zations from isopropyl alcohol afforded white crystalline solid, mp 200–201°.

Anal. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.10; H, 5.02; N, 28.83.

Polymerizations of Diamidoximes with Diacid Chlorides. To an ice-cold solution of 0.970 g (0.005 mol) of diamidoxime in 15–60 ml of distilled DMAc under a nitrogen blanket was added 1.628 g (0.0105 mol) of N,N-diethylcyclohexylamine. The diacid chloride (0.005 mol) was then added in portions and the resulting solution was stirred for 2 hr at room temperature. Work-up in two 400-ml portions of water and two 400-ml portions of methanol in a blender, followed by drying in a vacuum oven at 80° for 16 hr, afforded the poly(arylene acyloylamidoxime) in quantitative yield. When *p*-diacid chlorides were used, 0.4–1.0 g of lithium chloride was added before the amine addition.

Thermal Cyclodehydrations. Thin films of the poly(arylene acyloylamidoximes) were cast from 5% solutions of the polymer in DMAc (containing 5% lithium chloride for polymers IX and X). A sample of the film was placed in a polymer tube, connected to a vacuum pump at 0.1 mm pressure, and heated in a vapor both at the desired temperature for the desired length of time.

Solution Cyclodehydrations. A solution of 1.0 g of poly(arylene acyloylamidoxime), 8.0 g of lithium chloride for polymers IX and X, and 100 ml of DMSO or amide solvent was heated to 115–120° for 3 days and 150° for 2 hr. The resulting precipitated poly(arylene-1,2,4-oxadiazole) was washed with water and methanol in a blender and then dried at 80° for 16 hr in a vacuum oven. Yields were 95–100%.

Model Compounds. Condensations of appropriate monofunctional compounds with the diamidoximes or diacid chlorides were carried out by methods similar to those used for polymerizations. Cyclodehydrations were carried out either by heating the powders in evacuated polymer tubes, whereupon the 1,2,4-oxadiazole sublimed, or by heating solutions of the powders, whereupon the 1,2,4-oxadiazole precipitated under specific conditions of temperature and concentration.

Thermogravimetric analyses were obtained on a Du Pont 950 thermogravimetric analyzer at a heating rate of 5°/min.

Anomalous Polymerization Mechanisms. I. The Aqueous Acrylic Acid Dead End

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ABSTRACT: The polymerization of aqueous acrylic acid by potassium persulfate at 100° results in a limiting (dead-end) polymer yield which does not conform to the Tobolsky dead-end equation for the classical polymerization mechanism. Over the monomer concentration range $[\mathrm{M}]_0 = 0.01\text{–}0.77\ M$, the relation between original initiator concentration, $[\mathrm{I}]_0$, and residual fraction of unpolymerized monomer, U, is given by $[\mathrm{I}]_0 = 0.00185\{\mathrm{arc\ Tan}\ (60[\mathrm{M}]_0) - \mathrm{arc\ Tan}\ (60[\mathrm{M}]_0U)\}$. By development of a *generalized dead-end theory*, it has been shown that the form of the empirical relation corresponds to dominance of a first-order termination reaction and to an effective kinetic competition between propagation and termination reactions for monomer-containing radicals which is of zeroth order with respect to radical concentration and of *second* order with respect to monomer concentration. The kinetic competition is much less favorable to termination for first stage (monomer-free) radicals and evidence for termination of these radicals is obtainable only below 0.01 M monomer concentrations. The mathematical analysis also provides a measure of the net monomer-consuming efficiency of the aqueous persulfate ion. The value obtained is unexpectedly high, but would be consistent with the presence of a *radical-proliferation process.*

The Empirical Dead-End Equation. The term *dead-end polymerization* was coined by Tobolsky[1] to characterize radical-chain polymerizations in which the reaction stops significantly short of exhaustion of the monomer. By integration of the classical rate equation[2] for radical-induced polymerization, he obtained the expression given by eq 1 for a limiting value of the monomer concentration in unlimited time. Satisfactory agreement with eq 1 was obtained for measurements

$$2k_p(f/k_T{}''k_d)^{1/2}[\mathrm{I}]_0{}^{1/2} = \ln\,[\mathrm{M}]_0/[\mathrm{M}]_\infty = -\ln U = -\ln(1 - Y) \quad (1)$$

on styrene and isoprene.[3]

Aqueous acrylic acid solutions may be refluxed for many hours without appreciable change, but rapid polymerization is initiated by the addition of small quantities of potassium persulfate, presumably due to rapid dissociation of the persulfate anion into radicals under these conditions.[4] At 100° the polymerization ceases well within 1.5 hr after the persulfate addition,

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[1] A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 5927 (1958).

[2] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 114. The notation used in the present paper follows Flory with some modifications and necessary amplifications. The significance of the symbols in eq 1 is as follows: $[\mathrm{M}]$ = concentration of unreacted monomer; $[\mathrm{M}]_0$ = initial value; $[\mathrm{M}]_\infty$ = limiting value; $U = [\mathrm{M}]_\infty/[\mathrm{M}]_0$ = limiting value of unpolymerized monomer fraction; $Y = 1 - U$ = limiting value of polymer yield fraction; $[\mathrm{I}]$ = concentration of unreacted initiator; $[\mathrm{I}]_0$ = initial value; f = initiator efficiency; k_d = rate constant of first-order primary cleavage of the initiator; k_p = the specific rate of propagation; $k_T{}''$ = the sum of the specific rates, $k_{Tc}{}''$ and $k_{Td}{}''$ of combination and disproportionation of the radicals. The double prime distinguishes these second-order termination rate constants from others to be introduced later.

[3] R. H. Gobran, M. B. Berenbaum, and A. V. Tobolsky, *J. Polym. Sci.*, **46**, 431 (1960); *Thiokol Magazine*, **3**, 5 (1964).

[4] I. M. Kolthoff and I. K. Miller, *J. Amer. Chem. Soc.*, **73**, 3055 (1951).

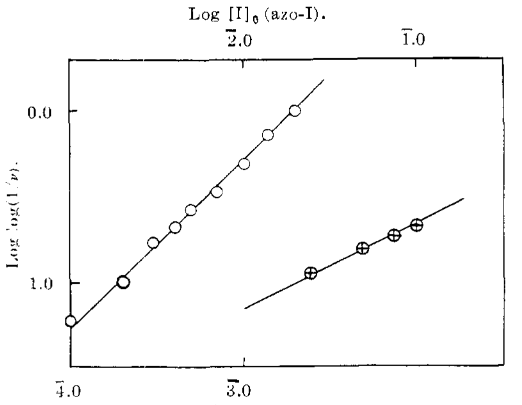

Figure 1. The dead-end relation for 0.0333 *M* aqueous acrylic acid at 100°: ○, 0.0333 *M* acrylic acid–persulfate at 100°; ⊕, isoprene–azo-I at 80°.

resulting in well-defined dead ends which do not conform to the Tobolsky relation, thus demonstrating that the mechanism of this polymerization differs notably from the classical mechanism assumed in the derivation of eq 1. When the initial acrylic acid concentration is 0.033 *M*, a proportionality between the *first* power of the original initiator concentration and the limiting yield function is observed (eq 2) as shown by the *unit*

$$K[I]_0 = -\ln U \qquad (2)$$

slope of the plot of log log $(1/U)$ against log $[I]_0$ for this system in Figure 1. For comparison, a similar plot of the data on dead ends observed by Gobran, Berenbaum, and Tobolsky[3] with the system isoprene–azoisobutyronitrile at 80° is also shown. The latter plot exhibits the slope of one-half required by eq 1.

The indicated acrylic acid data yield a value of 1.20 ± 5% for $10^{-3}\,K$ in eq 2, but this is a near-minimum value of this parameter which varies considerably with the initial monomer concentration, ranging up to 1.91 with monomer dilution to 0.00611 *N*, and up to 10.08 for a monomer concentration of 0.768 *N*. The acrylic acid data over a wide range of concentration of monomer, as well as of initiator, can be represented by eq 3, where A

$$A[I]_0 = \text{arc Tan}\,(B[M]_0) - \text{arc Tan}\,(BU[M]_0) \qquad (3)$$

and B are constants. For any fixed value of U, the initiator requirement, $[I]_0$, has a maximum (corresponding to the minimum of K) at an initial monomer concentration defined by eq 4 from which, in principle,

$$[M]_0(\text{max}) = 1/B\sqrt{U} \qquad (4)$$

B could be evaluated. In practice, precise determination of $[M]_0$ (max) is difficult, but an approximate value of B can be obtained and, by using values in this neighborhood, the value of B which gives the best linear relationship between $[I]_0$ and the arc Tan difference term of eq 2 can be located. Figure 2 shows a plot of these two variables using $B = 60$. The slope of the line corresponds to $A = 540$. The agreement with experimental data is best shown by comparing actual values of $[I]_0$ with those calculated from eq 5. Such a comparison

$$[I]_0 = (1/540)\{\text{arc Tan}\,(60\,[M]_0) - \text{arc Tan}\,(60[M]_0U)\} \qquad (5)$$

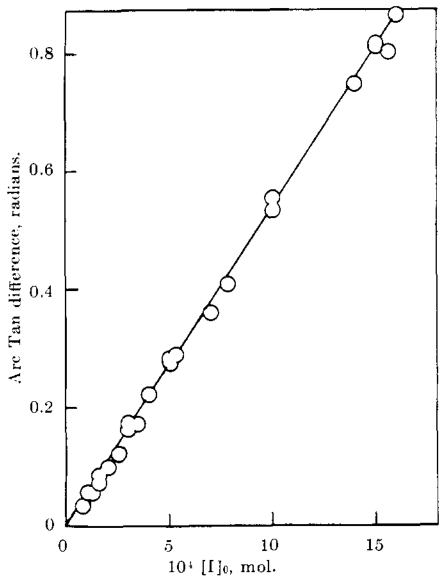

Figure 2. The empirical dead-end relation.

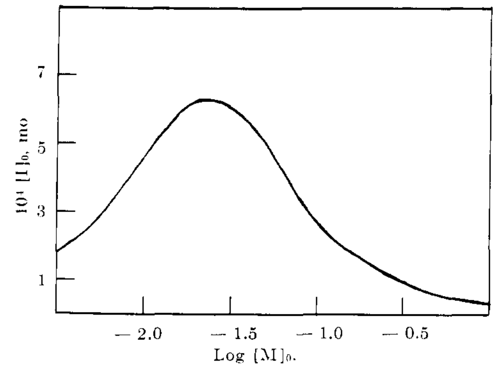

Figure 3. Calculated initiator requirements for 50% polymerization.

appears in Table I, from which it is evident that agreement is obtained within an average deviation of about 6%. Equation 5 could only be represented graphically over the range of the three variables by a surface, but, for any arbitrary value of U, the relation between $[I]_0$ and $[M]_0$ is a curve such as that in Figure 3 for $U = 0.5$.

Generalized Dead-End Theory. In seeking an interpretation of the acrylic acid anomalies it will be convenient to utilize a generalized rate equation which may be simply derived as follows. Consider a differential increment in radical concentration, $d[R\cdot]_f$, formed from the initiator. A fraction, w_1, of these radicals will react with monomer to form a concentration, $w_1 d[R\cdot]_f$, of second-stage radicals. If each reacting first-stage radical combines with z_1 molecules of monomer, the differential change in monomer concentration will be $-d_1[M] = z_1 w_1 d[R\cdot]_f$. Similar relations will hold for subsequent steps of the propagation sequence

$$-d_2[M] = z_2 w_2 w_1 d[R\cdot]_f; \quad -d_i[M] = z_i(w_i w_{i-1} \ldots w_1)d[R\cdot]_f$$

and the total differential change in monomer concentration will be

$$-d[M] = \sum_1^{\infty} z_i w_{i!}\, d[R\cdot]_f \qquad (6)$$

Table I

Observed and Calculated Initiator Requirements

No.	Stoichiometric ratio, $Y[M]_0/[I]_0$	$[M]_0$	$[M]_\infty$	$10^4[I]_0$ Obsd	$10^4[I]_0$ Calcd	Difference % of obsd
1	3880	0.768	0.161	1.56	1.52	2.6
2	2122	0.384	0.218	0.78	0.62	20.5
3	1520	0.384	0.147	1.56	1.29	17.3
4	453	0.192	0.0787	2.50	2.23	10.8
5	168	0.0985	0.0564	2.50	2.23	10.8
6	61.2	0.0497	0.0421	1.25	1.00	20.0
7	60.5	0.0500	0.0319	3.00	2.98	0.7
8	49.6	0.0497	0.0252	5.00	4.88	2.4
9	42.3	0.0333	0.0291	1.00	1.035	3.5
10	36.0	0.0333	0.0226	3.00	3.20	6.7
11	35.4	0.0497	0.0144	10.00	9.97	0.3
12	34.4	0.0333	0.0264	2.00	1.81	9.5
13	32.1	0.0333	0.0204	4.00	4.07	1.8
14	30.4	0.0333	0.0182	5.00	5.14	2.8
15	28.0	0.0497	0.0077	15.00	15.04	0.3
16	27.1	0.0315	0.0170	5.35	5.35	0.0
17	25.4	0.0333	0.0155	7.00	6.63	5.3
18	22.5	0.0333	0.0108	10.00	9.86	1.4
19	19.4	0.0333	0.0062	14.00	13.88	0.8
20	14.9	0.0333	0.0035	20.00	16.60	17.0
21	14.7	0.0248	0.0027	15.00	15.12	0.8
22	14.6	0.0167	0.0094	5.00	5.06	1.2
23	13.9	0.0248	0.0030	15.61	14.98	4.6
24	10.8	0.0124	0.0039	7.82	7.56	3.3
25	8.9	0.0061	0.0030	3.48	3.17	8.8
					Av	6.1

This relation describes the behavior of all systems in which monomer is consumed solely by radical-chain polymerization. With suitable adjustments it can also be extended to cases involving autoinhibition. Specific rate equations may be obtained from eq 6 by substituting appropriate specific relations for the generalized terms. Thus z_i and w_i will be defined by the specific propagation and termination mechanisms postulated, and $d[R\cdot]_f$ will be related to d[I] by the particular radical formation processes assumed. The general term, $w_i/(1 - w_i)$, is the ratio of the fraction of ith stage radicals *participating in propagation to the fraction terminated.* It is always equal to the ratio of the rate of propagation to the rate of termination for a particular radical species and is thus a measure of this *kinetic competition.* Integration of the specific rate equations between limits corresponding to $t = 0$ and $t = \infty$ should express the conditions for a dead end.

For the special case where all the z's are the same and equal to unity, where all the w's are the same, and where the steady-state relation is assumed, eq 6 reduces to the classical rate equation and, of course, on integration leads to the Tobolsky dead-end (eq 1). Bamford, Jenkins, and Johnston[5] have shown that deviations from the half-order dependence of rate on initiator concentration may occur due to extensive termination by primary radicals at low [M]/[I] ratios. The influence of such termination on the dead end may be examined by distinguishing w_1 for primary radicals from w_m for monomer-containing radicals in eq 6. Recombination of persulfate radicals may be ignored as it merely produces a somewhat reduced net rate of $SO_4\cdot^-$ formation. The result is the Tobolsky equation *except* that the quotient $Q = k_p/(k_T'')^{1/2}$ varies with $[M]_0$, approaching Q_m (for monomer-containing radicals) at high $[M]_0$ where primary radical termination is negligible, and Q_1 (for primary radicals) at low $[M]_0$ as $[R_m\cdot]$ approaches $[R_1\cdot]$. If $Q_1 > Q_m$, the initiator requirement as plotted in Figure 3 should show a rise with increasing monomer concentration as observed in the lower ranges of $[M]_0$, but would approach a maximum constant value at high $[M]_0$ and not fall off as actually observed. A curve of the observed form could result if the Q value for very large radicals was larger than Q_1 and the Q value for radicals of intermediate size were lower than either. Even under these circumstances, Q would be approximately constant in the neighborhood of the curve's maximum and the Tobolsky equation should apply to measurements in this region giving a slope of one-half in Figure 1. Accordingly, the acrylic acid dead end cannot be explained by such modifications of the classical bimolecular termination process.

For application to nonclassical systems we shall introduce a new parameter, G, termed the *generative factor* and defined as the number of first stage (monomer-free) radicals produced when 1 mol of initiator is consumed. Thus $d[R\cdot]_f = -G\,d[I]$ by definition so that eq 6 may be reexpressed as

$$G\,d[I] = d[M]/\sum_{1}^{\infty} z_i w_i' \tag{7}$$

and for the classical mechanism

$$G\,d[I] = (d[M])(1 - w)/w \tag{8}$$

Interpretation of the Empirical Equation. If, as the sole departure from the classical mechanism, we assume

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(5) C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55**, 1451 (1959).

exclusive termination by a reaction which is first order with respect to radical concentration, $w/(1 - w)$ becomes $k_p[M]/k_T' = F[M]$, and substitution in eq 8 followed by integration between the limits $[I]_0$ to $[I]_\infty$ and $[M]_0$ to $[M]_\infty$ gives the "first-order dead-end" eq 9, which is

$$FG[I]_0 = \ln [M]_0/[M]_\infty = -\ln U \qquad (9)$$

identical in form with our empirical eq 2. The appearance of the original initiator concentration as the *first* power is therefore consistent with mechanisms dominated by first-order termination. (Simultaneous participation of second-order termination processes is not excluded, but such participation has a negligible influence on the limiting polymer yield.) For all such systems the right-hand term of eq 7 is solely a function of monomer concentration and, when so expressed, will usually be explicitly integrable. Another important characteristic of such systems is that the limiting polymer yield is independent of the *rate* of initiator dissociation.

Since eq 9 would correspond to a horizontal line if plotted on Figure 3, it is evident that additional assumptions are required. The observations of Ito, Shimizu, and Suzuki[6] that the initial polymerization rate in these systems at 50° is second order with respect to monomer concentration suggests the possibility of a second-order propagation process such as eq 10, so that $z_i = 2$.

$$RM_{(i)}\cdot + 2M = RM_{(i+2)}\cdot \qquad (10)$$

For a fixed value of U, this possibility leads to the hyperbolic relationship

$$[I]_0[M]_0 = (1 - U)/(2SGU) \qquad (11)$$

where $S = k_p''/k_T'$. This is consistent with the rise in $[I]_0$ with decreasing $[M]_0$ shown in Figure 3 for the more concentrated solutions of acrylic acid, but it would not provide for the observed maximum and subsequent decrease in $[I]_0$ with further dilution of acrylic acid. These phenomena require greater propagation efficiency at one or more of the early propagation stages. In fact, the further assumption that termination of first-stage radicals is negligible at monomer concentrations above 0.01 M permits derivation of the empirical eq 3 from the general eq 7. Taking $w_1 \cong 1$, the summation term is altered to $2/(1 - w_m)$ or $2(1 + S[M]^2)$ since $w_m = S[M]^2/(1 + S[M]^2)$ and therefore eq 7 becomes

$$2G\mathrm{d}[I] = \mathrm{d}[M]/(1 + S[M]^2) \qquad (12)$$

In integral form

$$(2G\sqrt{S})\,[I]_0 = \text{arc Tan}\,([M]_0\sqrt{S}) - \text{arc Tan}\,([M]_0U\sqrt{S}) \qquad (13)$$

this conforms to empirical eq 3, from which it is evident that $B = \sqrt{S}$ and $A = 2G\sqrt{S}$, or $S = 3600$, $zG = 9.0$, and $G = 4.5$. An alternative propagation mechanism of the same order as eq 10

$$RM_{(i)}\cdot + 2M = RM_{(i+1)}\cdot + M \qquad (14)$$

merely changes the value of z from 2 to 1 so that G becomes 9.0.

Propagation mechanisms of the normal order

$$RM_{(i)}\cdot + M = RM_{(i+1)}\cdot \qquad (15)$$

in place of eq 10 or 14 are consistent with the data under specialized circumstances. The simplest possibility distinguishes the second stage from the later ones, *i.e.*, $w_2 \neq w_3$, but $w_3 = w_4 = w_5$, etc. For this $z_i = 1$ and, using $F = k_p'/k_T'$ with consistent subscripts, eq 7 now reduces to

$$G\mathrm{d}[I] = \mathrm{d}[M](1 + F_2[M])/(1 + 2F_2[M] + F_2F_3[M]^2) \qquad (16)$$

This integrates to the form of eq 3 *if* the terms in F_2, but not the product, F_2F_3, are negligible. Under these special circumstances $F_2F_3 = B^2 = 3600$ and $G = A/\sqrt{F_2F_3} = 9.0$.

The Termination Reaction. The retarder which is presumably responsible for first-order termination has not been identified. Evidence with respect to the obvious possibilities (autoinhibition, oxygen, impurities) has been negative. Formation of an intermediate complex between radicals and water with sufficient stability to be ineffective as a chain transfer agent is consistent with available information. Such a complex might also account for the unexplained first-order termination observed in oxygen-styrene copolymerization in *aqueous* solution by Bovey and Kolthoff.[7]

The arc Tan difference in eq 5 has an absolute maximum value of 1.57 radians indicating that dead-end phenomena would be suppressed at initiator concentrations above 29×10^{-4}. High radical concentrations would also favor second-order termination over first-order termination. The difference in order with respect to persulfate observed in the Japanese rate studies (one-half)[6] and in our dead-end studies (first) is probably due to such considerations, since the Japanese investigators used generally higher initiator concentrations. Such considerations imply that dead-end phenomena may be much more general than presently appears; possibly they need only to be sought under the right conditions.

The Generative Factor. All of the possibly valid polymerization mechanisms which have been considered agree on the value of the product $zG = 9.0$. The maximum limit of 2 placed on G by the simple dissociation of persulfate ion would require a minimum value of 4.5 for z, the number of monomer molecules consumed per radical in each propagation step. This is inconsistent with these mechanisms and direct dissociation of persulfate ions into more than two radicals is most unlikely. Some type of radical proliferation by a secondary process would account for the observed results. There seem to be no prior observations of radical proliferation in polymerization systems. Independent G values are not ordinarily obtainable directly from rate or dead-end data; only the special complexities of the acrylic acid system permit their calculation in this case.

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(6) H. Ito, S. Shimizu, and S. Suzuki, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **58**, 194 (1955). The abstract [*Chem. Abstr.*, **49**, 14375*c* (1955)] contains inaccuracies. Data in the original paper show that the initial polymerization rate was second order with respect to monomer and one-half order with respect to initiator.

(7) F. A. Bovey and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **69** 2152 (1947).

Experimental Section

The aqueous acrylic acid polymerizations were carried out in 1-l., three-neck flasks equipped with thermometer, stirrer, and reflux condenser. The mixtures were made up to 300 ml final volume by first mixing acrylic acid solutions and distilled water, bringing this to the reflux temperature and then adding appropriate small volumes of 0.030 *M* potassium persulfate. Since the persulfate decomposes rapidly at elevated temperatures,[4] precautions must be taken to minimize thermal decomposition in the absence of acrylic acid by running the persulfate directly into the vigorously stirred acrylic acid solution. Prior contact of the persulfate with the flask walls or the stirrer shaft must be avoided. In the standard experiments, temperature control was limited to reflux conditions (about 100°). The dead-end yield is relatively insensitive to temperature. The average K (eq 2) for four experiments with 0.0333 *N* acrylic acid and 0.0005 *M* persulfate conducted in a thermostated oil bath at 90° was 1.29×10^3 which does not differ significantly from 1.21×10^3 obtained under reflux conditions. Reduced polymer yields were sometimes obtained in a new flask. The yield rose to normal by the second or the third experiment in the same flask. The use of glass wool did not affect the polymer yield after "breaking-in" by one or two experiments. The unpolymerized acrylic acid content of reaction mixtures was determined by three methods which gave concordant results. These were (1) acid permanganate oxidation (8 equiv/mol of acrylic acid), (2) steam distillation of acrylic acid and alkali titration, (3) a bromination procedure. Acrylic acid was purified in two ways, crystallization and distillation; both achieved 99–100% purity. Potassium persulfate (assay 99–100%) was used as purchased.

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The Polymerization of Isoprene with *sec*-Butyllithium in Hexane

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ABSTRACT: The polymerization of isoprene in *n*-hexane, initiated by *sec*-butyllithium, has been investigated with particular emphasis on the initiation step. The mechanism of chain initiation appears to be quite different from that previously observed in benzene and involves direct attack of *sec*-butyllithium tetramers on isoprene. The effect of lithium *t*-butoxide has been investigated and found to accelerate the initiation rate but to depress the propagation rate. Some experiments were carried out to determine the rate of intermolecular exchange between *sec*-butyllithium and polyisoprenyllithium.

Lithium alkyl initiated polymerization of olefines in hydrocarbon solvents has received much attention recently. In many cases, the mechanism can be represented schematically as eq 1 and 2 where the ac-

$$(\mathrm{RLi})_n \rightleftharpoons n(\mathrm{RLi}) \qquad (1)$$

$$\mathrm{RLi} + \mathrm{M} \xrightarrow{k_i} \mathrm{RM_1Li} \qquad (2)$$

tive species is a small fraction of the dissociated alkyl in labile equilibrium with a large excess of associated material. The reaction order in lithium alkyl is, according to this scheme, fractional ($1/n$) and can be correlated with the association number. Two recent reviews[1,2] have examined the evidence for such a mechanism which has been suggested to hold in certain cases, for both initiation and propagation steps, *i.e.*, where R is an initiator fragment or a growing polymer chain, respectively. The validity of this mechanism, generally, has been challenged by Brown.[3]

One case in which this mechanism certainly does not hold is the initiation step in the *n*-butyllithium (*n*-BuLi) initiated polymerization of styrene, butadiene[4] and isoprene[5] in cyclohexane. Similar results have been observed with *sec*-butyllithium.[6] Instead of an initially linear increase in concentration of polymer–lithium species, which falls off as the reagents are depleted, as observed in benzene, the initiation curve is sigmoidal in shape. Some form of autocatalysis (by the alkenyllithium formed) was suggested to occur.[5] The reaction of isoprene with *sec*-butyllithium in hexane, which follows a similar course, has been investigated in an attempt to obtain more detailed information on this type of reaction.

Experimental Section

n-Hexane was stirred with concentrated sulfuric acid until no coloration developed. After washing the solvent to free it from sulfuric acid and drying, it was fractionally distilled from potassium metal. A middle cut was collected and passed twice over activated silica gel. The solvent was stored on the vacuum line over calcium hydride and distilled onto *n*-BuLi prior to use. Isoprene was purified and

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[1] S. Bywater, *Fortschr. Hochpolym. Forsch.*, 4, 65 (1965).

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[6] D. J. Worsfold and S. Bywater, *J. Organometal., Chem.*, 9, 1 (1967).