the dissociation of the polyisoprenyllithium itself will contribute. This is indicated by the presence of a nonzero intercept in Figure 3.

Results and Intrepretation

The experimental data for the cross-association of ethyllithium with polyisoprenyllithium are shown in Table II. The results of the plots of the data according to eq 3 for runs 1 and 2 are presented in Table III for the case of the tetramer (y = 4) and the hexamer (y = 6) of ethyllithium. A typical plot of this series is shown in Figure 2.

If ethyllithium is taken to be a hexamer, the cross-association product would be either a tetramer (v = 3) or a pentamer (v = 4).

However, if ethyllithium were a tetramer, the cross-association product would most likely be a tetramer (v = 3). Log–log plots are notoriously insensitive. Therefore the more specific equations (4), (5), and (6) must be used to distinguish between these possibilities.

A comparison of K values, for the systems indicated by the plots of eq 3 as being the most likely, are given in Table IV. Clearly, the correct equilibrium scheme appears to be that in which ethyllithium is a hexamer (y = 6) and the cross-association product is a tetramer (v = 3). This then yields the equation

$$(\mathrm{RM_jLi})_2 + (\mathrm{EtLi})_6 \overset{K}{\rightleftharpoons} 2\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_3$$

The data from the four runs listed in Table II are plotted according to eq 4 in Figure 3. Run 3 is consistent with the value of K found in the first two runs. However, since it yielded only two points, this run is not included in the evaluation of K. Run 4 likewise is not included since there is some slight deviation from the other data at high r values. A least-squares treatment of the slopes of the plots of eq 3 led to the K values shown in Figure 3.

TABLE II
CROSS-ASSOCIATION OF ETHYLLITHIUM (EtLi) AND POLYISOPRENYLLITHIUM IN n-HEXANE AT 40°[a]

$[\mathrm{RM_jLi}]_0 \times 10^3$	r	Flow times, sec t_a	Flow times, sec t_t	N
		Run 1		
1.35	1.15	681.8	100.8	1.76
1.35	1.80	527.0	100.8	1.63
1.35	2.46	432.1	100.8	1.53
1.35	3.55	328.1	100.8	1.42
		Run 2		
2.81	2.70	649.7	148.2	1.54
2.81	4.56	437.6	148.2	1.38
2.81	8.49	289.0	148.2	1.22
2.81	9.47	271.7	148.2	1.20
		Run 3		
1.37	1.46	467.3	43.6	1.66
1.37	2.55	242.3	43.6	1.51
		Run 4		
1.90	3.15	225.2	57.2	1.50
1.90	5.44	151.2	57.2	1.32
1.90	8.01	119.3	57.2	1.24
1.90	11.08	101.7	57.2	1.18

[a] $r = [\mathrm{EtLi}]_0/[\mathrm{RM_iLi}]_0$.

TABLE III
RESULTS OF PLOTS OF EQUATION 3

v	Theoretical slope	Slope from run 1	Slope from run 2
		y = 6	
1	0.33	1.78	1.45
2	0.67	1.61	1.36
3	1.00	1.38	1.20
4	1.33	0.97	1.04
5	1.67	0.51	0.87
		y = 4	
1	0.50	1.83	1.50
2	1.00	1.63	1.35
3	1.50	1.39	1.22
4	2.00	0.98	1.07
5	2.50	0.45	0.89

TABLE IV
DETERMINATION OF THE CONSTANCY OF K

y	v	K from run 1	K from run 2
6	3	6.5 ± 0.1	6.3 ± 0.1
6	4	110 $M^{-1/3}$	40 $M^{-1/3}$
4	3	142 $M^{-1/2}$	47.8 $M^{-1/2}$
1	1	137 M^{-1}	41.1 M^{-1}

Previous work[4] on the cross-association of n-butyllithium with polyisoprenyllithium suggested the n-butyllithium was completely unassociated. However, that study was performed at one concentration of polyisoprenyllithium. The current investigation has shown that this picture does not hold when the isoprenyllithium concentration is varied. Indeed, the only equilibrium scheme which was found to hold is

$$(\mathrm{RM_jLi})_2 + (\mathrm{EtLi})_6 \rightleftharpoons 2\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_3$$

This equilibrium system is consistent with the known facts concerning the association behavior of ethyllithium[10,11] and polyisoprenyllithium, respectively,[2,3] in hydrocarbon solvents.

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[10] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, **84**, 1371 (1962).

[11] T. L. Brown, J. A. Ladd, and G. Newman, *J. Organometal. Chem.*, 3, 1 (1965).

The question now arises concerning the mechanism of the formation of the cross-complex. While the dissociation of the polyisoprenyllithium dimer to a single chain is a reasonable proposal, it is energetically unfavorable[12] for the ethyllithium hexamer to dissociate to monomer since this requires the simultaneous breaking of a number of bonds. However, Brown's[10] proposed model of the hexamer of ethyllithium shows that there are two places on the aggregate which are particularly favorable for coordination, since the lithium atoms occupy only six of the eight faces of the octahedral structure. In the light of this model and the cross-association equilibrium which is now known, it seems reasonable to postulate that the cross-association occurs by attack of a polyisoprenyllithium single chain on one of the two coordination sites available from ethyllithium with subsequent cleavage of the ethyllithium hexamer. This can be denoted as

$$(\mathrm{RM_jLi})_2 \rightleftharpoons 2\mathrm{RM_jLi}$$

$$\mathrm{RM_jLi} + (\mathrm{EtLi})_6 \rightleftharpoons [\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_6] \rightleftharpoons \mathrm{RM_jLi}\cdot(\mathrm{EtLi})_3 + (\mathrm{EtLi})_3$$

The unstable $(\mathrm{EtLi})_3$ fragment produced can then combine with a like fragment to form a hexamer or combine with a polyisoprenyllithium single chain to give a cross complex. This mechanism is more favorable energetically since it requires cleavage of fewer bonds, and it is consistent with information on the structure of organolithium compounds in hydrocarbon solvents.

Appendix A

Cross-Association of High and Low Molecular Weight Chains. The equilibrium constant K for this type of cross-association may be expressed as

$$(\mathrm{RM_jLi})_2 + (\mathrm{RM_oLi})_2 \rightleftharpoons 2(\mathrm{RM_jLi}\cdot\mathrm{RM_oLi})$$

so that

$$K = \frac{[\mathrm{RM_jLi}\cdot\mathrm{RM_oLi}]^2}{[(\mathrm{RM_jLi})_2][(\mathrm{RM_oLi})_2]} \qquad \text{(A1)}$$

The three associated species shown above, *i.e.*, $\mathrm{RM_jLi}\cdot\mathrm{RM_oLi}$, $(\mathrm{RM_jLi})_2$, and $(\mathrm{RM_oLi})_2$ will of course be in equilibrium with their respective single chains, *i.e.*, $\mathrm{RM_jLi}$ and $\mathrm{RM_oLi}$, and these equilibria may be expressed as

$$K_1 = \frac{[\mathrm{RM_jLi}]^2}{[(\mathrm{RM_jLi})_2]} \text{ or } [(\mathrm{RM_jLi})_2] = [\mathrm{RM_jLi}]^2/K_1$$

$$K_2 = \frac{[\mathrm{RM_oLi}]^2}{[(\mathrm{RM_oLi})_2]} \text{ or } [(\mathrm{RM_oLi})_2] = [\mathrm{RM_oLi}]^2/K_2$$

$$K_3 = \frac{[\mathrm{RM_jLi}][\mathrm{RM_oLi}]}{[\mathrm{RM_jLi}\cdot\mathrm{RM_oLi}]} \text{ or } [\mathrm{RM_jLi}\cdot\mathrm{RM_oLi}] = ([\mathrm{RM_jLi}][\mathrm{RM_oLi}])/K_3$$

These equilibria are based on the assumption that the species $\mathrm{RM_jLi}$ and $\mathrm{RM_oLi}$ behave in a similar fashion, since they differ only in molecular weight.

Hence substituting these values in eq 1 and solving for K

$$K = K_1K_2/K_3{}^2$$

but

$$K_1 = K_2 = K_3$$

hence

$$K = 1$$

Appendix B

Derivation of K in Terms of the Experimental Variables for the General Case. Assuming polyisoprenyllithium to be a dimer, the general cross-association equilibrium can be represented by the equation

$$(\mathrm{RM_jLi})_2 + (2v/y)(\mathrm{EtLi})_y \overset{K}{\rightleftharpoons} 2\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_y$$

Letting $z = 2v/y$, K is given by

$$K = \frac{[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_y]^2}{[(\mathrm{RM_jLi})_2][(\mathrm{EtLi})_y]^z}$$

Rearranging, this becomes

$$K[(\mathrm{EtLi})_y]^z = \frac{[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v]^2}{[(\mathrm{RM_jLi})_2]}$$

Now

$$\frac{[(\mathrm{RM_jLi})_2]}{[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v]} = x = \frac{N-1}{2(2-N)}$$

Substituting in x, the rearranged equation becomes

$$K[(\mathrm{EtLi})_y]^z = [\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v]/x \qquad \text{(A2)}$$

It now becomes necessary to find the value of $[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v]$. Now $[\mathrm{RM_jLi}]_0 = 2[(\mathrm{RM_jLi})_2] + [\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v]$ where $[\mathrm{RM_jLi}]_0$ denotes the total concentration of polyisoprenyllithium regardless of its association state.
Hence

$$\begin{aligned}[\mathrm{RM_jLi}]_0 &= 2x[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v] + [\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v] \\ &= (2x+1)[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v]\end{aligned}$$

Thus

$$\begin{aligned}[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v] &= \frac{[\mathrm{RM_jLi}]_0}{2x+1} \\ &= (2-N)[\mathrm{RM_jLi}]_0\end{aligned}$$

Substituting this into (A2) we arrive at

$$\begin{aligned}K[(\mathrm{EtLi})_y]^z &= \frac{(2-N)[\mathrm{RM_jLi}]_0}{x} \\ &= \frac{2(2-N)^2[\mathrm{RM_jLi}]_0}{(N-1)}\end{aligned} \qquad \text{(A3)}$$

It now remains to solve for the value of $[(\mathrm{EtLi})_y]^z$

$$\begin{aligned}y[(\mathrm{EtLi})_y] &= [\mathrm{EtLi}]_0 - v[\mathrm{RM_jLi}\cdot(\mathrm{EtLi})_v] \\ &= [\mathrm{EtLi}]_0 - v(2-N)[\mathrm{RM_jLi}]_0\end{aligned}$$

where $[\mathrm{EtLi}]_0$ is the stoichiometric amount of ethyllithium added. This rearranges to give

$$[(\mathrm{EtLi})_y] = (1/y)[\mathrm{EtLi}]_0 - (v/y)(2-N)[\mathrm{RM_jLi}]_0 \qquad \text{(A4)}$$

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[12] T. L. Brown, *J. Organometal. Chem.*, **5**, 191 (1966); *Advan. Organometal. Chem.*, **3**, 365 (1965).

Now, substituting eq A4 into eq A3, the general form of the equation is obtained in terms of the experimental variables.

$$K\{(1/y)[\mathrm{EtLi}]_0 - (v/y)(2 - N)[\mathrm{RM_jLi}]_0\}(2v/y) = \frac{2(2 - N)^2[\mathrm{RM_jLi}]_0}{(N - 1)} \quad \text{(A5)}$$

Appendix C

Calculation of K for a Specific Case. The general equation (A5) for K in terms of the experimental variables was shown in Appendix B. Now, for $y = 6$ and $v = 3$, the left side of the equation becomes

$$K\{(1/6)[\mathrm{EtLi}]_0 - (1/2)(2 - N)[\mathrm{RM_jLi}]_0\} = K[\mathrm{RM_jLi}]_0\left\{(1/6)\frac{[\mathrm{EtLi}]_0}{[\mathrm{RM_jLi}]_0} - (1/2)(2 - N)\right\}$$

Letting $r = [\mathrm{EtLi}]_0/[\mathrm{RM_jLi}]_0$ we have

$$K[\mathrm{RM_jLi}]_0\{(r/6) - (1/2)(2 - N)\} = K\frac{[\mathrm{RM_jLi}]_0}{2}[(r/3) + N - 2]$$

Substituting this into eq A5 in Appendix B and rearranging yields

$$K = \frac{4(2 - N)^2/(N - 1)}{[(r/3) + N - 2]}$$

which is the form desired.

Stereospecific Polymerization of Methyl Methacrylate by Organomagnesium Catalysts with a Magnesium–Nitrogen Bond

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ABSTRACT: The polymerization of methyl methacrylate by organomagnesium compounds with the magnesium–nitrogen bond was carefully studied and a number of new catalysts were disclosed. The stereostructure of the resulting polymer as well as the catalytic activity is quite different depending on the amide group in the catalyst. The organomagnesium compounds with a piperidine ring such as ethylpentamethyleniminomagnesium or bis-pentamethylenimino)magnesium are found to be an effective catalyst for the syndiotactic polymerization of methyl methacrylate. The polymerization is affected by the polymerization conditions such as temperature and the solvent employed. The lower the polymerization temperature, the higher the syndiotacticity of the polymer, and toluene is a best solvent in the syndiotactic polymerization. On the other hand, organomagnesium compounds with a pyrasole ring such as ethylvinyleniminomagnesium, or bis(divinylenimino)magnesium are the novel catalyst for the isotactic polymerization of methyl methacrylate. The isotacticity of polymer is not affected by the polymerization conditions such as polymerization temperature and the solvent employed and the polymers obtained by these catalysts have all 100% isotactic units. The mechanism of the polymerization was discussed in considerable detail in view of the aggregation of the catalyst and a reasonable mode of polymerization is proposed that the propagation occurs at magnesium–nitrogen bond, and the propagation is affected by another coordinated nitrogen-bridged group in the catalyst throughout the polymerization.

Since the pioneering works by Fox, *et al.*,[1] Miller, *et al.*,[2] and Watanabe, *et al.*,[3] who independently succeeded in the preparation of the stereoregular poly(methyl methacrylate) in 1958, considerable literature on the syntheses and characterization of the stereoregular poly(methyl methacrylate) has appeared.[4-10]

The utilization of organometallic catalysts has been the most useful method in these researches and many new effective catalysts were disclosed. Natta, *et al.*,[11,12] and Nishioka, *et al.*,[13] have described nitrogen Grignard reagents, but did not study these catalysts intensively. Recently Joh, *et al.*,[14,15] disclosed several kinds of new catalysts containing the Mg–N bond which are particularly effective in the stereospecific polymerization of methacrylonitrile at moderately high temperatures. The polymerization of methyl methacrylate by the various kinds of organomagnesium catalysts containing the Mg–N bond brought us new interesting information on the polymerization of methyl methacrylate. The stereostructure of the resulting polymer depends sub-

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