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# Comparative Study of the Deactivation of Low Oligomeric Dienyllithiums by Alkyl Iodides

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ABSTRACT: The deactivation of living anionic oligomers of dienes $\mathrm{R{-}M_n^-,Li^+}$ by alkyl iodides R′I leads to $\mathrm{R{-}M_n{-}R'}$ and $\mathrm{R{-}M_n{-}R}$ products. Three monomers were investigated: 2,3-dimethyl-1,3-butadiene, isoprene, and *trans*-1,3-pentadiene. The yields of the products and the structures of R–M–R′ products were compared to those of the methanol-deactivated oligomers; a different oligomerization number distribution is observed, which is discussed on the basis of a complex set of coupling and exchange reactions. It is shown that the alkyl iodide deactivation leads to a decrease of the 4,1 stereospecificity.

In previous work dealing with anionic oligomerization of isoprene initiated by alkyllithium compounds RLi and terminated by alkyl halides R′X we have shown that two sorts of products occur,[1,2] i.e., products $\mathrm{R{-}M_n{-}R'}$, corresponding to a "normal" deactivation of the living oligomer, and products $\mathrm{R{-}M_n{-}R}$, resulting from halogen–lithium exchange reactions that may occur between the alkyl halide and unreacted initiator or living oligomers of various polymerization number.

$$\begin{array}{lll}
\mathrm{R{-}M_n{-}Li + R'X \longrightarrow R{-}M_n{-}R' + LiX} & \text{termination (coupling)} & \\
\mathrm{RLi + R'X \rightleftharpoons R'Li + RX} & \text{exchange} & \\
\mathrm{R{-}M_n{-}Li + RX \longrightarrow R{-}M_n{-}R + LiX} & \text{termination} & \text{(I)} \\
\mathrm{R{-}M_n{-}Li + R'X \rightleftharpoons R{-}M_n{-}X + R'Li} & \text{exchange} & \\
\mathrm{R{-}M_n{-}X + RLi \longrightarrow R{-}M_n{-}R + LiX} & \text{termination} & \text{(II)} \\
\mathrm{R{-}M_n{-}X + R{-}M_m{-}Li \longrightarrow R{-}M_{n+m}{-}R + LiX} & \text{termination} &
\end{array}$$

In the case of isoprene we established that these exchange reactions take place when a low monomer to initiator ratio ($M/I$) is used, conditions in which a mixture of oligomers of polymerization numbers 1–3 is obtained ($M/I = 1/4$ to 1).[3]

The overall yield in exchange products is influenced by the deactivating agent: it is higher with ethyl iodide than with methyl iodide and than with ethyl bromide. It seemed then interesting to extend this study to the oligomerization of other dienes in order to investigate the extent to which the yields in normal products $\mathrm{R{-}M_n{-}R'}$ and in exchange products $\mathrm{R{-}M_n{-}R}$ depend on the monomer.

Furthermore, it is important to compare the distribution of the polymerization numbers of the oligomers terminated by an alkyl halide to that obtained by deactivating the same living oligomer by methanol, inasmuch as it is not always the same, as already pointed out for isoprene (IP). 2,3-Dimethyl-1,3-butadiene (DB) and *trans*-1,3-pentadiene (PD) were chosen for this study.

## Experimental Section

**Oligomer Preparation.** Solvents were degased and stored on a high-vacuum line.

Monomers (Fluka) were distilled and dried over calcium hydride, prepolymerized on *n*-butyllithium, and distilled into ampules.

*sec*-Butyllithium was purified by distillation and *tert*-butyllithium by sublimation.

The reactants were added slowly to the solvent in a glass sealed reactor. For $M/I = 1/2$, $5 \times 10^{-2}$ mol of diene and $10^{-1}$ mol of alkyllithium in 250 mL of solvent were allow to react for 18 h at 20 °C. The alkyl halide was then added ($10^{-1}$ mol) and the excess butyllithium hydrolyzed after 6 h.

**Analysis of the Products.** The oligomer mixture was submitted to vapor phase chromatography (column, methylsilicone SE30 (10%); temperature, 70–250 °C; carrier gas, helium).

**(a) Identification of Normal and Exchange Products.** The groups of peaks corresponding to R–M–R′, R–M–R, $\mathrm{R{-}M_2{-}R'}$, $\mathrm{R{-}M_2{-}R}$, ... were attributed by coupling vapor phase chromatography and mass spectrometry (ion source temperature, 290 °C; electron acceleration voltage, 70 V; ion acceleration voltage, 3500 V). The most intense peaks are those in the series *m/e* 27, 41, 55, 69, 83, ...; the molecular ion peak could be used to identify the different groups of products; confirmation was obtained from the highest *m/e* resulting from the scission $\mathrm{R{\nmid}M_n{-}R'}$ for normal products and $\mathrm{R{\nmid}M_n{-}R}$ for exchange products.

**(b) Microstructure of R–M–R′.** The products corresponding to the main peaks in the R–M–R′ groups were isolated by preparative vapor phase chromatography. The microstructures were deduced from comparison of the $^1$H NMR spectra of the isomer mixtures with those of the isolated products; then the percentages were calculated from the chromatograms.

The following $^1$H NMR shifts were attributed to the characteristic types of protons according to previous work[2] and literature references[3-5] (in $C_6D_6$ from tetramethylsilane): $\delta$ 1.60–1.65 ($\mathrm{CH_3C{=}C}$), 2.05 ($\mathrm{CH_2C{=}C}$), 4.9 ($\mathrm{CH_2{=}C}$), 5.2 ($\mathrm{CH{=}CH}$), 5.3 ($\mathrm{CH{=}C}$).

## Results

### A. Comparison of the Distribution of Normal and Exchange Product. 1. Distribution of the Oligomers in Benzene.

We have effected in the same conditions the oligomerization of 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene, and isoprene; *sec*-butyllithium was used as the initiator ($M/I = 1/4$) and ethyl iodide was used as deactivating agent. The resulting distribution of the oligomers was compared to that obtained by the deactivation of the living oligomers of the same dienes with methanol. The results appear in Table I.

Concerning the overall yield in exchange products, the highest yield is obtained for DB whereas the yields are similar for PD and isoprene.

The deactivation by methanol yields one sort of products $\mathrm{R{-}M_n{-}H}$, the distribution of which is that of the living oligomer; comparison with the distribution of the oligomers resulting from the deactivation by ethyl iodide shows clearly an increase of the yield of dimers, due to the formation of exchange products $\mathrm{R{-}M_2{-}R}$. The overall yield of monomeric species is concomitantly decreased, both exchange and normal products being present.

**2. Distribution of the Oligomers in Cyclohexane.** Another comparison of the oligomers of the three dienes deactivated by methyl iodide was carried out in different experimental conditions in cyclohexane, but always with an excess of initiator ($M/I = 1/2$). The composition of the corresponding products is reported in Table II. The results lead to conclusions similar to those obtained in benzene. DB gives the highest yield in exchange products. For DB and PD the highest yield in exchange produts is that of the dimer; it must be noted that in these conditions also the yield of monomeric products is lower than that of oligomers deactivated by methanol.

The above results obtained with $M/I = 1/4$ or $1/2$ suggest that the dimeric exchange products $\mathrm{R{-}M_2{-}R}$ are

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Table I
Composition (%) of the Oligomers of Isoprene, *trans*-1,3-Pentadiene, and 2,3-Dimethyl-1,3-butadiene[a]

| monomer | termination by $C_2H_5I$ | | | | | | exchange products total |
|---|---|---|---|---|---|---|---|
| | R—M—Et | R—M—R | R—$M_2$—Et | R—$M_2$—R | R—$M_3$—Et | R—$M_3$—R | |
| DB | 32 | 36 | 3 | 26 | 3 | | 62 |
| | 68 | | 28 | | 3 | | |
| PD | 45 | 26 | 11 | 17 | | | 43 |
| | 71 | | 29 | | | | |
| IP | 51 | 25 | 6 | 17 | | | 42 |
| | 76 | | 23 | | | | |

| monomer | termination by MeOH | | |
|---|---|---|---|
| | R—M—H | R—$M_2$—H | R—$M_3$—H |
| DB | 92 | 5 | 3 |
| PD | 84 | 10 | 6 |
| IP | 93 | 7 | |

[a] Initiator, *sec*-BuLi; solvent, benzene; $M/I = 1/4$.

formed from R-M-Li by the set of reactions II, a process which modifies the distribution of the molecular weight of the living oligomer; we have already pointed out that this conclusion is not general when higher $M/I$ ratios are used.[1]

**B. Comparison of the Microstructures of the Normal Products R-M-R′.** The microstructure of the normal oligomer R-M-R′ was obtained with oligomers prepared in cyclohexane and deactivated by methyl iodide; the results for the structures shown or Chart I appear in Table III. The percentages of each type of microstructure for each diene are different from those obtained with methanol as deactivating agent: an increase of the amount of 1,2 addition is observed for PD and DB and of 4,3 addition for IP oligomers; for isoprene the yield of 68% for the 4,1 addition mode is low compared to the high 4,1 stereospecificities (83%) reported in the literature when methanol is used as deactivating agent.[3] These results are in good concordance with the well-established observation according to which the exact microstructure of the oligomer is not preexistent in the living oligomer but is determined after the addition of the deactivating agent. However, one may remark that the smallest decrease in 4,1 structure is obtained with DB.

## Discussion and Conclusions

The oligomerization of DB, PD, and isoprene initiated by RLi and terminated by R′I leads to the normal R-M-R′ and exchange R-M-R products.

The major product is R-M-R′ (except in the case of DB in cyclohexane, where a high yield of R-$M_2$-R is obtained). In all cases a modification of the oligomerization number distribution is observed: an increase of dimers corresponding to the formation of exchange products.

DB gives the highest yield of exchange products.

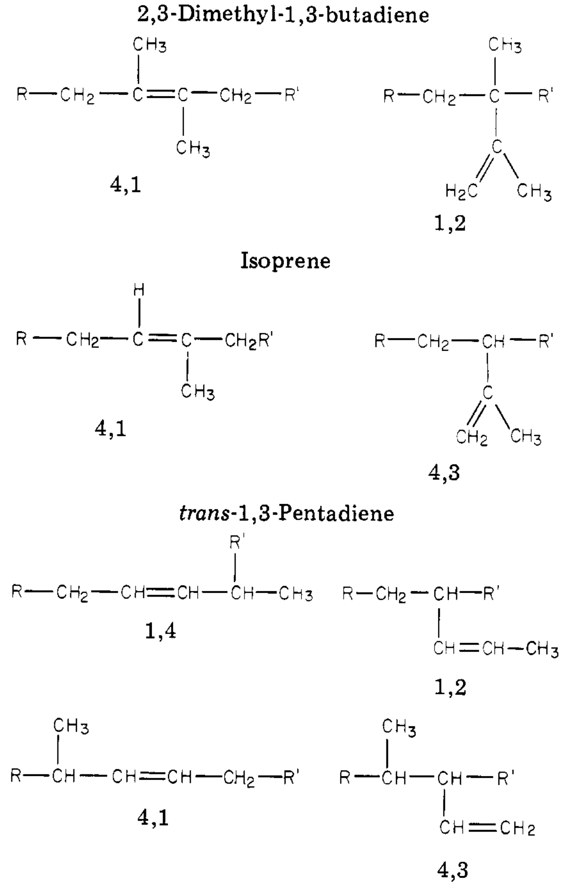
More 1,2 or 4,3 addition modes are present in the alkyl iodide terminated oligomer than in the methanol-terminated oligomer.

**1. Description of the Reactions Leading to the Different Products.** Addition of an alkyl halide to a dienyllithium results in a complex set of possible reactions (Scheme I).

**2. Normal Termination Reaction. Microstructure of the Products.**

$$\text{R-M-Li} + \text{R'X} \rightarrow \text{R-M-R'} + \text{LiX}$$

Chart I
Structure of R—M—R′



The microstructure of the normal products depends on both the site of addition of the initiator RLi and the site of addition of the termination agent on the living oligomer. The proposed structures for the living oligomer may be described as localized covalent species in equilibrium with a small percentage of delocalized species (in hydrocarbon solvents). The proposed structures, resulting from $^1H$ NMR examination of dienyllithium active chain ends by Bywater and Worsfold,[4] Schue,[4,6] and Morton,[7,8] are reported in Chart II. In such species the concentration of the negative charge $\Delta^-$ is maximum on the $C_1$ atom ($C_4$ for DB and the 1,4 form of PD). The fact that different termination agents can add on $C_3$ or $C_2$, leading to different yields in 4,3 and 1,2 products, was mentioned in several works.[5,9] We confirmed this effect using different alkyl halides in the termination of polyisoprenyllithium.[2] In the present work, we observe that methyl iodide increases the 4,3 amount for isoprenyllithium and the 1,2 amount for (dimethylbutadienyl)lithium and pentadienyllithium (relative to methanol-deactivated dienyllithiums). This

Table II
Composition (%) of the Oligomers of Isoprene, *trans*-1,3-Pentadiene, and 2,3-Dimethyl-1,3-butadiene[a]

<table>
<tr><th rowspan="2">monomer</th><th colspan="6">termination by $CH_3I$</th><th rowspan="2">exchange products total</th></tr>
<tr><th>R—M—Me</th><th>R—M—R</th><th>R—$M_2$—Me</th><th>R—$M_2$—R</th><th>R—$M_3$—Me</th><th>R—$M_3$—R</th></tr>
<tr><td>DB</td><td>29</td><td>9</td><td>7</td><td>46</td><td>2</td><td>7</td><td>62</td></tr>
<tr><td></td><td colspan="2">38</td><td colspan="2">53</td><td colspan="2">9</td><td></td></tr>
<tr><td>PD</td><td>37</td><td>7</td><td>23</td><td>25</td><td></td><td>8</td><td>38</td></tr>
<tr><td></td><td colspan="2">44</td><td colspan="2">48</td><td colspan="2">8</td><td></td></tr>
<tr><td>IP</td><td>43</td><td>22</td><td>20</td><td>15</td><td></td><td></td><td>37</td></tr>
<tr><td></td><td colspan="2">64</td><td colspan="2">35</td><td colspan="2"></td><td></td></tr>
</table>

| monomer | termination by MeOH<br>R—M—H | R—$M_2$—H | R—$M_3$—H |
|---|---|---|---|
| DB | 88 | 12 | |
| PD | 66 | 19 | 11 |

[a] Initiator, *t*-BuLi; solvent, cyclohexane; $M/I = 1/2$.

Table III
Microstructure of the Oligomers of DB, PD, and IP in Cyclohexane[a]

| | termination agent | microstructure, %<br>4,1 | 4,1 + 1,4 | 1,2 | 4,3 |
|---|---|---|---|---|---|
| DB | MeI | 85 | | 15 | |
| | MeOH | 90 | | 10 | |
| PD | MeI | | 65 | 30 | 5 |
| | MeOH | | 81 | 15 | 4 |
| IP | MeI | 68 | | | 32 |
| | MeOH | 83 | | | 13 |

[a] Normal product R—M—R'; initiator, *t*-BuLi; $M/I = 1/2$.

Scheme I

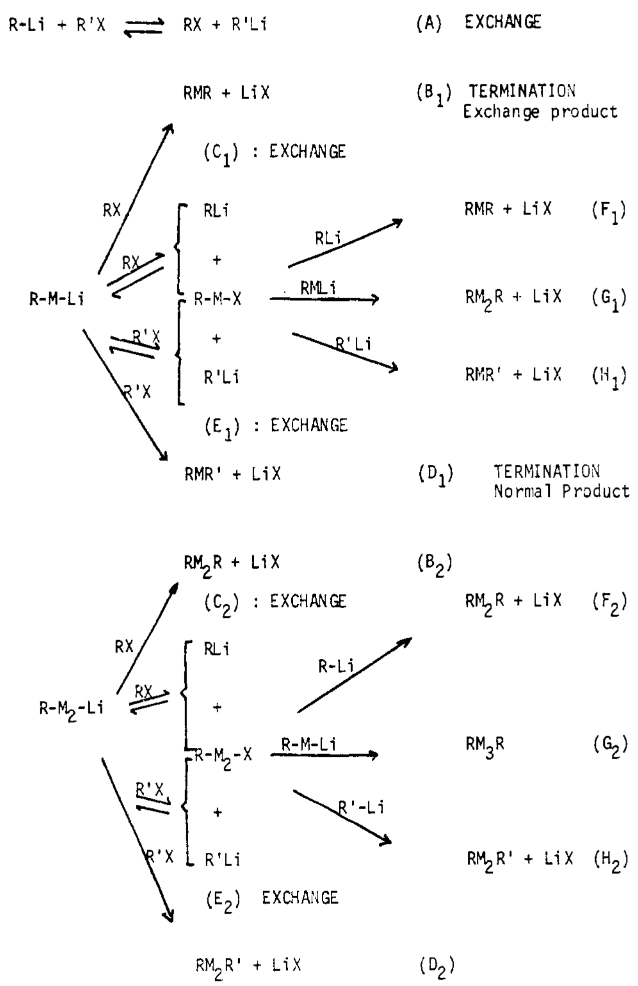
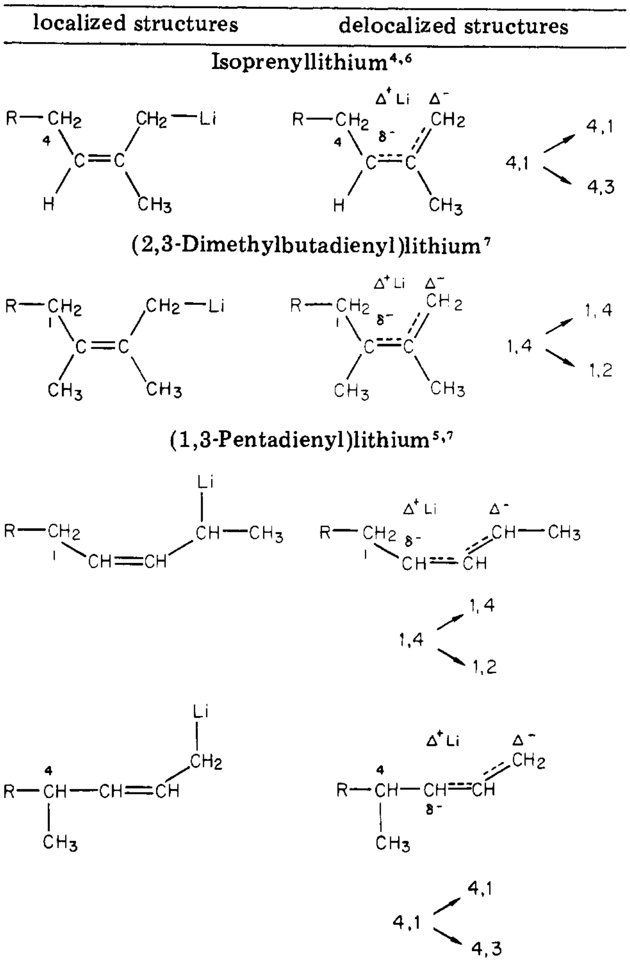


Chart II
Structures of Dienyllithiums in Hydrocarbon Solvents



can be attributed to an increase of the negative charge $\delta^-$ on the $C_3$ carbon ($C_2$ for the 1,4 additions). This suggests that the approach of methyl iodide induces a modification of the repartition of the charges of the organolithium species; this modification could occur through the coordination of lithium with an electron pair of the halogen and could result in an increase of the polarity of the C–Li bond and of the delocalization of the negative charge.

The comparison of this effect on the three dienes appears in the results of Table III: it is lower for DB than for isoprene or PD; this indicates that (dimethylbutadienyl)lithium is less easily delocalized than the two other dienyllithiums, which is consistent with increased negative charge stability on less substituted carbon atoms.

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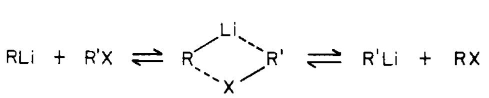
**3. Formation of Exchange Products.** Lithium-halogen exchange reactions are generally explained by two types of mechanisms: (i) an ionic four-center mechanism:[10]



and (ii) a radical mechanism according to

$$RLi + R'X \rightleftharpoons [R\cdot,X,Li,R'\cdot] \rightleftharpoons R'Li + RX^{11}$$

It is known that these reactions are equilibria and that the formation of the more stable carbanion is favored.[12]

(a) A reaction such (A), exchange between an alkyl iodide and an alkyllithium, will lead to comparable amounts of the two organolithiums, as demonstrated by the study of the exchange of *n*-butyllithium ethyl iodide.[13] Thus this reaction is likely to occur but its importance cannot be evaluated.

(b) Reactions $C_1$ and $E_1$ involve an exchange between the dienyllithium and an alkyl halide. These reactions are expected to favor the formation of the stabilized species R–M–Li. But our results indicate that R–$M_2$–R is formed in a process that modifies the distribution of the oligomerization numbers, and among the different possibilities, it can only be the route $C_1/E_1,G_1$.

The coupling reaction was reported in two cases to proceed by an $S_n2$ mechanism: (i) between an allylic halide and an organolithium[14] and (ii) between an allylic organolithium and an alkyl halide.[15] In the view of this mechanism, one may expect the high reactivity of the allylic halide R–M–X in reaction $G_1$ to displace toward the right the equilibria $C_1$ and/or $E_1$.

Finally, one may try to explain why DB gives a higher yield of the exchange product R–$M_2$–R than the two other dienes: if as suggested in section 2 (dimethylbutadienyl)lithium is less stabilized by delocalization, reactions $C_1$ and $E_1$ will be less disfavored than for the two other dienyllithiums.

## References and Notes

(1) Teixeira-Barreira, S. R.; Chaineaux, J.; Mechin, R.; Tanielian, C. *J. Organomet. Chem.* **1981**, *212*, 11.
(2) Teixeira-Barreira, S. R.; Mechin, R.; Tanielian, C. *Eur. Polym. J.* **1979**, *15*, 677.
(3) Schué, F.; Bywater, S. *Bull. Soc. Chim. Fr.* **1970**, 271.
(4) Schué, F.; Worsfold, D. J.; Bywater, S. *Macromolecules* **1970**, *3*, 509.
(5) Ulrich, A. *Bull. Soc. Chim. Fr.* **1973**, 2773.
(6) Sledz, J.; Kaempf, B.; Schué, F.; Libs, S. *Makromol. Chem.* **1975**, *176*, 459.
(7) Morton, M.; Sanderson, R. D.; Sakata, R.; Falvo, L. A. *Macromolecules* **1973**, *6*, 186.
(8) Morton, M.; Falvo, L. A. *Macromolecules* **1973**, *6*, 190.
(9) Sledz, J.; Schué, F.; Kaempf, B.; Libs, S. *Eur. Polym. J.* **1974**, *10*, 1207.
(10) Winkler, H. J. S.; Winkler, H. *J. Am. Chem. Soc.* **1966**, *88*, 964.
(11) Ward, H. R.; Lawler, R. G.; Cooper, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 746.
(12) Applequist, D. E.; O'Brien, D. *J. Am. Chem. Soc.* **1963**, *85*, 743.
(13) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1941**, *63*, 1441.
(14) Cristol, S. J.; Overhults, W. C.; Meek, J. S. *J. Am. Chem. Soc.* **1951**, *73*, 813.
(15) Sommer, L. H.; Korte, W. D. *J. Org. Chem.* **1970**, *35*, 22.

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# Hydrolytic Degradation of Polyester Polyurethanes Containing Carbodiimides

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ABSTRACT: Polyester polyurethanes containing a mono- or polycarbodiimide were aged at 100% relative humidity at 85, 55, and 35 °C. Acid concentration, [A], carbodiimide concentration, [B], and the number-average molecular weight, $M_n$, were measured at intervals. Results are consistent with the occurrence of three parallel processes: acid-catalyzed hydrolysis, reaction of acid with carbodiimide, and uncatalyzed hydrolysis. Their rate constants are designated $k$ (pseudo first order), $k'$ (second order), and $k_0$ (pseudo zero order), respectively. Pertinent differential equations are $d[A]/dt = k_0 + k[A] - k'[A][B]$, $d\Delta(M_n^{-1})/dt = k_0 + k[A]$, and $-(d[B]/dt) = k'[A][B]$. The constants $k$, $k'$, and $k_0$ were calculated from the rates of scission and acid formation without carbodiimide, of mutual disappearance of A and B without water, and of long-term disappearance of B in the presence of water, respectively. These constants and the initial values of [A], [B], and $M_n$ were inserted into the differential equations above and the equations were integrated digitally. The curves generated describe hydrolysis in the presence of monocarbodiimide reasonably well. Lifetimes, defined as the time required to accumulate a specific number of scissions, are increased 3-fold at 85 °C, 7-fold at 55 °C, and about 10-fold at 35 °C by use of about 3 wt % monocarbodiimide. The polycarbodiimide is insoluble in the polyurethanes, and curves generated as described above do not fit the hydrolysis very well. By observation at 85 °C the polycarbodiimide is about as effective as the monocarbodiimide. The rate constant $k_0$ is critical to the lifetime increment. It equals about $10^{-6}$ equiv/(g·day) at 85 °C and has an activation energy of about 85 kJ/mol.

## Introduction

The hydrolytic degradation of unstabilized polyester polyurethanes is due to the acid-catalyzed hydrolysis of the ester linkage.[1] Acid concentration, [A], and the reciprocal of the number-average molecular weight, $M_n^{-1}$, change by equivalent amounts, obeying the equations[2]

$$d[A]/dt = d\Delta(M_n^{-1})/dt = k[A] \qquad (1)$$

Here $t$ is time and $k$ is a pseudo-first-order rate constant giving the fractional rate of increase in acid content.

Certain mono- and polycarbodiimides stabilize polyester polyurethanes against hydrolysis by reacting with acid to form acylureas.[3] The kinetics of this reaction have been studied in dry polyester diols and in a dry polyester polyurethane.[4] With a soluble monocarbodiimide, M, acid and carbodiimide contents obey the equations

$$-d[A]/dt = -d[M]/dt = k'[A][M] \qquad (2)$$

More complex behavior, described later, was found with