

## Thermal Stability of "Living" Polymer-Lithium Systems

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### Synopsis

The thermal stabilities of polybutadienyllithium, polyisoprenyllithium, and polystyryllithium solutions have been determined in hydrocarbon solvents. Kinetic analysis indicated that a complex mechanism was involved in the thermolysis of polybutadienyllithium. The thermal stability was observed to increase with increasing lithium concentration, suggesting the presence of competitive reactions in addition to the expected elimination of lithium hydride. The thermal stability of the three systems studied was consistent with their reported degrees of association: dimeric polystyryllithium was less stable than tetrameric polyisoprenyllithium or hexameric polybutadienyllithium.

### INTRODUCTION

Much kinetic data are available which elucidate the initiation and propagation reactions of anionic polymerization systems. They are described as "living" polymerizations, and the presence of a termination reaction is often neglected. These polymerizations result in the formation of narrow molecular weight distribution polymers. The preparation of polybutadiene with *n*-butyllithium is an example of this type of polymerization.

The absence of a termination reaction is a good assumption when impurities are absent and low polymerization temperatures are involved. However, some commercial polymerization processes frequently operate at much higher temperatures (65° to 120°C) than those at which kinetic data have been reported. Under such process conditions, termination does occur along with other complex reactions which significantly alter the molecular weight distribution of the polymer.<sup>1</sup>

There is also a significant amount of kinetic data describing the thermal stability of alkylolithium compounds.<sup>2,3,4</sup> The mechanism of these elimination reactions is conveniently elucidated by manometric methods, and mechanistic interpretations have been proposed. However, there are no known published accounts of the thermal stability of polymer-lithium systems. For high molecular weight polymers (10,000 to 100,000 MW) the lithium concentrations are necessarily two to four orders of magnitude

less than the concentrations used in the kinetic studies reported for alkyl-lithium compounds.

There is a need to have kinetic data describing the thermal termination of "living" polymers at lithium concentrations approaching those of commercial polymerization systems. This paper will discuss the thermal stabilities of polybutadienyllithium, polyisoprenyllithium, and polystyryllithium solutions in the absence of monomers.

## EXPERIMENTAL

Butadiene monomer (Firestone Tire & Rubber Co.) containing less than 20 ppm  $\alpha$ -acetylenes, nil 1,2-butadiene, and nil propadiene was dried and blended with solvent (Aycock hexane: 73% *n*-hexane and 27% methylpentanes; or Ashland Oil cyclohexane, 99%). The blends (10–25 wt-% monomer) were further dried by circulation through a desiccant dryer to less than 8 ppm water impurity level ( $3 \times 10^{-4}$ M) as determined by Michler's ketone titration technique.<sup>5</sup> Sufficient blend was prepared for a series of experiments to eliminate variations in quality from experiment to experiment. Ninety-nine % isoprene was blended with Aycock hexane and dried in the same manner. Styrene monomer, 99.8%, was blended with cyclohexane and dried for this series of experiments. Fifteen % *n*-butyllithium solution in hexane from The Foote Mineral Co. was used as received after assay for carbon-bound lithium content. The experiments were carried out in either a 5-, 20-, or 50-gallon agitated, stainless steel autoclave. Air and moisture were rigorously excluded from the system. The polymerization procedure was as follows:

1. Blend was charged by weight to the polymerization vessel.
2. The impurity level was determined and the blend was initiated with *n*-butyllithium solution.
3. The polymerization was run to total conversion below 65°C to conserve the "living" polymer.
4. Samples were taken into sealed glass bottles for titration analysis using a syringe needle adapted to the reactor sample line. Additional samples were taken for molecular weight distribution analysis. All bottles were water washed, oven baked at 150°C, purged with nitrogen, capped, and pressured with nitrogen prior to use.
5. The polymer solution was heated to the desired temperature, and samples were analyzed as a function of heating time.

The Gilman double-titration technique is widely used to determine the activity or carbon-bound lithium concentration of alkyl-lithium solutions.<sup>6</sup> A variation of this procedure has been developed for determining the carbon-bound lithium concentration of polymer-lithium solutions.<sup>7</sup> The carbon-bound lithium concentration is the difference between the measured total and noncarbon-bound lithium concentrations. This technique was used to titrate the thermolyzed polymer-lithium solutions. The precision of this analysis was observed to be about  $\pm 5\%$ .

Polybutadiene solutions were alcohol coagulated and dissolved in hexane for the determination of permanent polymer structure changes using a Beckman DK-2 UV spectrophotometer. The UV spectra of "living" polybutadienyllithium solutions were also determined using specially fabricated cells. These cells allowed a sample of cement to be purged through the cell to minimize the loss of "live" polymer due to trace impurities. Unheated, "live" polymer was used in the reference cell of the spectrophotometer.

Gas chromatography was used to analyze the heated, hydrolyzed cements for hydrogen content. The system was operated at room temperature and consisted of 5A molecular sieve column packing, Argon carrier gas, and a thermal conductivity detector. The apparatus was calibrated by hydrolyzing a known amount of lithium hydride, suspended in mineral oil. The details of the experiments are included in Tables I, II, and III.

TABLE I  
Thermolysis of Polymer-Lithium Solutions

	Heating time, hr	Titration, meq non-C-Li/ 100 g soln.	Gas chromatography, meq LiH/ 100 g soln.
Poly BD-Li	0	0.16	0.09
	1	0.24	0.26
	2	0.31	0.30
	16	0.70	0.88
	40	0.98	0.97
Poly Sty-Li	0	0.16	0.07
	4	0.46	0.31
	14	0.73	0.53
	23	0.82	0.51

## RESULTS

Initially, polybutadienyllithium and polyisoprenyllithium solutions were colorless to light yellow, but upon heating the color changed through dark yellow to orange to dark amber. Polystyryllithium solutions changed from light to dark red upon heating. The color intensity increased with the loss of activity. The color intensity was also greater at higher lithium concentrations. The dark color of heated polymer solutions was destroyed by complete termination.

Ultraviolet spectrophotometric analysis of the terminated polybutadiene solutions showed an increasing peak at 235 nm with heating time. Analysis of the "living" polymer solutions showed an increasing peak at 267 nm with heating. Upon termination, a significant reduction in absorbance was noted. Figure 1 is a plot of the data at 267 nm.

The titration data in Figures 2 through 4 show the carbon-bound lithium concentration of polybutadienyllithium solutions as a function of

TABLE II  
Experimental Summary of Thermolysis of Polybutadiene-Lithium Solutions

wt-% Poly- mer	Solvent	Temp., °C	Lithium concentration			Apparent initial first- order rate constant, hr <sup>-1</sup>
			Active, meq C-Li/ 100 g soln.	Active, $M \times 10^4$	Total, $M \times 10^4$	
10	hexane	80	0.07	4.7	7.6	0.36
20		80	0.18	12.	19.	0.17
10		80	0.27	18.	21.	0.14
		80	0.53	36.	39.	0.01
10		93	0.11	7.5	9.9	0.53
		93	0.092	6.2	8.3	0.53
		93	0.119	8.0	17.	0.47
		93	0.57	38.	43.	0.33
		93	0.77	51.	54.	0.23
20		93	1.8	130.	130.	0.07
25	hexane	93	2.2	160.	180.	0.067
10	cyclohexane	93	0.15	12.	15.	0.58
		93	0.90	72.	80.	0.16
		93	2.4	200.	200.	0.13
10	hexane	120	0.07	4.9	7.1	0.47
		120	0.10	6.8	9.2	0.77
		120	0.15	10.	14.	0.50
		120	0.58	39.	43.	0.50

TABLE III  
Experimental Summary of Thermolysis of Polymer-Lithium Solutions

wt-% Poly- mer	Solvent	Temp., °C	Lithium concentration			Apparent initial first- order rate constant, hr <sup>-1</sup>
			Active meq C-Li/ 100 g soln.	Active, $M \times 10^4$	Total, $M \times 10^4$	
Polystyrene						
10	cyclohexane	65	0.28	21	27	0.19
25	cyclohexane	65	2.7	230	240	0.12
		93	2.5	210	230	0.70
		93	2.6	220	240	0.87
		120	2.4	200	220	1.3
Polyisoprene						
10	hexane	93	0.24	16	20	0.5
		120	0.20	13	18	1.9

heating time at 80°, 93°, and 120°C. Initially, the carbon-bound lithium concentration decreased rapidly with heating time. The initial rapid rate period was followed by a much slower rate of decrease in carbon-bound lithium concentration. Within experimental error, the stability of polybutadienyllithium in hexane or cyclohexane was the same. Figure 5

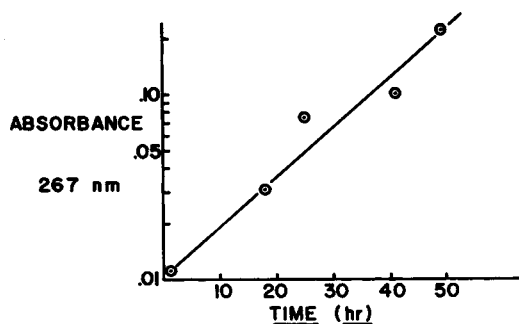


Fig. 1. UV absorption of polybutadienyllithium as a function of heating time at 70°C.

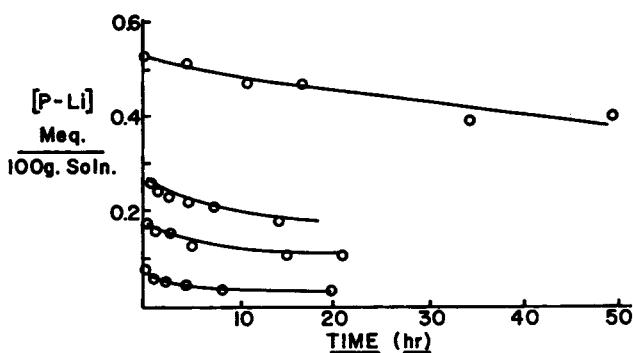


Fig. 2. Decrease in polymer-lithium concentration as a function of heating time at 80°C for polybutadienyllithium.

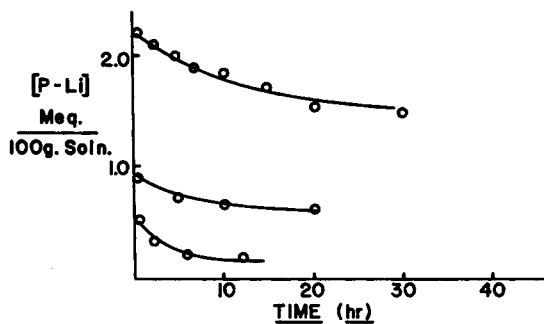


Fig. 3. Decrease in polymer-lithium concentration as a function of heating time at 93°C for polybutadienyllithium.

shows the carbon-bound lithium titration data of polyisoprenyllithium solutions at 93° and 120°C.

The thermal stability of polystyryllithium in cyclohexane was also determined. These data are plotted in Figure 6 at 65°, 93°, and 120°C. The titration data indicated that polystyryllithium is less thermally stable than polyisoprenyllithium or polybutadienyllithium.

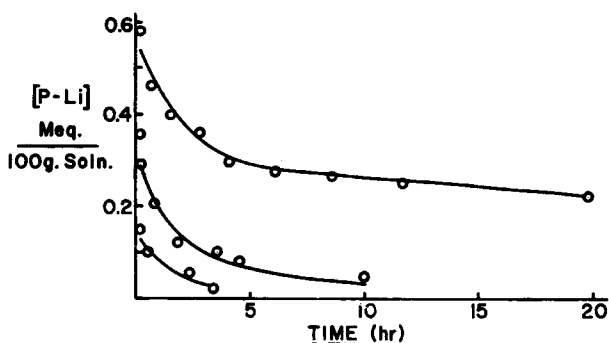


Fig. 4. Decrease in polymer-lithium concentration as a function of heating time at 120°C for polybutadienyllithium.

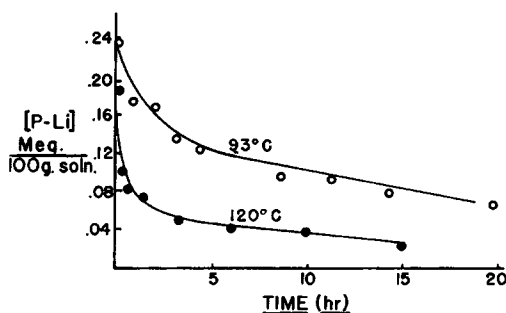
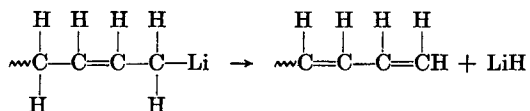


Fig. 5. Decrease in polymer-lithium concentration as a function of heating time at 93° and 120°C for polyisoprenyllithium.

## DISCUSSION

The thermolysis of polymer-lithium compounds was found to involve an elimination reaction with the formation of unsaturation in the polymer chain and lithium hydride. For polybutadienyllithium,



The formation of lithium hydride was verified by hydrolysis of the heated cements, and the evolved hydrogen gas was measured by gas chromatography. Table I summarizes the noncarbon-bound lithium concentrations obtained by titration and from the hydrogen analysis by gas chromatography. This reaction is consistent with that proposed for the thermolysis of alkyl lithium compounds<sup>2,3,4</sup> and the isomerization of polystyrylsodium.<sup>8</sup>

The UV spectrophotometric analysis of "living" polybutadienyllithium showed the formation of a peak at 267 nm upon thermolysis. The appearance of this peak is not fully understood. Absorption at this

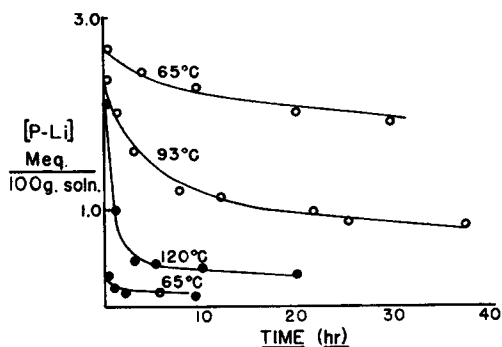


Fig. 6. Decrease in polymer-lithium concentration as a function of heating time at 65°, 93°, and 120°C for polystyryllithium.

wavelength may be a measure of the extent of elimination. Since the optical density decreased upon termination with methanol, the absorption was possibly due to a reaction product of the elimination reaction and polybutadienyllithium or perhaps the formation of a complex involving an elimination product.

The increased absorption of heated, terminated polymer solution at 235 nm was indicative of conjugated double bonds.<sup>9</sup> This further verified that the decrease in "live" ends occurred by an elimination reaction.

Kinetic analysis of the titration data indicated that the complete termination reaction did not follow the same mechanism as the thermolysis of alkylolithium compounds which has been shown to be first order. Applying the data in Figures 2 through 6 to first-order kinetics, it was found that, at best, the data only fit during the rapid initial rate period. Other fractional and simple whole-order kinetic schemes provided poorer fits of the data. These results are indicative of a complex mechanism involving consecutive or concurrent competitive reactions. Along with the elimination reaction, metalation and addition are suggested for polybutadienyllithium and polyisoprenyllithium. The macrostructural evidence for these reactions is discussed elsewhere.<sup>10</sup>

Since the titration data measured the overall loss of carbon-bound lithium, it was insufficient to evaluate any of the individual rate constants. Although the titration data did not support a first-order treatment, this analysis was made to develop quantitative values which would be more useful than qualitatively comparing curves. An apparent initial first-order rate constant was then determined. Because the initial concentration was often uncertain, a technique outlined by Swinbourn for determining first-order rate constants was used to analyze the data.<sup>11</sup> The apparent initial first-order rate constants are listed in Tables II and III.

For polybutadienyllithium at constant temperature (Table I), the apparent initial first-order rate constants are concentration dependent. A plot of these data at three temperatures is shown in Figure 7. These results further suggest that a complex kinetic scheme is involved.

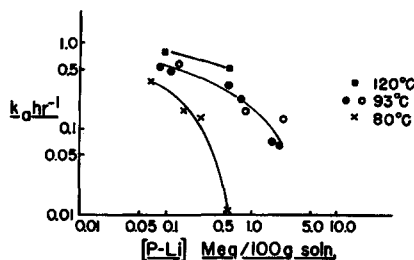


Fig. 7. Effect of lithium concentration on apparent initial first-order rate constant for polybutadienyllithium: (■), (●), (×) in hexane solvent; (○) in cyclohexane.

The kinetic data for polystyryllithium and polyisoprenyllithium solutions are shown in Table III. It was found that polystyryllithium is less stable than either polyisoprenyllithium or polybutadienyllithium. Table IV summarizes the kinetic data for the systems studied. The degrees of association of polystyryllithium, polyisoprenyllithium, and polybutadienyllithium in cyclohexane have been proposed to be dimeric, tetrameric, and hexameric, respectively.<sup>11,12</sup> It is interesting to note that the observed thermal stabilities are consistent with these suggested degrees of association. However, there is disagreement between investigators who have determined the extent of association by various techniques: kinetic,<sup>12,13</sup> light-scattering,<sup>12</sup> or viscometric<sup>14</sup> measurements. Viscosity measurements by Morton and co-workers<sup>14</sup> have determined that these polymer-lithium species in hydrocarbon solvents are associated in pairs.

TABLE IV  
Thermal Stability of Polymer-Lithium Systems

System	Temp., °C	Initial lithium concn., meq pol-Li/100 g soln.	Kinetic parameter, hr <sup>-1</sup>
Poly BD-Li	93	0.12	0.47
	93	0.57	0.33
	93	2.20	0.07
	120	0.58	0.50
Poly Isop-Li	93	0.24	0.50
Poly Sty-Li	93	2.5	0.70
	120	2.4	1.3

## CONCLUSIONS

The thermolysis of polybutadienyllithium was observed to involve a complex kinetic scheme. Competitive side reactions in addition to the expected elimination of lithium hydride were observed to have an effect on the thermal stability. Polystyryllithium was observed to be less stable than either polyisoprenyllithium or polybutadienyllithium.



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