

# The Reaction Engineering of the Anionic Polymerization of Isoprene

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## SYNOPSIS

The anionic solution polymerization of isoprene with *n*-butyllithium (*n*-BuLi) initiator and tetramethylethylenediamine (TMEDA) modifier or *n*-butyllithium (*n*-BuLi) initiator and tripiperidinophosphine (TPPO) modifier was studied and kinetic and reactor models are proposed for both systems. Reactor conversion, molecular weight distribution, and polymer glass transition temperature had been calculated from the model and compared favorably to actual data for various combinations of reactor system and operating conditions. Simulations of the models can be used to design reactor systems, and predict polymer properties of a large-scale operation from results of small-scale batch reactor runs. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The interest in anionic polymerization has grown tremendously in recent years because it can be employed to tailor-make polymers of controlled architecture. This is especially important in the tire and rubber industry in which elastomers of controlled molecular weight, molecular weight distribution, and microstructure are required to meet today's tire requirement for traction, treadwear, and rolling resistance.

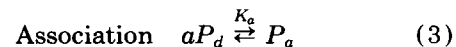
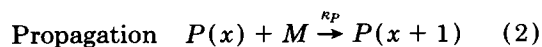
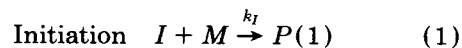
The need to control so many variables presents problems of reproducibility and scale-up to chemist and process alike. This challenge can be met by the fundamental models, including the kinetic and reactor models, of the polymerization system. In this work, we will focus on the polymerizations of a well-known elastomer, polyisoprene, and on the development of fundamental models of them.

It is well known that polymerization of isoprene with *n*-BuLi initiator in hexane solvent will produce

polyisoprene with high 1,4-polyisoprene or low 3,4-polyisoprene content (polymer glass transition temperature is about  $-60$  to  $-65^{\circ}\text{C}$ ). In this study, we examined the effect of adding various modifiers that allow us to make polyisoprenes with varied microstructures or glass transition temperatures. Specifically, the detailed results of two of the modifiers, tetramethylethylenediamine (TMEDA) and tripiperidinophosphine (TPPO), are presented in this paper.

## DEVELOPMENT OF KINETIC MODEL

It is assumed that there is no termination or chain-transfer reaction involved and the mechanism can be described by (e.g., see Ref. 1):



where  $x = 2, 3, \dots$ . In the above equations,  $M$  is the monomer;  $I$ , the initiator (*n*-BuLi);  $P(x)$ , the

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unassociated polymer having chain length  $x$ ;  $P_d$  and  $P_a$ , the dissociated and associated polymer; and  $a$ , the degree of association.  $k_i$  and  $k_p$  are the rate constants of the initiation and propagation reactions, respectively, while  $K_a$  is the equilibrium constant of the association reaction.

From eq. (3), the concentration of dissociated polymer can be related to concentration of total polymer by

$$[P] = [P_d] + a[P_a] = [P_d] + aK_a[P_d]^a \quad (4)$$

For a highly associated polymer, we have

$$[P_d] = (aK_a)^{-1/a}[P]^{1/a} \quad (5)$$

In the above equations,  $[P_d]$ ,  $[P_a]$ , and  $[P]$  are the concentration of dissociated polymer, the concentration of associated polymer, and the concentration of total polymer, respectively. It is assumed that the associated polymer is dormant for propagation and is in equilibrium with the active dissociated polymer. It is also assumed that the ratio of dissociated polymer to total polymer is constant at each chain length, i.e.:

$$h = \frac{[P_{1d}]}{[P_1]} = \frac{[P_{2d}]}{[P_2]} = \dots = \frac{[P_{xd}]}{[P_x]} \quad (6)$$

Summing this relationship and combining with eq. (5) yields

$$h = \frac{[P_d]}{[P]} = \frac{(aK_a)^{-1/a}[P]^{1/a}}{[P]} \quad (7)$$

To derive equations that can be used for both the unmodified system and the modified system, a constant  $K_S$  is defined as

$$\begin{aligned} K_S &= k_{pu}h && \text{unmodified system} \\ &= k_{pm} && \text{fully modified} \\ &= f k_{pm} + (1-f)k_{pu}h && \text{partially modified} \end{aligned} \quad (8)$$

In the above equation,  $k_{pu}$  and  $k_{pm}$  are the rate constants of the unmodified and fully modified systems, respectively. An unmodified system consists of both associated and dissociated polymers and its propagation kinetic expression has the term  $h$  to convert the total polymer concentration to the dissociated polymer concentration. A fully modified system is defined as the one in which all living polymers are complexed with the modifier and exist in the dissociated form ( $h = 1$ ). A partially modified

system is assumed to contain a mixture of modified and unmodified living polymers; the fraction of the polymer that forms a complex with the modifier is  $f$ . It should be noted here that  $K_S[P]$  is the observed first-order rate constant for monomer conversion with the above definitions regardless of modification levels.

The rate of initiation, propagation reactions, and monomer consumption (or rate of polymerization) based on the proposed mechanism and long-chain approximation are

$$-d[I]/dt = k_i[I][M] \quad (9)$$

$$d[P_1]/dt = k_i[I][M] - K_S[P_1][M] \quad (10)$$

$$d[P_x]/dt = K_S[P_{x-1}][M] - K_S[P_x][M] \quad (11)$$

$$-d[M]/dt = K_S[P][M] \quad (12)$$

The initial conditions are

$$[I] = [I]_0$$

$$[P_x] = 0 \quad x = 1, 2, 3, \dots$$

$$[M] = [M]_0 \quad (13)$$

Equations (9)–(13) are the governing equations of the general kinetic model. If the initiation reaction is fast, the equations can be simplified to

$$d[P_1]/dt = -K_S[P_1][M] \quad (14)$$

$$d[P_x]/dt = K_S[P_{x-1}][M] - K_S[P_x][M] \quad (15)$$

$$-d[M]/dt = K_S[I]_0[M] \quad (16)$$

with initial conditions

$$[P_1] = [I]_0$$

$$[P_x] = 0 \quad x = 2, 3, 4, \dots$$

$$[M] = [M]_0 \quad (17)$$

## DEVELOPMENT OF REACTOR MODELS

Reactor models can be developed easily from the reaction kinetics and the material balance of the particular reactor system. Detailed anionic polymerization models, including the molecular weight distribution, for batch/plug flow and CSTR reactor systems can be found in the literature (e.g., see Ref. 1) and will not be included here.

## EXPERIMENTAL

### Material Preparation

Isoprene monomer was purified by distillation and then mixed with hexane to prepare a premix of the desired concentration. The premix was purified by passing it through a drying column packed with 3Å molecular sieve and silica gel.

Concentrated *n*-BuLi (1.6M), TMEDA (99+%), and TPPO (98%) were obtained from the Reilly Chemical Company. Dilution of the concentrated solutions, as required for proper metering, was carried out using high-performance liquid chromatography (HPLC)-quality hexane sparged with nitrogen and stored over 3Å molecular sieve. The diluted solutions were stored in sealed bottles under a nitrogen blanket and kept refrigerated until used.

Rosin acid and methanol were added as shortstop (SS) and 2,6-dibutyl-*para*-cresol was added as antioxidant at 1 part per 100 rubber (1 phr) each to the live cement at the end of each run.

### Procedure

Polymerizations were carried out batchwise in 1 gallon jacketed stirred reactors. The reactors were run in the batch mode to obtain kinetic data or in the continuous mode to confirm the reactor model. Prior to each run, the reactor was washed with polymerization-grade hexane and then pickled with a solution consisting of 10 mL of 1.6M of *n*-BuLi and 2.5 kg of hexane. The reactor was then evacuated and 2.0–2.5 kg of the premix was charged. A sample was taken from a dip-leg and analyzed for monomer concentration by gas chromatography. Then, the required amount of modifier was injected into the reactor and the reactor was brought to the desired temperature. A small amount of dilute *n*-BuLi was added into the reactor to scavenge the impurity in the reactor. The scavenging procedure was repeated until polymerization was detected. Then, the required amount of *n*-BuLi was injected to start the polymerization.

During the course of polymerization, small samples of cement were withdrawn and coagulated in sealed vials containing ethyl alcohol. The remaining liquor was analyzed for residual monomer concentration to obtain the monomer conversion. The polymer cement obtained was oven-dried and the samples were characterized by various analyses including glass transition temperature ( $T_g$ ) by DSC, molecular weight distribution by GPC, and microstructures by NMR and FTIR.

### Design of Experiments

The operating conditions of the designed experiment are shown in Table I. Selected conversion data are shown in Figures 1–3. The major design variables are the reaction temperature and modifier ratio. The former is varied to obtain the activation energy of the rate constant, while the later is varied to examine the effect of modifier ratio on the kinetics and the glass transition temperature of polymers produced. Because unmodified isoprene polymerization has been extensively studied (e.g., see Refs. 2–4), only a few unmodified runs were conducted to verify its kinetics. It should be pointed out here, unlike for the polymerization of butadiene,<sup>1</sup> there is no controversy about the kinetic order reported by various researchers; it is 1/4 order in active polymer concentration. This greatly reduces the number of unmodified runs required.

In addition to the batch polymerization runs, a few continuous polymerizations were carried out with 1 gallon CSTR reactors arranged in a series. The data obtained including the conversion and polymer  $T_g$  were used to verify the model developed.

## RESULTS AND DISCUSSION

### Effect of Modifier Ratio on Kinetics

The modifier ratio,  $MR$ , is defined as either  $[TPPO]/[n\text{-BuLi}]$  or  $[TMEDA]/[n\text{-BuLi}]$  depending on the type of modifier used. The effects of modifier ratio on the regressed first-order rate constant  $K_S[I]_0$  and polymer  $T_g$  are shown in Figure 4. It can be seen that, for TPPO modifier, both the polymer  $T_g$  and the rate constant increase with increasing modifier ratio ( $MR$ ) and approach a maximum value when the modifier ratio is around 1.0. The results suggest that all living poly(isoprenyl lithium) is complexed with TPPO when the amount of TPPO reached the critical value ( $\sim 1.0$  modifier ratio); the reaction rate and polymer  $T_g$  were at the maximum values and changed very little afterward. Gradual increases achieved beyond this level are attributed to solvent effects of the modifier itself. Therefore, it is assumed that the polymerization is fully modified when the modifier ratio is equal to or greater than one, i.e.:

$$f(\text{TPPO}) = 1.0 \quad \text{for } MR(\text{TPPO}) \geq 1.0 \quad (18)$$

The effects of the modifier ratio,  $[TMEDA]/[n\text{-BuLi}]$ , on the regressed first-order rate constant  $K_S[I]_0$  and polymer  $T_g$  are also shown in Figure 4.

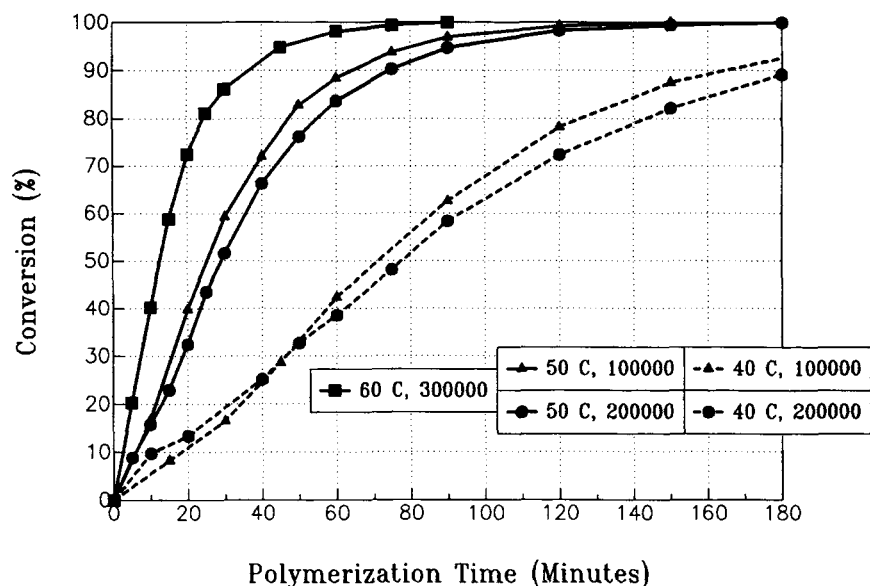
**Table I** Summary of Operating Conditions and Experimental Data

$[M]_0$ (mol/L)	$[I]_0$ (mmol/L)	$MR^a$	Temp (°C)	$M_n$ (kg/Mol)	HI <sup>a</sup>	$T_g$ (°C)
<u>Without modifier</u>						
1.827	0.6317	0.0	40	215	1.26	-62.5
1.779	1.228	0.0	50	98.6	1.35	-64.2
1.798	1.241	0.0	40	105	1.40	-62.8
1.788	0.6182	0.0	50	200	1.36	-63.5
1.589	0.3662	0.0	60	339	1.44	-63.2
<u>With TPPO modifier</u>						
1.545	0.3562	1.5	30	235	1.35	-10.9
1.565	0.3606	1.0	30	245	1.32	-13.6
1.526	0.3517	0.5	30	202	1.36	-25.9
1.536	0.3539	1.0	40	219	1.25	-15.5
1.545	0.3562	1.5	40	200	1.27	-15.2
1.545	0.3562	0.5	40	214	1.28	-27.2
1.545	0.3562	1.0	50	247	1.16	-18.2
1.526	0.3517	1.5	50	228	1.29	-17.9
1.575	0.3629	2.0	50	249	1.37	-16.4
1.594	0.3674	3.0	50	163	1.52	-15.2
1.536	0.3539	2.0	40	232	1.39	-13.5
1.507	0.3472	0.5	50	268	1.21	-27.1
1.507	0.3472	2.0	30	249	1.42	-10.8
1.516	0.3494	0.25	50	217	1.52	-59.6
1.477	0.3405	0.75	50	305	2.30	-19.1
<u>With TMEDA modifier</u>						
2.003	0.4419	1.5	40	255	1.15	-27.8
1.990	0.4516	1.5	50	260	1.08	-38.0
1.984	0.4502	5.0	40	240	1.26	-11.5
1.516	0.3439	1.0	60	242	1.36	-37.1
1.518	0.3444	1.5	60	197	1.46	-42.0
1.452	0.3296	0.75	60	293	1.11	-51.0
1.507	0.3419	0.25	60	320	1.13	-61.5
1.590	0.3560	0.5	60	306	1.15	-53.1
1.590	1.082	1.5	60	83.4	1.05	-12.9
1.572	0.5351	1.5	60	160	1.05	-21.5
1.566	0.3554	2.0	60	250	1.23	-17.6
1.583	0.3591	4.0	60	240	1.12	-12.3
1.574	0.3572	2.0	50	220	1.15	-11.0
1.603	0.3638	2.0	70	271	1.28	-27.7
1.654	0.3752	3.0	60	224	1.09	-13.2
1.568	0.3558	2.0	80	293	1.10	-34.9

<sup>a</sup>  $MR = [TPPO]/[I]_0$  or  $[TMEDA]/[I]_0$ ;  $HI = M_w/M_n$ .

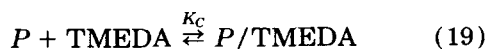
It can be seen that the TMEDA-modified polymerization is quite different from TPPO-modified polymerization. Although the polymer  $T_g$  increases with increasing modifier ratio ( $MR$ ) and approaches a maximum value for both systems, the  $T_g$  of TPPO-modified polymer reaches its maximum value at  $MR$

$\cong 1.0$ , but the  $T_g$  of TMEDA-modified polymer reaches its maximum value at a much higher  $MR$  (about 3–4 depending on the reaction temperature). In addition, the critical  $MR$  may vary with the reaction temperature (the higher the temperature, the higher the critical modifier ratio) as shown in Figure



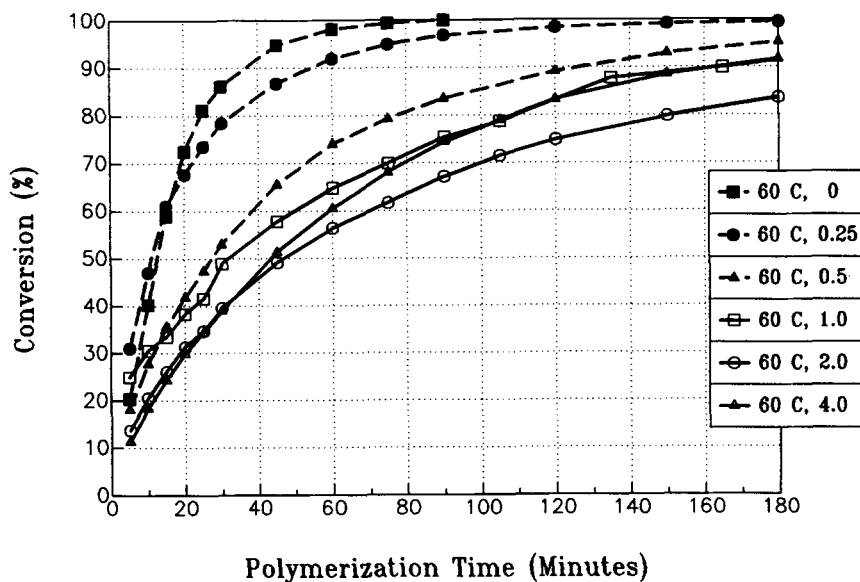
**Figure 1** Conversion data of unmodified isoprene polymerization. Parameters are temperature and target  $M_n$ .

5. This suggests that the complexing reaction is probably an equilibrium reaction as shown below:

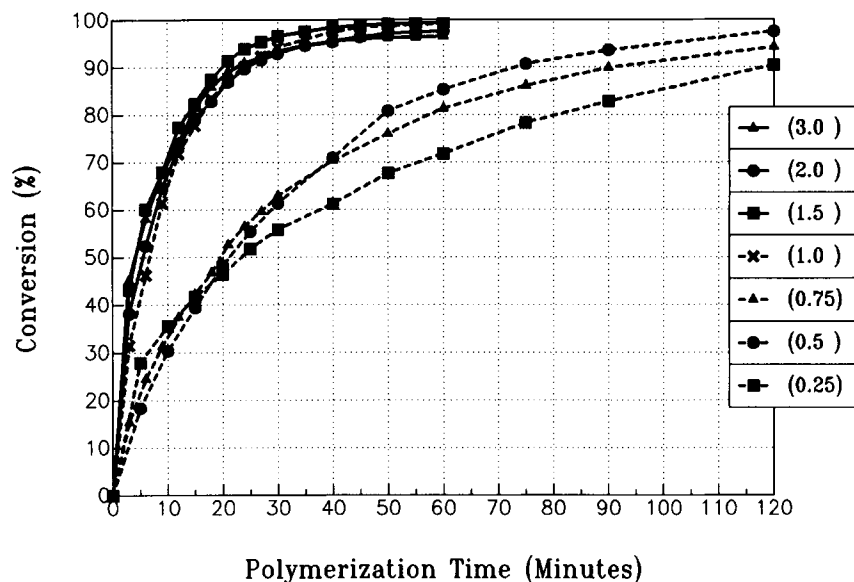


This is different from that of the TPPO-modified polymerization model in which the complexing reaction was assumed to be instantaneous and irreversible.

The major difference between the effect of the two modifiers is the rate of polymerization. As can be seen, the rate constant increases with increasing TPPO modifier ratio, but it decreases with increasing TMEDA modifier ratio. In other words, the modifier TMEDA, by being complexed with the living polymers, modifies the microstructure of the polyisoprene produced and depresses the reactivity of the living polymers at the same time. This indicates



**Figure 2** Conversion data of TMEDA-modified isoprene polymerization. Parameters are temperature and modifier ratio.



**Figure 3** Conversion data of TPPO-modified isoprene polymerization. Temperature = 50 C; target  $M_n = 300,000$ . Parameter is modifier ratio.

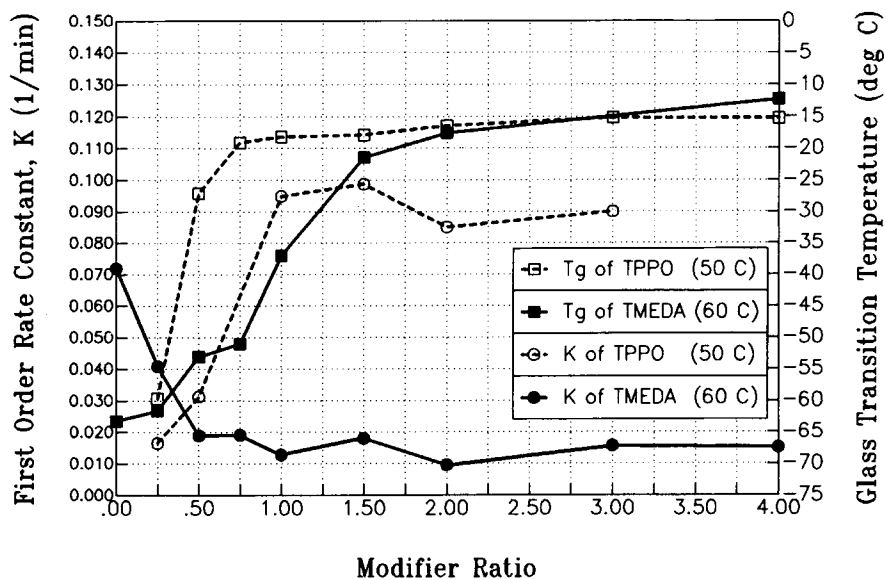
that the reactivity of the complexed polymer is lower than that of the uncomplexed (or unmodified) living polymer. This is consistent with the published results by Dumas et al.<sup>5</sup> and Van Beylen et al.<sup>6</sup> At this time, we are unable to quantify the equilibrium constant  $K_C$ , which would allow us to relate the variable  $f(\text{TMEDA})$  with the modifier ratio and reaction temperature. However, we would assume that the

polymerization is fully modified when the modifier ratio is equal to or greater than 4, i.e.:

$$f(\text{TMEDA}) = 1.0 \text{ for } MR(\text{TMEDA}) \geq 4.0 \quad (20)$$

#### Effect of Temperature and Modifier on Polymer $T_g$

For unmodified polymerization, the effect of reaction temperature on the polymer  $T_g$  is negligible. The



**Figure 4** Effects of modifier ratio on rate constant and polymer  $T_g$ ; with TMEDA or TPPO modifier.

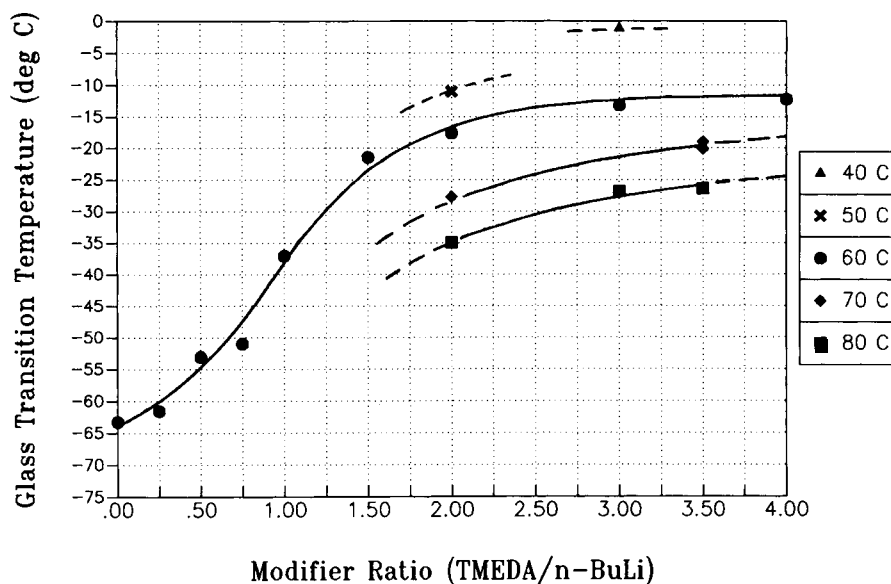


Figure 5 Effects of modifier ratio and temperature on polymer  $T_g$ ; with TMEDA modifier.

polymer  $T_g$  is essentially constant,  $-63 \pm 2^\circ\text{C}$ , over a wide range of operating temperatures ( $30\text{--}70^\circ\text{C}$ ). Thus, a constant  $T_g$  will be used for the unmodified polymer in the present model:

$$T_{g_u} = -63.0 \quad (21)$$

For fully modified polymerization, the polymer  $T_g$  is a function of the reaction temperature, as shown in Figure 6. The data were regressed and the

result for TPPO-modified polymerization is shown below:

$$T_{g_m} = -22.88 + 33.05e^{-0.03376T_c} \quad (22)$$

where  $T_{g_m}$  is the glass transition temperature of fully modified polymer in  $^\circ\text{C}$  and  $T_c$  is the reaction temperature in  $^\circ\text{C}$ .

For TMEDA-modified polymerization, it can be seen that the polymer  $T_g$  decreases almost linearly

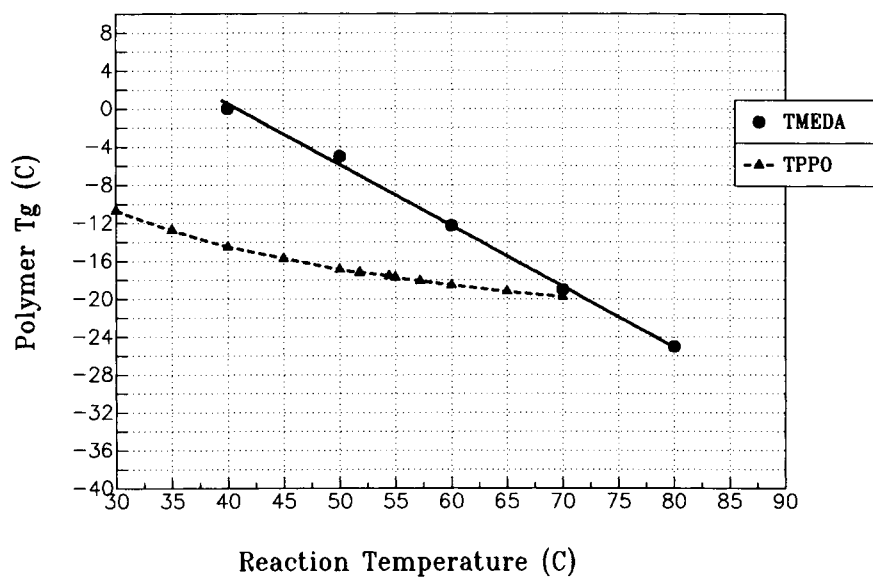


Figure 6 Effect of reaction temperature on polymer  $T_g$ ; fully modified by TMEDA or TPPO.

with increasing reaction temperature within the range of 40–80°C. The data were regressed and the result is

$$T_{gm} = 26.148 - 0.64Tc \quad (23)$$

It can be seen from Figure 6 that the  $T_g$  for the TMEDA-modified polymer is much more sensitive to temperature variations (0.64°C  $T_g$ /1°C reaction temperature) than that of the TPPO-modified polymer (~0.2°C  $T_g$ /1°C reaction temperature). It can also be seen that TMEDA is a stronger modifier at low temperature, but becomes weaker at temperatures above ~70°C.

### Kinetic Data Regression

Each batch kinetic run was conducted under isothermal conditions and with constant initiator concentration. If the initiation is fast and there is no termination, the concentration of living polymer is constant,  $[P] = [I]_0$ , and, thus, eq. (16) can be used with the conversion data to regress the constant  $K_S[I]_0$ .

It should be pointed out here that the initiation is slow for the unmodified polymerization and substantial termination is involved in the modified polymerization. However, these reactions can be decoupled and the propagation rate constant can be regressed from the conversion data.

For unmodified polymerizations:

$$\begin{aligned} K_S[I]_0 &= k_{P_u}h[I]_0 \\ &= k_{P_u}(aK_a)^{-1/a}[I]_0^{1/a} \\ &= k_{u_0}e^{-E_u/(RT)}[I]_0^{1/a} \end{aligned} \quad (24)$$

For modified polymerizations:

$$\begin{aligned} K_S[I]_0 &= k_{P_m}[I]_0 \\ &= k_{m_0}e^{-E_m/(RT)}[I]_0 \end{aligned} \quad (25)$$

where  $k_{u_0}$  (in L/mol-min) and  $E_u$  (in cal/mol) are the frequency factor and activation energy of the combined unmodified propagation rate constant  $k_{P_u}$  and the association equilibrium constant  $K_a$ ;  $k_{m_0}$  (in L/mol-min) and  $E_m$  (in cal/mol) are, respectively, the frequency factor and activation energy of the modified propagation rate constant  $k_{P_m}$ ;  $R$  is the gas law constant in cal/(mol K) ( $R = 1.987$ );  $T$  is the reacting temperature in K; and  $[I]_0$  is the effective concentration of *n*-BuLi in kmol/m<sup>3</sup> or mol/L.

The obtained constant  $k_p[I]_0$  can again be regressed with reaction temperature and initiator concentration; the results are summarized below:

For unmodified polymerization:

$$K_S[I]_0 = 6.253 \times 10^{10} e^{-16886/(RT)} [I]_0^{0.25} \quad (26)$$

For TPPO-modified polymerization:

$$K_S[I]_0 = 2.233 \times 10^8 e^{-8675/(RT)} [I]_0 \quad (27)$$

For TMEDA-modified polymerization:

$$K_S[I]_0 = 2.560 \times 10^8 e^{-10332/(RT)} [I]_0 \quad (28)$$

The  $R$  square values for the regressions are 0.997, 0.995, and 0.962 for the unmodified, TPPO-modified, and TMEDA-modified polymerizations, respectively.

### Partially Modified Polymerization

As was explained earlier, a partially modified polymerization system is assumed to contain a mixture of modified and unmodified living polymers with the following rate expression:

$$k_p = f k_{P_m} + (1 - f) k_{P_u}h$$

Since the weight fractions of the modified and unmodified polymers produced are

$$W_m = \frac{f k_{P_m}}{f k_{P_m} + (1 - f) k_{P_u}h} \quad (29)$$

$$W_u = \frac{(1 - f) k_{P_u}h}{f k_{P_m} + (1 - f) k_{P_u}h} \quad (30)$$

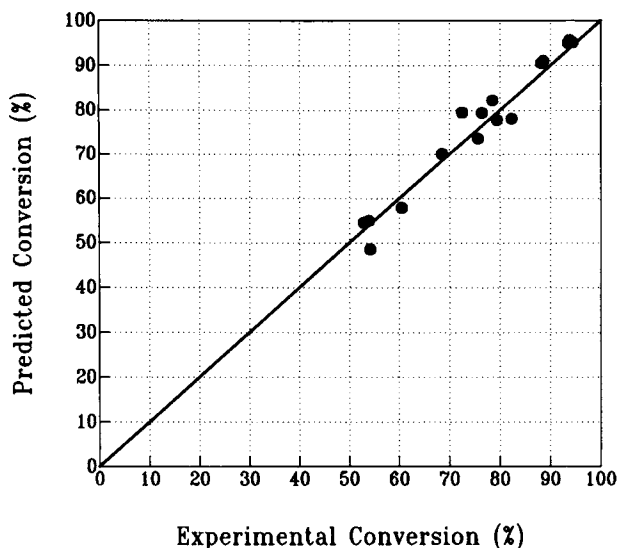
the polymer  $T_g$  can be calculated using the following equation:

$$\frac{1}{(T_g + 273)} = \frac{W_m}{(T_{gm} + 273)} + \frac{W_u}{(T_{gu} + 273)} \quad (31)$$

Therefore, the partially modified system can be fully characterized from the kinetics of fully modified and unmodified polymerizations if the effects of operating variables on the parameters,  $f$  (TPPO) and  $f$  (TMEDA), can be established.

For TPPO-modified polymerization, it has been shown that the complexing reaction is fast and irreversible; thus, the fraction of initiator,  $f$  (TPPO), that forms a complex with the modifier TPPO in-





**Figure 7** Comparison between predicted and experimental conversions.

creases linearly with  $MR$  in the partially modified region, i.e.:

$$f(\text{TPPO}) = MR \quad \text{for } 0 \leq MR < 1.0 \quad (32)$$

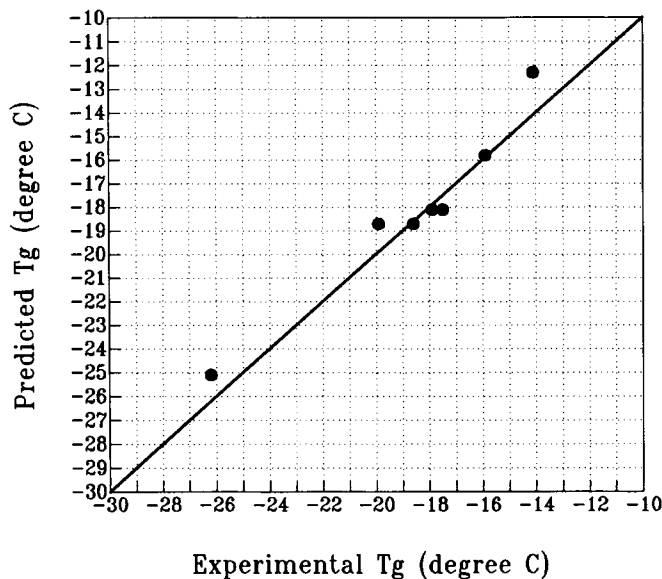
For TMEDA-modified polymerization, we are unable to quantify the partially modified region as pointed out previously; thus, empirical correlation was used as a first approximation. However, it should

be noted that both the rate of polymerization and the polymer  $T_g$  vary substantially when the modifier ratio is increased from 0 to 1.0 for TPPO and from 0 to 2.0 for TMEDA-modified polymerization. Thus, a slight change in modifier ratio within this range will drastically change both values. Thus, these regions should be avoided from the standpoint of maintaining process stability and product uniformity.

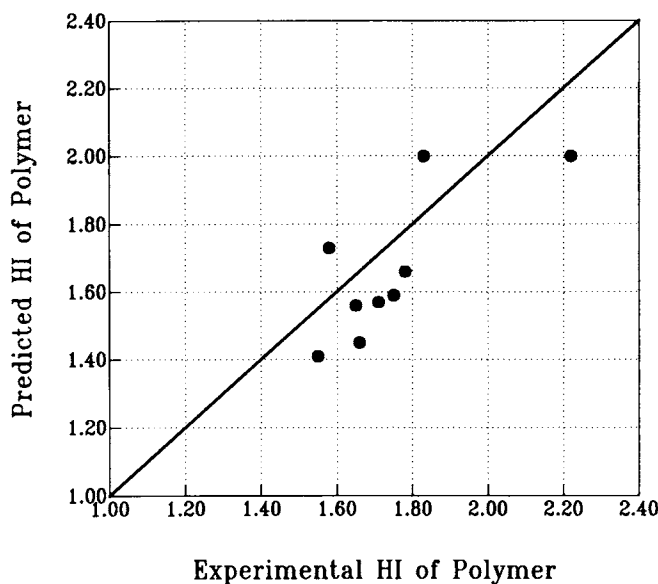
### Model Verification and Scale-up Runs

Reactor conversion, MWD, and polymer  $T_g$  of isoprene polymerizations for any reactor configurations, such as a batch/plug flow reactor system or a CSTR reactor chain, can be calculated easily by the model developed. To test the model developed, six continuous polymerization runs were carried out. In addition, one commercial-scale production run was conducted based on the conditions selected from model predictions. The reactor size ranged from 1 gallon for the bench-scale operation to several thousand gallons for the commercial scale operation, and the number of reactors employed in the reactor chain ranged from 1 to 4. The reaction temperature ranged from 55 to 80°C and the reactor residence time from 30 to 60 min per reactor.

The experimental results and model predictions are shown in Figures 7–9. For the small-scale runs, the average differences between the predicted and experimental values are 2.7% for the conversion



**Figure 8** Comparison between predicted and experimental glass transition temperature.

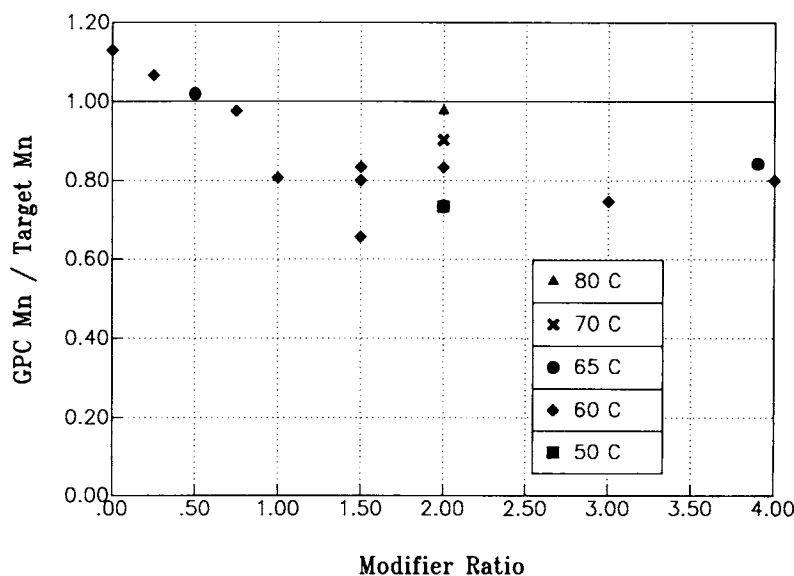


**Figure 9** Comparison between predicted and experimental  $HI$  of polymers.

and  $0.64^{\circ}\text{C}$  for the polymer  $T_g$ . For the large-scale commercial run, the average differences between the predicted and experimental values are 2.3% for the conversion and  $0.10^{\circ}\text{C}$  for the polymer  $T_g$ . From the simulation results, we can conclude that the model can be used to adequately predict reactor conversions and polymer  $T_g$ .

Before discussing the molecular weight and molecular weight distribution data, it should be pointed

out that it is very difficult to make high molecular weight polyisoprenes in the presence of TMEDA or TPPO modifier. Figure 10 shows the effect of TMEDA modifier on the molecular weight of isoprene polymers from the results of our previously designed batch kinetic study. It can be seen that the ratio of GPC  $M_n$  to target (or theoretical)  $M_n$  decreases with increasing TMEDA modifier ratio. For unmodified or low-modified ( $MR < 1.0$ ) polymer-



**Figure 10** Effect of TMEDA modifier on the molecular weight of anionic isoprene polymers.

**Table II Comparison between Experimental Data and Model Predictions**

	Conversion (%)		$M_n$		$M_w$		$HI^a$	
	Exp	Pred	Exp	Pred	Exp	Pred	Exp	Pred
RX1	52.9	54.6	214	200	393	399	1.83	2.00
RX2	76.4	79.4	270	291	463	456	1.71	1.57
RX3	88.2	90.6	288	332	478	482	1.66	1.45
RX4	93.8	95.7	272	350	424	494	1.55	1.41

<sup>a</sup>  $HI = M_w/M_n$ ;  $M_n$  and  $M_w$  in kg/mol.

ization the GPC  $M_n$  is close to the theoretical value, indicating a truly living polymerization system without termination and chain transfer reactions. For highly modified polymerization, the GPC  $M_n$  is only about 80% of the theoretical value. Similar results were also obtained for TPPO-modified isoprene polymerization. One possible explanation is that the modifier promotes either chain transfer or chain sections. As a result, the number-average molecular weight is decreased while the molecular weight distribution ( $HI$ ) is increased (see Table I). This is also confirmed from the experimental and predicted data of one of the runs, in which a three-CSTR reactor chain is used, as shown below in Table II.

It can be seen that the GPC  $M_n$  and  $M_w$  of the first reactor polymer are very close to the simulation results. After the first reactor, the difference between GPC  $M_n$  and predicted  $M_n$  became larger and larger; the ratio of GPC  $M_n$  to predicted  $M_n$  for the four-reactor polymer samples are 1.07, 0.93, 0.87, and 0.78, respectively. This data can be explained based on the assumption of chain transfer/scission. This is because the amount of monomer reacted in each reactor decreased along the reactor chain (52.9, 23.5, 11.8, and 5.6% for the four reactors), while chain transfer/scission was most likely to remain the same or even increase. Thus, the relative contribution of chain transfer/scission will increase along the reactors. Since polymer Mooney and properties will be affected by the MW and MWD, it should be part of the model. The mechanism and kinetics of possible chain transfer or scission will be investigated and incorporated into the models in future studies.

## CONCLUSIONS

With the addition of tetramethylethylenediamine (TMEDA) modifier, the glass transition temperature of the polyisoprene produced is increased, but

the rate of polymerization is depressed. With the addition of another modifier, tripiperidinophosphine (TPPO), both the polymer  $T_g$  and the polymerization rate are increased. On the other hand, TMEDA is a much stronger modifier that can be used to make polyisoprene with higher  $T_g$  at a reaction temperature lower than 70°C.

Kinetic and reactor models are proposed for both *n*-BuLi/TMEDA and *n*-BuLi/TPPO systems. Reactor conversion, molecular weight distribution, and polymer glass transition temperature have been calculated from the model and compare favorably to actual data for various combinations of reactor system and operating conditions. Simulations of the models can be used to design reactor systems and to predict polymer properties of a large-scale operation from results of small-scale batch reactor runs.

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