Q_k = heat transferred in equipment k (energy/unit time)
SGi = subgroup of variables numbered i
t_k = residence time for equipment k (unit time)
T_j = temperature of stream j (deg.)
U_k = heat transfer coefficient for equipment k (energy/area—unit time—deg.)
V_k = liquid volume in equipment k (volume)
Vi = variable numbered i
x = unknown variable
x_i = unknown variable numbered i
$x_{i,j}$ = mole fraction of component i in stream j
ΔT_{1m_k} = log mean temperature difference for equipment k (deg.)
ρ_j = mean molar density of stream j (mole/volume)
τ_j = variable degrees of freedom of variable j
ϕ = empty set indicator

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APPENDIX A. THE LEE-CHRISTENSEN-RUDD ALGORITHM

(i). Calculate the variable degrees of freedom considering only the equations not eliminated by the LCR Algorithm. Go to (ii).

(ii). Locate a column with variable degree of freedom equal to one. If no degree one variable exists, go to (vii). Otherwise, go to (iii).

(iii). Locate the row which contains the degree one variable. Go to (iv).

(iv). Eliminate both the row and column which contain the degree one variable. Go to (v).

(v). If all the equations have been eliminated, Go to (vi). Otherwise, return to (i).

(vi). Output all columns which have not been eliminated as the optimal design variable set. Stop.

(vii). Persistent iteration encountered. Algorithm fails.

APPENDIX B. THE EQUATION ORDERING AND VARIABLE GROUP ALGORITHMS

(i). Calculate variable degrees of freedom considering only the equations not eliminated by the equation ordering Algorithm. Go to (ii).

(ii). Proceeding left to right, locate the leftmost column whose variable degree of freedom is one. If no degree one variable exists, go to (iv). Interchange the row of the matrix which contains the degree one variable with the bottom row of the matrix which has not been eliminated by the equation ordering Algorithm. Go to (iii).

(iii). Eliminate the bottom row which does not contain an eliminated equation. Go to (v).

(iv). Persistent iteration encountered. Stop.

(v). If all the equations or all equations except one have been eliminated, stop. Otherwise, go to (i).

(i). Set subgroup counter t to zero. Go to (ii).

(ii). Calculate the equation degrees of freedom considering only those columns of the matrix which have not been eliminated by the variable group algorithm. Go to (iii).

(iii). Proceeding from top to bottom, find the topmost equation whose equation degree of freedom is one. If no degree one equation exists, go to (ix). Store the degree one row outside the matrix and vacate (remove all entries in) the row of the matrix which had held the degree one equation. Go to (iv).

(iv). If the row immediately above the vacated row has an equation degree of freedom equal to zero, go to (vi). Otherwise, go to (v).

(v). Remove the entries from the row immediately above the vacated row and place the entries in the vacated row. The vacated row is now one row higher in the matrix. Go to (iv).

(vi). Put the stored degree one equation into the vacated row. Go to (vii).

(vii). Interchange the column containing the variable in the degree one equation with the leftmost column which has not been eliminated by the variable group algorithm. Go to (viii).

(viii). Eliminate the leftmost column which has not been eliminated by the variable group algorithm. Go to (xiii).

(ix). Find the topmost row which has an equation degree of freedom greater than zero. Define this value as f_{top}. Go to (x).

(x). Increment subgroup encounter t by one. vgout(t,1) = t. vgout(t,2) = the row number of the row whose equation degree of freedom is equal to f_{top}. vgout(t,3) = the column number of the leftmost column which has not been eliminated by the variable group algorithm. vgout(t,4) = $f_{\text{top}} - 1$ (the number of design and iterative variables associated with subgroup t). Go to (xi).

(xi). Interchange the f_{top} columns which have entries in the topmost equation whose equation degree of freedom is greater than zero with the f_{top} leftmost columns which have not been eliminated by the variable group algorithm. Go to (xii).

(xii). Eliminate the f_{top} leftmost columns which have not been eliminated by the variable group algorithm. Go to (xiii).

(xiii). If all the columns or all the columns except one have been eliminated by the variable group algorithm, stop. Otherwise, go to (ii).

Matrix vgout contains pointers for defining the rows and columns of subgroups of variables and equations associated with a subgroup.

Supplementary material has been deposited as Document No. 02694 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

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Cis-1,4 Polymerization of Butadiene Initiated by $CoCl_2 \cdot 4C_5H_5N\text{-}(C_2H_5)_2AlCl$

The effect of catalyst composition on the polymerization of butadiene initiated by $CoCl_2 \cdot 4Py\text{-}Et_2AlCl\text{-}H_2O$ in a batch reactor has been studied. It was found that the polymerization is first order with respect to monomer and cobalt concentrations, and both the deactivation of catalyst and the chain transfer reaction have great influence in conversion as well as molecular weight. A general conversion model was proposed, and it fits the experimental data well.

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and
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SCOPE

The polymerization of butadiene initiated by aluminum alkyl and cobalt chloride to make high cis-1,4 polybutadiene was first reported in several patents issued around 1958 (Marullo et al., 1957, 1958; Porter, 1959; Tucker, 1959; Wargotz and Saltman, 1959). It was Gibbin (1962) who first investigated the polymerization kinetics of the system using diethyl aluminum chloride-cobalt chloride-4 pyridine as catalyst. He found that the inclusion of controlled amounts of oxygen or water is essential to the initiation of polymerization. He also found that the rate of polymerization is first order with respect to monomer concentration. Zgonnik et al. (1962, 1965), on the other hand, studied the characteristics of the polymerization using the same catalyst used by Gibbon except that the four-pyridine complexes were replaced by two-pyridine and they concluded that the polymer products are characterized by a broad molecular weight distribution (MWD) and that the chain termination is due to the recombination of two active centers, with no attempt, however, to distinguish whether the chain breaking step is chain termination or chain transfer. Their results also confirmed the findings of Gibbin's that a trace of water promotes polymerization, but the presence of increased amount of water will cause a marked decrease in the polymerization rate. The water also has a profound effect on the MWD; the presence of water broadens the distribution significantly.

In the middle of 1960, the Chinese team reported in a series of papers (Wang et al., 1962, 1964*a*, 1964*b*; Shieh et al., 1965*a*, 1965*b*) the effects of additives on the catalytic activities, notably the compounds characterized as electron donors. They observed a drastic decrease in the rate of polymerization when a trace of certain electron donors was added. A few exceptions were noticed however; for example, when Et_2S was added to the system, the reaction rate increased substantially. The loss of activity due to the addition of electron donors was attributed to the complex formation between the electron donors and the active centers. The catalyst activities have been shown to follow closely the specific conductivities of the reaction mixture with the addition of electron donors. Similar phenomena were also observed as to the effect of water in the system. This led them to suggest the ionic nature of the polymerization, but they made no attempt to suggest a specific ionic reaction. The ionic mechanism has also been suggested by Childers (1963) and by Cooper et al. (1963). However, their findings contradicted each other as to whether the mechanism is anionic or cationic.

Attempts have also been made by the Chinese team to study the kinetics of the polymerization reaction including the effect of additives other than electron donors.

In this work a batch reactor has been used to investigate systematically the polymerization of butadiene in benzene solution initiated by $CoCl_2 \cdot 4Py\text{-}Et_2AlCl\text{-}H_2O$ catalyst. With such a reactor system we are able to sample the reaction mixture during the course of polymerization in order to follow the changes of the MWD of the polymer products with the help of gel permeation chromatograph (GPC). The MWD data provide additional information in the study of the polymerization mechanism and on the effects of aluminum alkyls and water on polymerization.

CONCLUSIONS AND SIGNIFICANCE

The study of the monomer conversion and the changes in molecular weight distribution during the course of polymerization in a batch reactor for the system of butadiene polymerization in benzene with $CoCl_2 \cdot 4Py\text{-}Et_2AlCl\text{-}H_2O$ catalyst shows that the polymerization is first order with respect to monomer concentration and also to the cobalt concentration. The deactivation step is believed to be a combination of different mechanisms and is much more complicated than suggested by previous investigators. The main source of deactivation comes from the decomposition of the active complexes in the presence of the traces of unknown impurities. With respect to its complexity, a pseudo first-order deactivation can be used to treat the conversion data. In fact, the conversion model presented here with first-order approximation correlates the experimental data well. Owing to its simplicity, the model might be used in process studies.

The MWD of the polymers is governed mainly by the chain transfer reaction, though the concentration of cobalt plays an equally important role in the average molecular weights of the final products. Evidence shows that the chain breaking step is mainly due to the transfer reaction with the secondary products from the reaction between water and aluminum alkyl. However, aluminum alkyl itself, if in excess, also acts as a transfer agent.

EXPERIMENTAL WORK

Equipment

A bench scale batch reactor made of borosilicate glass with a capacity of about 1 l was used for all the polymerization runs. The reactor was equipped with cooling coil and a magnetic stirrer. The temperature was controlled at the desired levels to within 1°C by a Time-Proportioning on-and-off controller obtained from API Instruments Co. A detailed description of the reactor system is given elsewhere (Loo, 1973). Because of the sensitivity of the polymerization process towards moisture and oxygen, the entire work was conducted under nitrogen atmosphere.

Material

Polymerization was conducted in benzene solution. The thiophine free benzene of ACS reagent grade was first distilled and then passed through a column packed with Linde molecular sieve of type 4A to reduce the moisture content to about 12 p.p.m. The dry benzene was stored under nitrogen atmosphere.

The monomer was Phillips rubber grade butadiene-1,3 and of 99 mole % purities. It was first distilled to remove the 0.02 wt. % of inhibitor. The butadiene directly from the cylinder contains about 370 p.p.m. of water as determined by Karl-Fischer titration. The moisture content was reduced to 30 p.p.m. by passing through the drying column filled with Linde molecular sieve, type 4A.

Diethyl aluminum chloride, obtained from K and K Co., certified to a minimum purity of 99% was used as received.

The $CoCl_2 \cdot 4Py$ complexes were prepared according to Katzin and his co-workers (1950). Dry pyridine was added

TABLE 1. MOLAR ABSORPTIVITY

	Molar absorptivity		
	10.3 μ	11.0 μ	12.0-16.0 μ
trans	136	2.4	1.67
1,2 vinyl	6.7	176	4.7
Cís-1,4	4.7	1.9	10.7

TABLE 2. COMPARISON OF THE COMPOSITIONS OF MICROSTRUCTURES OF STANDARD PB SAMPLES WITH CALCULATED ONES

	Trans (%)		Vinyl (%)		Cis (%)	
Sample	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
1	1.4	1.7	3.3	3.0	95.3	95.3
2	2.3	2.1	95.3	95.5	2.5	2.5
3	88.5	88.5	2.6	2.7	8.9	8.7
4	44.5	45.5	8.4	8.4	47.1	46.1

to cobaltous chloride which forms the dark red violet solids. The solids were separated by filtration and then extracted with cold dry chloroform. The chloroform was removed by evaporation to form pure $CoCl_2 \cdot 4Py$ solids of pink violet color. The complexes were analyzed for cobalt content with an atomic adsorption spectroscopy. A typical result shows the cobalt content of 12 ± 0.4% as compared to the calculated value of 13.2%.

Pure grade nitrogen gas was passed through a drying tube containing Drierite to remove the traces of water vapor before use.

Polymerization Procedures

The apparatus was dried overnight in an oven at 150°C. The reactor system was assembled while hot. The benzene solutions of monomer, cobalt complexes, and diethyl aluminum chloride were prepared in the additional bottles which were connected to vacuum-nitrogen lines at one end and to the benzene storage bottle at the other. Before the reactants were introduced, the reactor and the additional bottles were evacuated and then flushed with dry nitrogen twice.

Monomer solution was prepared by distilling butadiene into the bottle with a known quantity of benzene already in the bottle. The amount of butadiene transferred was measured by the difference in volume.

$CoCl_2 \cdot 4Py$ and Et_2AlCl solutions were prepared in a dry box under nitrogen atmosphere. The amount of $CoCl_2 \cdot 4Py$ was determined by weight, but the quantity of Et_2AlCl was measured by volume with a 2 ml syringe graduated at 0.1 ml. Both solutions were prepared immediately before a particular run.

The different reagents were added to the batch reactor under nitrogen atmosphere. The usual sequence of addition was solvent, butadiene solution, aluminum alkyl, and finally the cobalt solution. For the experiments in which water had to be added, it was in the form of saturated wet benzene and was added to the reactor before butadiene was introduced.

Samples were taken from the reactor at various reaction times. Methanol was added to precipitate polymers, and most of the solvent was then removed by filtration. Approximately 1% of phenyl-2-naphthyl-amine was added as antioxidant. The polymer was then dried in a vacuum oven at 40°C and weighed to constant weight. All the polymerization experiments were carried out at 25°C.

Molecular Weight Distribution Measurements

MWD were determined with a Waters Model 200 GPC. The universal calibration procedures were employed by using standard polystyrene samples provided by Waters and four broadly distributed polybutadiene standard samples provided by Phillips. The MWD of each sample was corrected for instrumental spreading. The detailed procedures for the calibration and corrections are given elsewhere (Loo and Hsu, 1971, 1974).

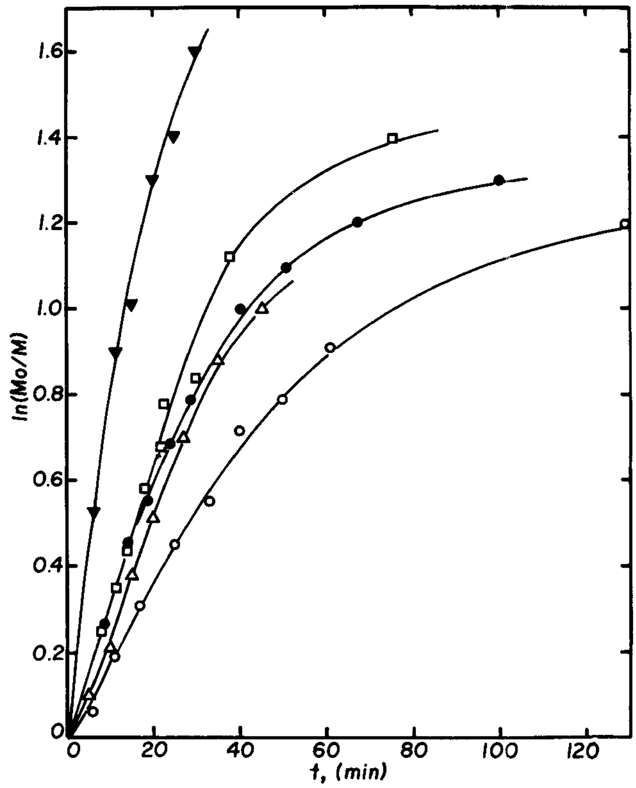

Fig. 1. Monomer conversion at [Al] = 8.3 mmole/l and [H_2O] = 1.4 mmole/l. Cobalt concentrations in milliliters per liter are: ○—0.029, △—0.04, ●—0.05, □—0.53, ▽—10.0.

IR Analysis

The microstructure of polybutadiene was determined according to the procedures suggested by Silas et al. (1959). The polybutadiene was dissolved in carbon disulfide with a concentration of about 0.5 to 1.0%. The potassium chloride cell with 1.0 mm path was used along with a reference cell of adjustable path length. Three absorption peaks were taken for calculation: 10.3, 11.0, and the combined one of 12 to 16 μ. In the case of the broad peak between 12 to 16 μ, the area bound by the two wavelengths was taken for calculation.

Four standard samples supplied by Phillips Petroleum Co. with known compositions of microstructures were used to generate the molar absorptivities. The results are given in Table 1. A comparison of the compositions between the certified values and those calculated from the absorptivities according to Table 1 are given in Table 2.

RESULTS AND DISCUSSION

Figure 1 shows the plots of ln(Mo/M) vs. reaction time for cobalt concentration ranging from 2.9×10^{-5} to 10×10^{-5} mole/l. Mo is the initial monomer concentration, and M is the concentration at any reaction time t. At low cobalt concentration a short induction period was observed. Without consideration of the induction period, the conversion curve shows a linear relationship at low conversion but becomes curved at higher conversion. The nonlinear behavior of the curve at higher conversion is mainly due to the significant deactivation of catalysts; there is no reason

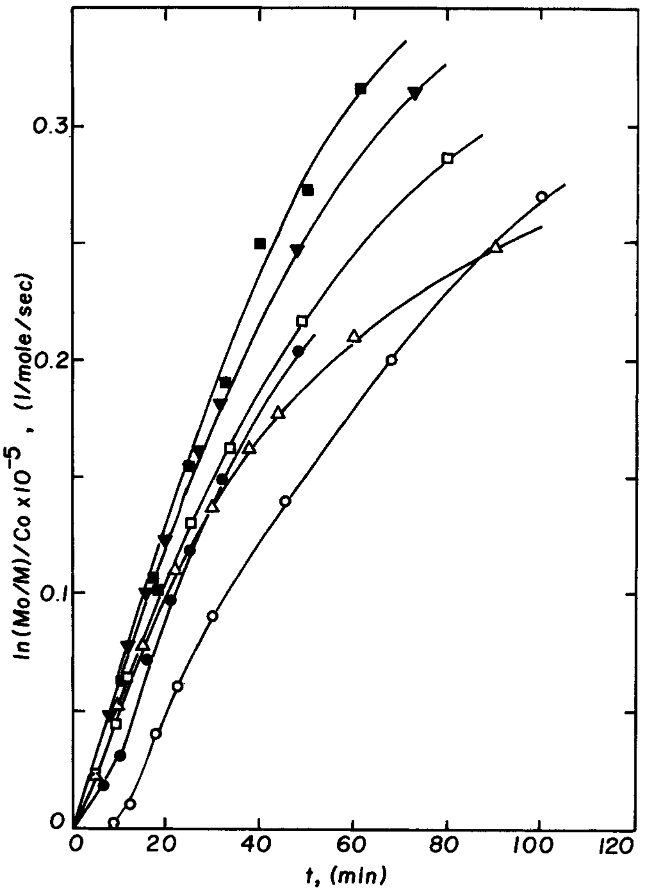

Fig. 2. Monomer conversion per mole of cobalt catalyst at fixed water content (1.4 mmole/l). Aluminum concentrations in milliliters per liter are: ○—5.0, ▼—9.8, ■—8.3, ●—11.6, □—15.0, △—24.7.

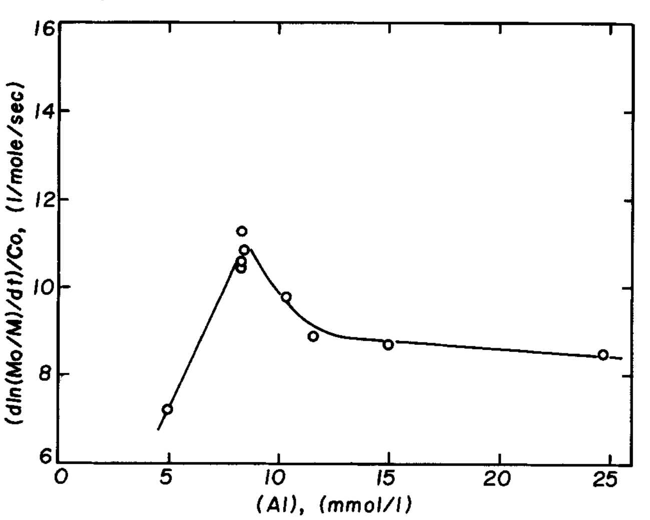

Fig. 3. Initial polymerization rate vs. [Al] concentration at $[H_2O] = 1.4$ mmole/l.

or evidence to believe that a change of reaction order occurs as polymerization progresses.

The linear relationship between ln *Mo*/*M* and *t* implies the first-order polymerization with respect to monomer concentration. The first-order mechanism has been reported for similar systems by many other investigators (Gibbin, 1962; Wang and Hsueh, 1962; Loo and Hsu, 1974).

Furthermore, the slopes of the linear portion of the curves in Figure 1 divided by the cobalt concentration at given concentrations of aluminum alkyl and water give a constant value of 10.9 ± 0.3 l/mole-s, which indicates that the polymerization is also a first-order reaction with respect to cobalt concentration.

The induction period is noticeable only for low cobalt or aluminum concentration (Figure 2). It becomes more evident when water content is high. Such evidence along with the results from MWD study to be discussed later gives a clear indication that the formation of active complexes is probably a relatively slow process as compared to the propagation reaction. In the presence of excessive water, the formation of complexes is greatly hindered.

Zgonnik et al. (1962) in their study of the polymerization of butadiene with $CoCl_2 \cdot 2Py$ catalyst at 2°C found that the viscosity average molecular weight is inversely proportional to the square root of cobalt concentration and concluded that the deactivation of catalysts is a result of the combination of two active centers. Our results, however, indicated that the nature of the termination reaction is much more complicated than a simple combination reaction as suggested by Zgonnik and his co-workers. Some of our polymerization runs did show the number average molecular weight being inversely proportional to the $[Co]^{1/2}$, but other results are quite different from a simple relationship. Even for those runs where *Mn* is inversely proportional to $[Co]^{1/2}$, such a relationship does not hold for *Mw*. Furthermore, if the combination reaction were predominant, then it would be expected that as conversion increases, the reaction media would become more and more viscous, which reduces the rate of diffusion and also the probability for two long chain polymers to meet for the termination by combination. The slowdown of termination reaction will result in the acceleration of the rate of polymerization as observed in many free radical polymerization systems, but this was not observed here.

Examining the data from those experiments with high aluminum and water concentrations, we found not only that the yield and the average molecular weight of polymer were drastically reduced, but also that the polymer species became broadly distributed as a result of a combined effect of deactivation and chain transfer. It is our opinion that the deactivation of catalyst is most likely the result of the decomposition of the complexes in the presence of impurities existing in the system; water is certainly one of the major constituents. However, we should point out that the arguments presented here do not preclude the possibility of the termination by combination. Deactivation is indeed a complicated matter requiring further study to identify the exact nature of this reaction or reactions. The existence of chain transfer reaction further complicates the analysis. Nevertheless, our later analysis of the conversion model will show that as far as the rate of polymerization is concerned, a pseudo first-order deactivation with respect to the concentration of complexes provides a very good approximation.

Figure 3 is a plot of the polymerization rates per mole of cobalt catalyst as defined by $(d\ln(Mo/M)/dt)/Co$ against aluminum alkyl concentrations at constant water level of 1.4 mmole/l. Polymerization rate rises rapidly as [Al] increases from 5 to 8.3 mmole/l. With further increase in [Al], however, the polymerization rate tends to decrease and then remains almost constant at higher concentrations of aluminum alkyl, a general behavior common to most of the Ziegler types of catalyst systems.

Figure 4 is a plot showing the combined effects of aluminum alkyl and water. It can be seen that the polymerization rates show a sharp maximum with respect to water-to-aluminum ratio; the location of maximum rate, however, shifts towards higher $[H_2O]/[Al]$ ratio as concentration of aluminum increases, and at the same time the maximum rates decrease.

At high water level, polymerization shows a short induction period. On the other hand, at very low water level one would also expect the existence of a similar induction period. In fact it has been shown by many other investigators that as the amount of water is reduced to zero, polymerization will not be initiated at all. When the water is maintained at the level over the range of 1.0 to 2.5 mmole/l, there were no appreciable effects on polymerization rate.

Conversion Model

With excessive amount of aluminum alkyl in the system, the reaction of complex formation may be approximated by first-order reaction with respect to the concentration of free cobalt-pyridine complexes. Hence

$$[Co] = [Co]_i\, e^{-k_c t} \qquad (1)$$

where [Co] is the concentration of free $CoCl_2 \cdot 4Py$. The subscript i indicates the initial concentration or the cobalt added to the reactor. k_c is the corresponding rate constant. Assuming the initiation reaction to be instantaneous, we obtain the rate equation for the active polymer species:

$$\frac{d[P_T]}{dt} = k_c[Co] - k_t[P_T] \qquad (2)$$

where $[P_T]$ is the concentration of total active polymer species and k_t is the rate constant for the termination reaction, which we assume as first order with respect to total active polymers. Integrating Equation (2) after the substitution of Equation (1), we obtain the concentration of $[P_T]$ at any time t:

$$[P_T] = \frac{k_c[Co]_i}{k_c - k_t}\left(e^{-k_t t} - e^{-k_c t}\right) \qquad (3)$$

The rate equation for the monomer is then given by

$$-\frac{d[M]}{dt} = k_p[M]\,\frac{k_c[Co]_i}{k_c - k_t}\left(e^{-k_t t} - e^{-k_c t}\right) \qquad (4)$$

where k_p is the rate constant for propagation. After integration, we have

$$\ln\frac{[Mo]}{[M]} = \frac{k_p k_c [Co]_i}{k_c - k_t}\left[\frac{1}{k_t}\left(1 - e^{-k_t t}\right) - \frac{1}{k_c}\left(1 - e^{-k_c t}\right)\right] \qquad (5)$$

Equation (5) was used to fit the experimental conversion data of each polymerization run, and the goodness of the fitting was shown in Figure 2, where the solid lines represent Equation (5) and the points are the experimental data. It is quite obvious that Equation (5) represents the data well.

Attempts have been made to correlate the data by assuming either that the formation of active centers is instantaneous or that steady state approximation with respect to active polymers are shown to be the case for many Ziegler types of polymerizations. It was found, however, that at high conversion region the present model gives about the same fit as that assuming steady state or instantaneous activation approximation, but the present model shows a definite improvement over the region of initial stage of polymerization. Both the steady state model and the instantaneous activation model fail to take into account the induction period showing in some of the experiments. The initiation rate constant k_c obtained has a mean value of 8.88×10^{-3} s^{-1}, with a standard deviation of 3.81×10^{-3}. There is no doubt that water plays an important role in the initiation step, but the exact nature of its role is still unknown. Racanelli and Pori (1970) have shown that one of the functions of water is that of producing in situ aloxanes which have been shown to be active to the polymerization. They agree, however, that water could also have other functions yet to be clarified.

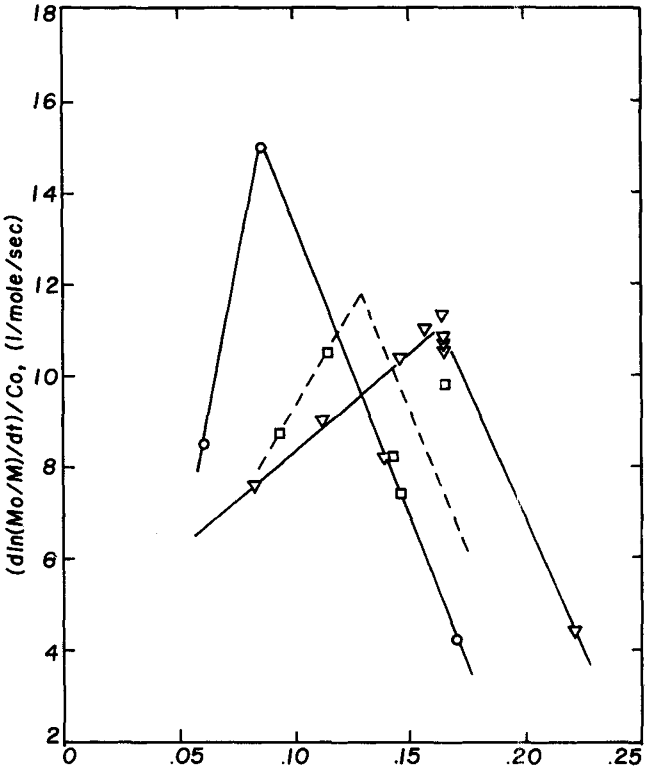

Fig. 4. Initial polymerization rate per mole of cobalt catalyst vs. $[H_2O]/[Al]$ ratio at [Al] concentrations of ○—24.0, □—15.0, and ▽—8.0 mmole/l.

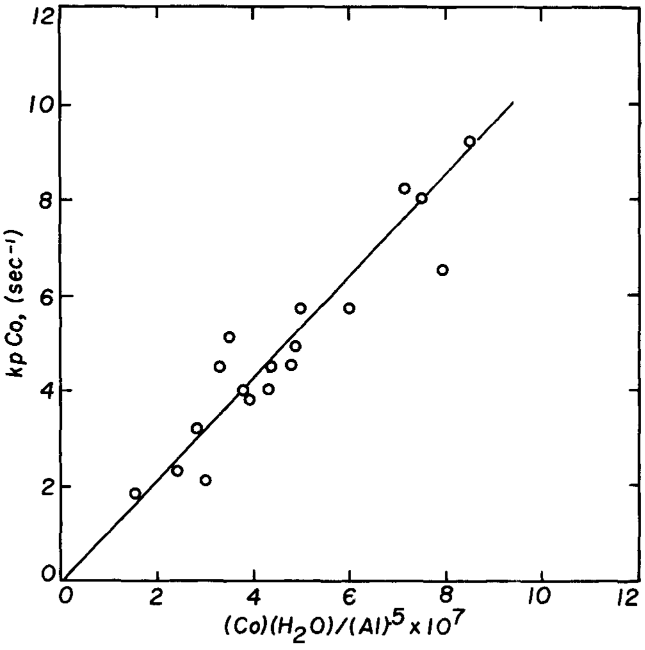

Fig. 5. Correlation of propagation rate constant.

It should be pointed out here that the k_c value obtained was from fitting the experimental data to Equation (5). The initiation reaction may be considered as a two-step process: the formation of complexes and the formation of active polymers; thus the k_c value obtained here represents the overall rate constant of the whole initiation process.

The propagation rate constant k_p was found to be correlated with both the concentrations of aluminum alkyl and water as expected. As was discussed previously, the rate

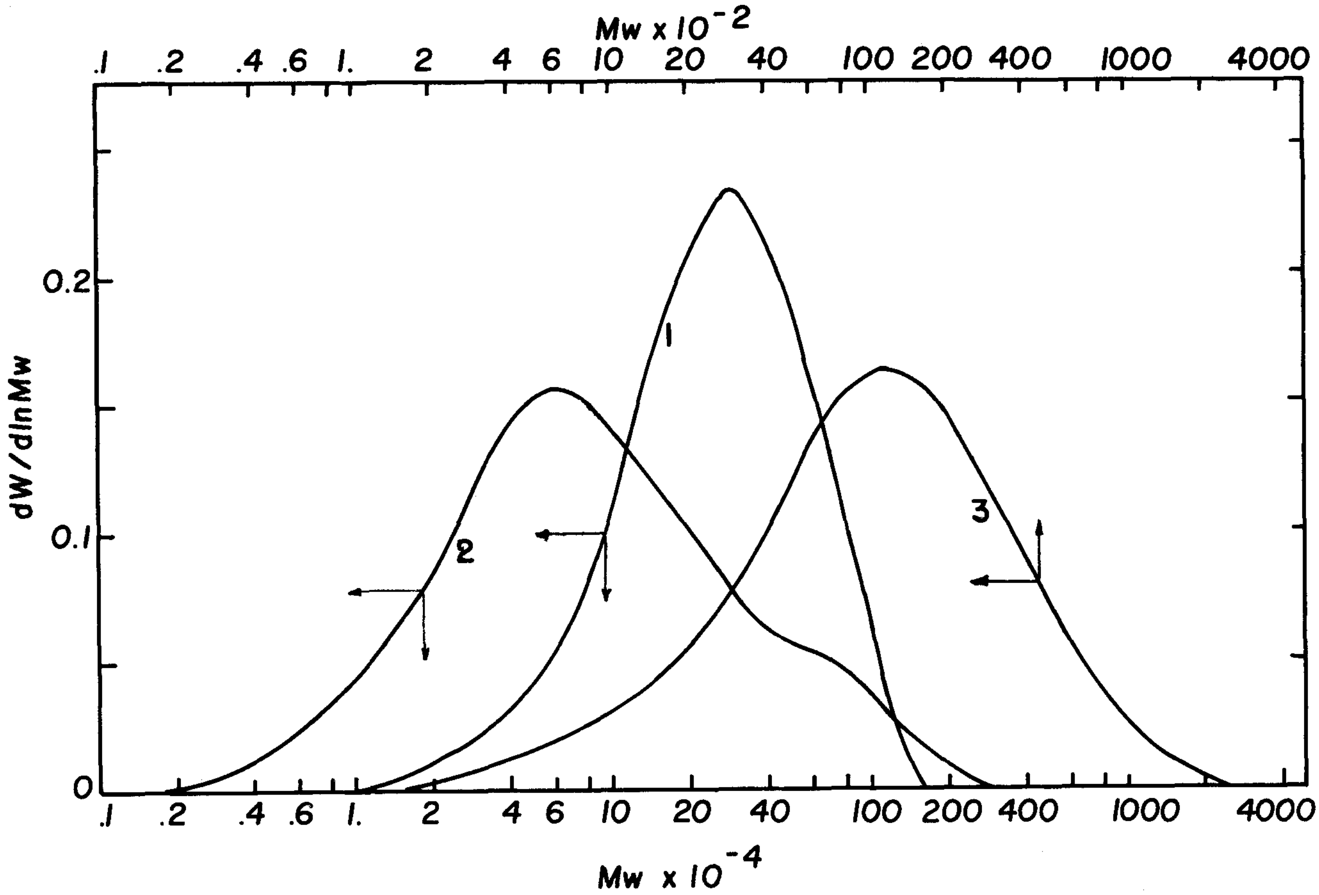

Fig. 6. Differential molecular weight distribution of polybutadiene. Curve 1: [Co]—3.2×10^{-5} mole/l, [Al]—14.5×10^{-3} mole/l, [H_2O]—2.1×10^{-3} mole/l; curve 2: [Co]—3.0×10^{-5} mole/l, [Al]—24.7×10^{-3} mole/l, [H_2O]—1.5×10^{-3} mole/l; curve 3: [Co]—3.1×10^{-5} mole/l, [Al]—24.0×10^{-3} mole/l, [H_2O]—4.1×10^{-3} mole/l.

of polymerization is related to the concentrations of [Al] and [H_2O] in a complicated way; it shows a sharp maximum as the polymerization rates are plotted against [H_2O]/[Al], and the location of the maximum is related to the concentration of [Al]. A simple correlation which would adequately cover the full range of [H_2O]/[Al] is difficult to obtain, but if we exclude the data for those experiments which yield the negative slopes on the plot of the rates of polymerization against [H_2O]/[Al] (Figure 4), k_p was found to be linearly related with [H_2O]/[Al]$^{1/2}$ as shown in Figure 5. The term [H_2O]/[Al]$^{1/2}$ can be rewritten in the form of ([H_2O]/[Al])[Al]$^{1/2}$, which indicates that at a given ratio of [H_2O]/[Al], the rate of polymerization is proportional to the square root of aluminum alkyl concentration. This relationship agrees with the results obtained by Shieh and Shen (1965*b*), although they did not consider the effect of [H_2O]/[Al] ratio. Beyond the maximum rates the data are so scattered that it is difficult to draw a sensible conclusion.

The termination reaction rate constants obtained from different polymerization conditions remain fairly constant. The average value over twenty-two experimental runs is $3.29 \pm 0.94 \times 10^{-4}$ s^{-1}, which is one order of magnitude less than the rate constant of active center formation. Even taking the uncertainties associated with k_c into consideration, one can still conclude that the polymerization reaction is far from steady state.

The termination rate constants determined from the data fittings of individual experiment show no sign of correlation with the polymerization system variables. This in a way is expected, because a pseudo first-order deactivation step was assumed, whereas in reality the termination step probably involves a complicated combination of different mechanisms due to the presence of traces of unknown impurities.

Molecular Weight Distribution

A typical MWD of polybutadiene obtained in this study by using a batch reactor after the correction for GPC instrumental spreading was presented in Figure 6. Under normal conditions, the molecular weights of polymers are distributed over a range of 10^3 to 10^7 as represented by curve 1. The aluminum concentration has no appreciable effect on MWD with the exception of extremely high concentration of aluminum alkyl; for example, increasing the concentration from 14.5 to 24.7 mmole/l results not only in the decrease of the average molecular weight, but also in the broadening of product distribution as shown by curve 2. Curve 2 also shows a second peak in the high molecular weight end, and a similar distribution has been observed in many other experimental runs. Its implication will be discussed later.

Curve 3 in Figure 6 represents the case where the water content is doubled over the experiments represented by curve 1 at high aluminum alkyl concentration. The compounded effects of high levels of aluminum and water drop the average molecular weight by one magnitude order and also show a long tailing at the low molecular weight end. Molecular weight as low as a few hundreds was obtained.

In Figure 7 the number average weight and the dispersion index (DI), *Mw/Mn*, were plotted against conversion for the experimental run under the conditions specified. It is interesting to note that at the early stage of polymerization, the molecular weight reaches to a high peak followed by a sharp drop and then essentially approaches a constant value. The data shown in the graph represent the polymerization with water content of 1.4 mmole/l. As the quantity of water increases to 2.1 mmole/l with same aluminum level, similar variation in *Mn* during the course of polymerization was also observed (Figure 8); however, the

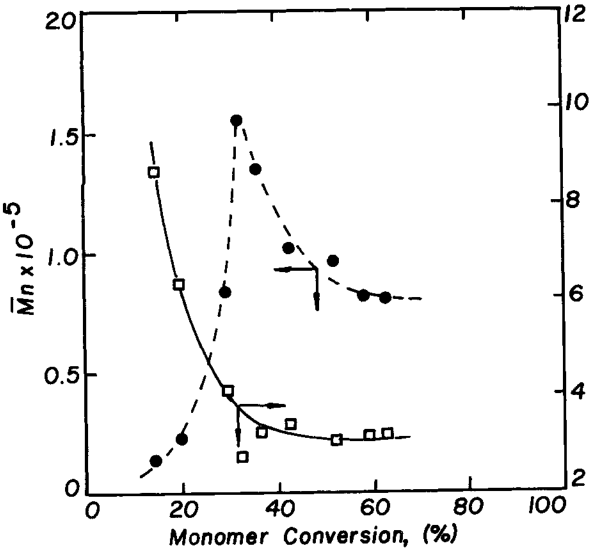

Fig. 7. Number average molecular weight and dispersion index as a function of monomer conversion. [Co] = 3.42×10^{-5} mole/l, [Al] = 15.0×10^{-3} mole/l, [H_2O] = 1.4×10^{-3} mole/l.

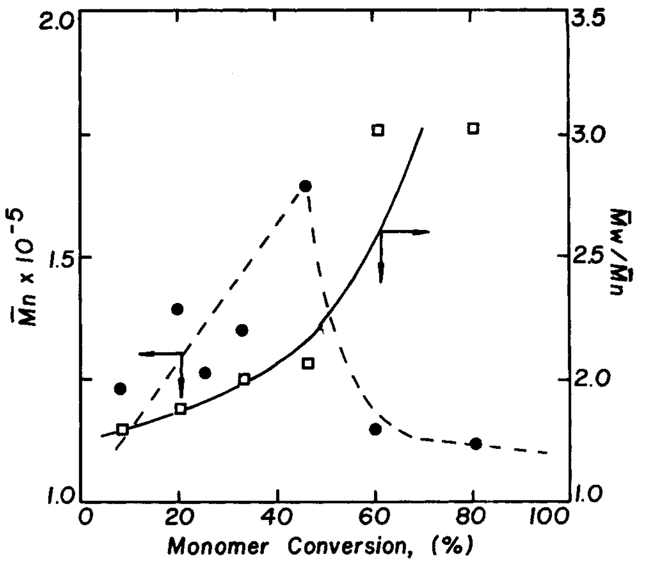

Fig. 8. Number average molecular weight and dispersion index as a function of monomer conversion. [Co] = 3.2×10^{-5} mole/l, [Al] = 14.5×10^{-3} mole/l, [H_2O] = 2.1×10^{-3} mole/l.

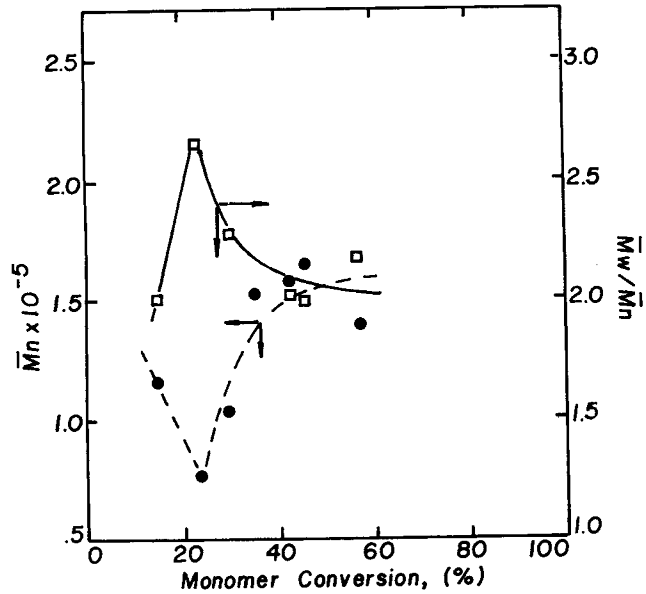

Fig. 9. Number average molecular weight and dispersion index as a function of monomer conversion. [Co] = 2.0×10^{-5} mole/l, [Al] = 8.3×10^{-3} mole/l, [H_2O] = 0.68×10^{-3} mole/l.

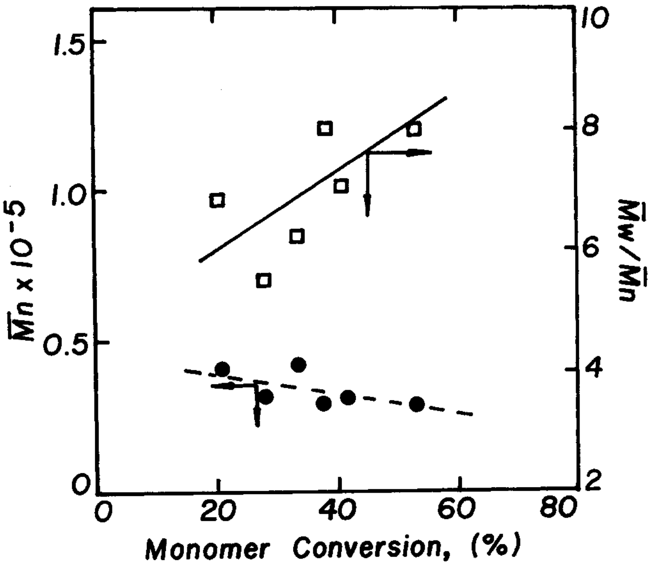

Fig. 10. Number average molecular weight and dispersion index as a function of monomer conversion. [Co] = 3.0×10^{-5} mole/l, [Al] = 24.0×10^{-3} mole/l, [H_2O] = 4.1×10^{-3} mole/l.

DI increases monotonically, whereas in the previous case the DI of the polymer had a high value at the beginning followed by a rapid decrease to a constant value of about 3.0.

At very low water content as shown in Figure 9, the curve starts with high *Mn* and then decreases as usual, but it rises again to high molecular weight in the later stage of the polymerization. The distribution, on the other hand, begins with a quick increase to relatively high dispersion, reaches to its maximum corresponding to minimum *Mn*, and then drops to about 1.5 DI. Within the range of 0.7 to 2.1 mmole/l, the effect of water on the overall degree of polymerization of final products is small. However, as the water content was raised to 4.1 mmole/l, the molecular weight of the final products dropped drastically and the polymer showed a very broad distribution; an average of 5.0 of DI was obtained.

The molecular weight jump at the beginning of the polymerization in those experiments where the concentration of water and Et_2AlCl are relatively low is a clear sign of the absence of chain transfer reaction at this period of polymerization. It is then reasonable to say that with limited quantities of aluminum and water in the system, both compounds do not involve directly in chain transfer reaction. However, that the molecular weight drops after a certain period of time certainly indicates the increasing importance of chain transfer reaction as polymerization proceeds. This can be explained that the transfer reaction is most likely caused by the formation of secondary products between water and Et_2AlCl. The main products from the reaction of water and Et_2AlCl are ethane, ethylene, hydrogen, etc.; all of them are known to be effective chain transfer agents, hydrogen in particular. Also to be noted is the fact that the molecular weights of the polymer in the low water experiments recover at high conversion after a drastic drop from their peaks at the early stage of polymerization. The drop of molecular weight is caused by the transfer reaction to the above-mentioned compounds, but the concentrations of those compounds are quickly depleted and the chain transfer reaction slows down. Therefore, the molecular weight of the products increases again at high conversion.

TABLE 3. CONFIGURATIONAL COMPOSITION OF POLYBUTADIENE POLYMERIZATION CONDITION: [Co] = 4×10^{-2} MMOLE/L, [AL] = 8.3 MMOLE/L, [H_2O] = 1.4 MMOLE/L AT 25°C

Percent conversion	Trans (%)	Vinyl (%)	Cis (%)
10.6	3.89	1.74	94.37
19.3	4.53	2.01	93.46
31.5	4.96	1.97	93.07
40.4	3.18	2.09	94.73
50.5	1.60	1.17	97.23
58.6	5.52	2.85	91.63
65.1	4.95	2.43	92.62
76.8	3.54	2.24	94.23
84.6	3.45	1.98	94.57

In the presence of excess amounts of water and aluminum alkyl, the polymerization path could be totally different as shown in Figure 10. When water content was increased to 4.1 mmole/l, the polymer products became highly dispersed; DI exceeded 5.0. It also resulted in a very low average molecular weight. The destruction of active centers by the water is clearly evident.

Increasing Et_2AlCl concentration only has a minor effect on average molecular weight which causes a slight decrease in average values. The significance, however, lies in the high values of dispersion index. With cobalt and water concentrations at 3×10^{-2} and 1.5 mmole/l, respectively, the [Al] concentration at 24.7 mmole/l increases the DI to as high as 8.0, and no high peak in molecular weight at the beginning was observed. With the same cobalt and water contents, the concentration of secondary products formed from the reaction between water and Et_2AlCl is expected to be the same. Therefore, the broadening effect on distribution can only be attributed to the chain transfer reaction to the free aluminum alkyl itself. That aluminum alkyl acts as a chain transfer agent has been observed in the polymerization system of similar nature (Loo and Hsu, 1974).

Even though the average molecular weights at the early stage of the polymerization are high, the distribution of molecular weight is broader than that of the products sampled at higher conversion. This provides the additional evidence to substantiate our early conclusion that the initial process is slow as compared to the rate of propagation. Before the molecular weight reaches to the highest point, the occurrence of the chain transfer reaction is highly unlikely; the broad distribution can only be explained by the slow formation of active centers. Furthermore, without the use of excess amounts of water, it has been found that the initiation reaction is proportional to the concentration of water. Thus, we will expect to observe low DI of the initial products from those experiments which use relatively high water concentration. Figure 8 shows that the DI increases monotonically as compared to Figure 7, where DI decreases right from the beginning. The increase in DI is certainly due to the acceleration of chain transfer reaction resulting from high water concentration. It should be pointed out again that once the water content exceeds a certain level, the excess water will destroy or suppress the formation of active complexes.

Keeping the concentrations of aluminum and water constant and examining the relationship between the number average mole weight and [Co], we found than *Mn* is linearly related to the square root of [Co] for certain experiments, which agrees with the results of Zgonnik et al. (1962, 1965). However, we do not share the view that the termination is a combination step. Some of the reasons have been discussed in the previous section. Our disbelief in their conclusion is further supported by the results of MWD study. The distribution curves of all of our samples show a long tail on the short chain end. If the combination step is predominant, such long tailing in distribution should not be observed. The low molecular species and the broad distribution can only be explained by the significant extent of chain transfer reaction and the destruction of active complexes by decomposition. However, we do not reject completely the possibility of such termination reaction. In our opinion termination by combination plays only a secondary role in the termination process. The second peak shown in Figure 6 on the higher molecular weight region is believed to be the result of this termination reaction. Even for those showing no second peak, the inflexion point on the high molecular weight side always occurs near the end of the distribution curve, and in some cases that part of the distribution curves behaves almost like a straight line, a clear sign of high proportion of long chain molecules.

Microstructure

The compositions of the microstructure of the polymer samples at different stages of polymerization for a typical experiment were presented in Table 3. It is quite obvious that the composition remains essentially constant during the course of polymerization to an average cis content of 94%. The configuration is not affected by the conditions of the polymerization with respect to catalyst composition. Solvent also has little effect on total cis content. Toluene causes a substantial decrease in the rate of polymerization, but the microstructure remains unchanged. For all experimental runs the average composition of the polymers contains 2.53 ± 1.18% trans, 1.50 ± 0.42% vinyl, and 95.96 ± 1.53% cis.

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Solubilities of Ethylene and Other Organic Solutes in Liquid, Low-Density Polyethylene in the Region 124° to 300°C

Gas-liquid chromatography was used to measure the solubilities of ethylene, *n*-butane, vinyl acetate, *n*-hexane, benzene, toluene, and *n*-octane in three different samples of liquid, low-density polyethylene. Solubilities in the different samples are similar. A correlation is presented for estimation of solubilities of nonpolar solutes in liquid polyethylene.

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SCOPE

This year, as last year, worldwide sales of polyethylene are expected to reach several billion dollars. Most polyethylene is produced by the high-pressure process. Since ethylene is the starting material, and since conversion per pass in the reactor is only about 20%, each high-pressure polyethylene facility must include one or more separation stages where unreacted ethylene is removed from the product polyethylene. Low molecular-weight products and chain-transfer agents are also removed from the polyethylene in these separators. Rational equipment design requires equilibrium solubilities of these solutes in liquid polyethylene.

In this work, gas-liquid chromatography has been used to measure solubilities of seven solutes in liquid polyethylene in the range 124° to 300°C. The chromatographic technique has been applied to sparingly soluble components, in particular ethylene, which appear in the high-pressure polyethylene process. Special experimental precautions must be observed to obtain reliable solubilities of sparingly soluble solutes in polymers.

CONCLUSIONS AND SIGNIFICANCE

Solubility data have been obtained for ethylene, *n*-butane, vinyl acetate, *n*-hexane, benzene, toluene, and *n*-octane in liquid, low-density polyethylene between 124° and 300°C. These data can be used to calculate equilibrium compositions for solute-polyethylene mixtures at moderate pressure (typically to 25 atm) as encountered in separation operations in polyethylene production. Solubility data in three low-density polyethylenes are only slightly different. Agreement with data reported by other researchers is good. It appears that the solubility of solutes in liquid polyethylene is nearly independent of polymer molecular-weight distribution and degree of long-chain branching.

New and previously published solubility data are correlated with solute critical temperatures and acentric factors. The resulting correlation gives good estimates of solubilities for nonpolar solutes in liquid polyethylene.

To measure low solubilities using gas-liquid chromatography, it is important to determine accurately the time the solute spends in the gas phase. Therefore, it is necessary to measure the retention-time difference between the solute and an "inert" reference gas (nitrogen). Since nitrogen is not truly inert, corrections for finite nitrogen solubility are not negligible for those solutes (for example, ethylene) whose solubilities are small.

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