

Thermolytic Reactions of Polybutadienyllithium

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Synopsis

In addition to the expected elimination of lithium hydride, metalation and addition reactions have been observed as competitive, thermolytic reactions of polybutadienyllithium. The importance of these reactions at temperatures frequently utilized for the polymerization of butadiene was illustrated and the effect of these reactions on the macrostructure of polybutadiene determined.

INTRODUCTION

The polymerization of butadiene with lithium and lithium alkyls has been extensively studied.¹ The kinetics and mechanism of the pyrolysis of alkyllithium compounds^{2,3,4} have also been investigated thoroughly, but little is known of the thermolytic reactions of polybutadienyllithium. By analogy with alkyllithium compounds, the elimination of lithium hydride would be expected to be an important thermolytic reaction. This was confirmed in a separate study.⁵ The present investigation was limited to thermolytic reactions of polybutadienyllithium, other than elimination of lithium hydride, which we believe to be of importance in determining the effect of the polymerization temperature on macrostructure and the mechanism of branching and gelation of polybutadiene.

EXPERIMENTAL

The polybutadienyllithium was prepared in either a 5- or 50-gallon stirred reactor using *n*-butyllithium as a catalyst. Polymerization of the butadiene (usually 10 wt-% in Aycock hexane) was initiated at 38°C and maintained at a temperature less than 50°C throughout the polymerization. After polymerization was complete, the temperature of the reactor was increased to that desired for thermolysis. Aliquots were removed before and during thermolysis for titration for carbon-bound lithium, polymer characterization, or for the polymerization of butadiene or styrene with the thermolyzed cement. The aliquots were obtained by pressuring approximately 500 ml of solution into a tared beverage bottle which had been dried, purged with nitrogen, and capped with a perforated crown cap with a self-sealing rubber liner. Additional monomer was added to the cooled solution

without exposure to air or moisture and polymerized at 30°C in a rotation-type polymerization box. After deactivation with methanol and the addition of antioxidant, the polymers were isolated by coagulation in methanol and vacuum dried.

GPC data were obtained on a Waters Associates Model 200 gel permeation chromatograph equipped with a du Pont Model 410 UV photometer (254 nm) and four Styragel columns of 10^6 , 10^5 , 10^4 , and 10^3 Å permeabilities. Samples were injected as 1/16 wt-% solutions in tetrahydrofuran, the GPC solvent. The GPC had been calibrated with polystyrene from the Pressure Chemical Company and polybutadiene standards with narrow molecular weight distributions prepared in these laboratories. A Mechrolab Model 502 membrane osmometer was used for osmotic molecular weight determinations. The block styrene analysis and isolation of the polystyrene from the butadiene-styrene copolymers were completed using the method of Kolthoff, Lee, and Carr.⁶ The carbon-bound lithium of the polybutadienyllithium was determined by a modified Gilman titration.⁷ Lithium hydride was found to have no measurable effect on the titration.

RESULTS

When a solution of polybutadienyllithium in hexane was heated at 80°C, the molecular weight of the polymeric product increased as the heating time was increased. This is illustrated in Table I. It was also observed

TABLE I
Effect of Postheating Live Polybutadiene Solutions*

Polymer no.	Postheating time at 80°C, hr	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
213	0	50	59	1.2
2113	3	52	64	1.2
2116	20	58	83	1.4
2119	44	61	90	1.5

* M_n and M_w calculated from GPC data using computer program for linear polymers.

that the weight-average molecular weight increased more rapidly than the number-average molecular weight, indicating a broadening of the molecular weight distribution with heating time. Since aliquots of the same "live" polymer solution were taken as a function of heating time, it was possible to determine the effect of heating on the molecular weight and molecular weight distribution by normalization of the chromatograms and subtracting the normalized GPC peak of the unheated cement from that of the heated one. These results are shown in Figure 1. This figure illustrates that the molecular weight distribution is broadened and the molecular weight increased by the formation of a high molecular weight shoulder on the GPC peak.

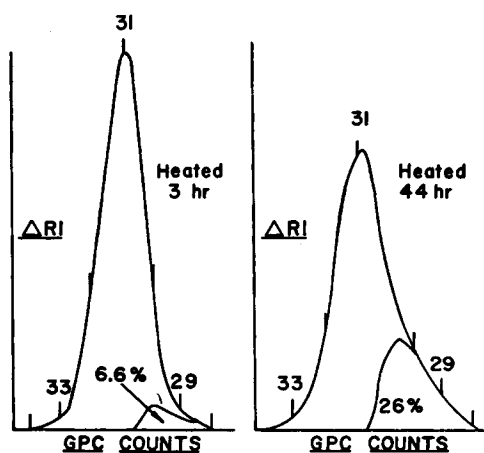


Fig. 1. Effect of thermolysis of polybutadienyllithium at 80°C on the molecular weight distribution of the isolated polymer.

From the calibration of the GPC, the number-average molecular weight of polybutadiene eluting at 31.0 counts was found to be 56,000, and that eluting at 29.5 counts was 130,000. It thus appeared that an average of two molecules of the base polymer were joining to form a higher molecular weight species when the polybutadienyllithium was thermolyzed. The skewing of the peak of the material formed on heating toward higher molecular weights suggested that more than two molecules could join on heating. We have plotted in Figure 2 the amount of high molecular weight polymer formed at varying heating times versus the fractional amount of carbon-bound lithium remaining after heating. We have included data obtained for three different heating temperatures (65°, 80°, and 120°C). The data obtained at 120°C illustrate that this coupling or addition reaction does not result in the loss of live ends (carbon-bound

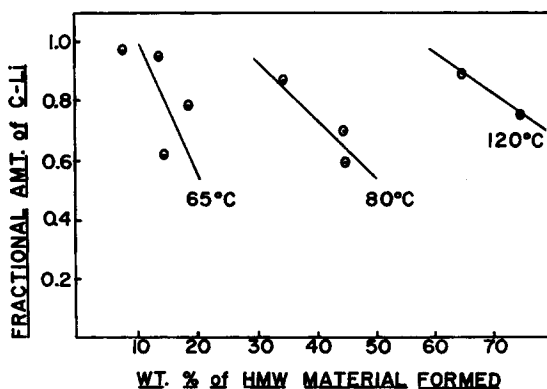


Fig. 2. Correlation of loss of carbon-bound lithium with formation of a high molecular weight species.

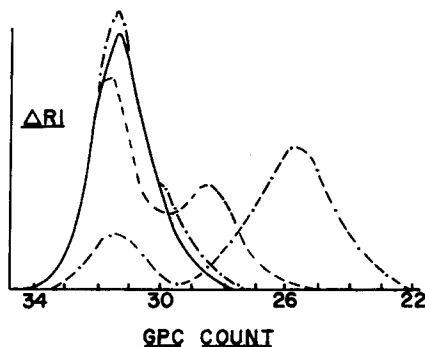


Fig. 3. Thermolysis of polybutadiene followed by addition of butadiene: (—) polybutadiene base polymer before heating; (---) polybutadiene isolated after thermolysis for 25 hr at 80°C; (— · —) polymer obtained after 12 wt-% of added butadiene polymerized; (· · ·) polymer obtained after all the added butadiene polymerized.

lithium) and is a more favored reaction compared to elimination of lithium hydride at higher temperatures.

Since elimination of lithium hydride was also observed when polybutadienyllithium was thermolyzed, additional butadiene was added to the live cement at room temperature in an attempt to observe from GPC data the sites of the residual carbon-bound lithium after thermolysis for 25 hr at 80°C. The polymerization of the additional butadiene resulted in the appearance of a second GPC peak of higher molecular weight than the base polymer (Fig. 3). From titration data before and after thermolysis, the kinetic molecular weight (M_k) was calculated for the base polymer and the additional polymer formed from the butadiene added to the thermolyzed cement. The values were 37×10^3 and 235×10^3 , respectively. Assuming that one molecule of the base polymer having an active catalyst site initiates the polymerization of the monomer added after heating, the kinetic molecular weight of the high molecular weight species should be 272×10^3 . The number-average molecular weight, as determined from the maximum of the high molecular weight GPC peak, was 1100×10^3 , which is four times greater than expected if all the remaining carbon-bound lithium is monofunctional polybutadienyllithium. Also shown in Figure 3 is the GPC curve for the polymer obtained after approximately 12% of the butadiene added to the thermolyzed cement had polymerized. From titration data for carbon-bound lithium, the kinetic molecular weight of the additional butadiene polymerized would be 28.5×10^3 , which is less than that of the base polymer. It is apparent from Figure 3 that an additional peak is observed in this instance at a higher molecular weight ($M_n = 25.0 \times 10^4$) than that of the base polymer. This would indicate that the active carbon-bound lithium must be part of a polymeric chain. These data strongly suggested that the active polymer chains were polyfunctional in lithium.

In order to elucidate the reactions occurring when polybutadienyllithium was thermolyzed, it was decided that styrene should be added to the

thermolyzed cements. Polystyrene blocks or grafts can easily be separated from the polybutadiene by osmium tetroxide oxidation⁶ of the unsaturated polymer and then recovering the polystyrene intact. The isolated polystyrene should be representative of the grafts or blocks of polystyrene on the thermolyzed polybutadienyllithium.⁸

From the molecular weight of the isolated polystyrene and the amount of styrene polymerized, we believed that we could reliably determine the functionality of the live polybutadiene cement. However, we found that degradation of the polystyrene blocks can also occur on the oxidation with osmium tetroxide. This is illustrated in Table II, which shows the effect

TABLE II
Block Styrene Analysis of a Standard Polystyrene^a

Oxidation time, min	$M_n \times 10^{-3}$	M_w/M_n	Block styrene, %
0	82	1.2	
10	81	1.2	97.5
20	81	1.2	96.9
40	23	1.8	97.5

^a Pressure Chemical Company PCC 97,200; M_n and M_w calculated from GPC data using the computer program for linear polymers.

of oxidation time on the molecular weight distribution of polystyrene homopolymer. These data indicate that the oxidation time should be limited to 20 min or less to prevent the degradation of polystyrene blocks. In addition to degradation, one also observes a broadening of the molecular weight distribution of the polystyrene. It was decided that the oxidation procedure for the isolation of styrene blocks would be limited to a 10-min oxidation time to minimize oxidative degradation of the polystyrene grafted to the thermolyzed polybutadienyllithium.

To aliquots of a polybutadienyllithium which had been thermolyzed at 80°C for varying times we added, and polymerized at 30°C, with 50 wt-% styrene. Other aliquots were taken for titration of carbon-bound lithium. Figure 4 illustrates the effect of heating time on the GPC curves of the copolymers formed after adding the styrene to the thermolyzed "live" polybutadiene solution. The GPC curve for the copolymer formed from the addition of styrene to the live solution heated for 3 hr showed a shift of the peak to lower counts (higher molecular weight) and the appearance of a shoulder on the peak. The GPC curves for copolymers prepared from the "live" polybutadiene solutions heated for 20 and 44 hr at 80°C had two distinct GPC peaks. The lower molecular weight peak in both instances had nearly the same elution volume (molecular weight) as the base polymer obtained from the unthermolyzed solution. The second GPC peak is of higher molecular weight (lower count), and the molecular weight of this peak is definitely dependent on the thermolysis time of the live polybutadiene cement. As the heating time was increased, a definite increase in

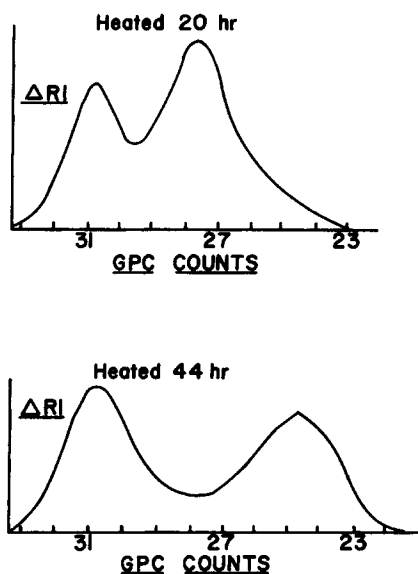


Fig. 4. GPC chromatograms of copolymers prepared by addition of styrene to polybutadienyllithium thermolyzed at 80°C.

the molecular weight of this peak was observed; and after 44 hr of heating, this peak was estimated to have a minimum molecular weight of 1500×10^3 .

The styrene blocks from these copolymers were recovered from the copolymer by oxidation with osmium tetroxide for 10 min and were isolated in the usual manner. The styrene blocks were analyzed using GPC. The number- and weight-average molecular weights of the blocks were calculated. These data, shown in Table III, indicate that the molecular weight distribution is broader than would be expected for polystyrene prepared with a lithium catalyst. This could be due to partial degradation of the block during the osmium tetroxide oxidation. However, we did find that the number-average molecular weight (M_n) from osmotic pressure measurements and the number-average molecular weight calculated from the GPC data were in reasonable agreement with the kinetic molecular weight (M_k) calculated from titration data.

TABLE III
Molecular Weight of the Styrene Portion of the Block Copolymers

Polymer	Wt. % ^a Styrene	Postheating			
		Time, hrs @ 80°C	$M_k \times 10^{-3}$	$M_n \times 10^{-3b}$	M_w/M_n^b
214	48.5	0	74	81	1.9
2114	47.3	3	58	49	1.9
2117	47.2	20	96	107	2.0
2120	50.7	48	130	95	2.4

^a Weight % styrene in copolymer before oxidation.

^b Calculated from GPC data using the computer program for linear polymers.

Using the previous data for the molecular weight of the styrene blocks, we can estimate the functionality of the active polymer chains since we also know the molecular weight of the base polybutadiene (sample 2119, Table I). After 44 hr of heating, we observed that the high molecular weight peak of the copolymer had a minimum estimated molecular weight of 1500×10^3 (GPC calibration for pure polybutadiene). The molecular weight of the polybutadiene, isolated after thermolysis of the live solutions but before the addition of styrene, was 61×10^3 from GPC. Since the GPC number-average molecular weight of the styrene blocks was 95×10^3 and the kinetic molecular weight was 130×10^3 , we conclude from the ratios of these values to that of 1500×10^3 for the high molecular weight peak that the polybutadiene chains have a functionality between 11 and 15. That is, after thermolysis for 44 hr at 80°C , the active polymer chain has an average of 11 to 15 lithiated sites per molecule. If one assumed that the high molecular weight peak is due to a polymer containing 50 wt-% styrene, an alternative to the proposed polyolithiation would be the coupling of seven to nine sample B-S-type butadiene-styrene block copolymer chains possibly formed by an addition reaction of a "live" copolymer chain to a double bond in another polymer chain.

To distinguish between polyolithiation and addition, the copolymer formed after adding styrene to polybutadiene thermolyzed for 24 hr was analyzed with a GPC equipped with an UV detector which measured UV absorption at 254 nm. This combination of instruments can be used to measure the concentration of styrene as a function of elution volume since no UV absorption is observed for either 1,2- or 1,4-polybutadiene. We have used this technique with polymer 2120. The GPC chromatogram is shown in Figure 5. Ultraviolet absorption was found for the thermolyzed polybutadiene

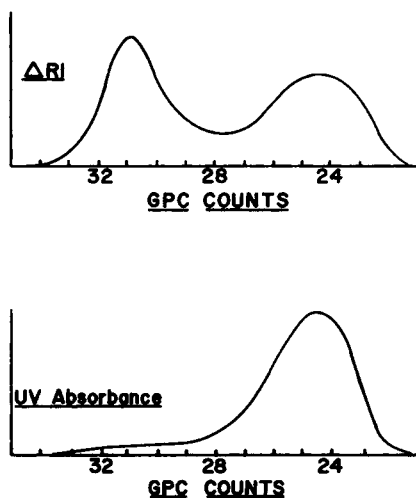


Fig. 5. GPC chromatograms (UV and RI detectors) of a copolymer prepared by addition of styrene to polybutadienyllithium which had been thermolyzed for 44 hr at 80°C .

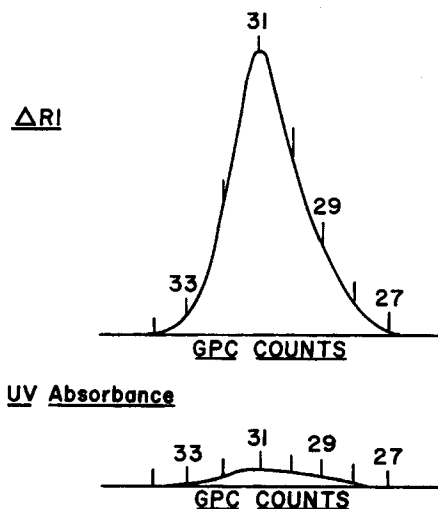
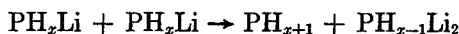
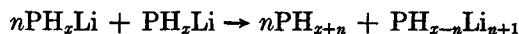


Fig. 6. GPC chromatograms (UV and RI detectors) for a polybutadiene isolated after thermolysis of polybutadienyllithium for 44 hr at 80°C.

cement which we believe is due to the formation of conjugated olefinic bonds by an elimination reaction. After correction for UV absorption found for the thermolyzed polybutadiene to which no styrene was added (Fig. 6), it appeared that the higher molecular weight peak was nearly 100% polystyrene. Polymer 2120 was prepared by heating the "live" polybutadiene cement for 24 hr. After heating, it was determined by titration that 59% of the lithium originally added was active for additional polymerization. Fifty wt-% styrene was then added to the live cement and polymerized. Taking into account the loss of live ends before the addition of styrene, the copolymer formed should contain 63 wt-% styrene if metalation did not occur. The metalation reaction



or, more generally,



would yield copolymers varying in composition depending on the degree of metalation, $n + 1$. For the above copolymer, the composition of the high molecular weight peak would vary with the degree of metalation, as shown in Table IV. If only an addition reaction occurred on heating which resulted in the combination of active chains by addition of a polybutadienyllithium across an internal double bond of a second molecule of polybutadienyllithium, the resulting copolymer formed on the addition of styrene would always be 63% styrene, regardless of the number of times the addition occurred on the same chain. We concluded that metalation definitely

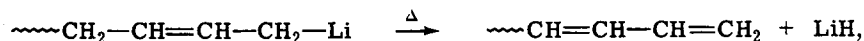
TABLE IV
Degree of Metalation of Sample 2120

$n + 1$	Wt. % Styrene
1	63
2	77
3	83
4	87
6	91
10	95

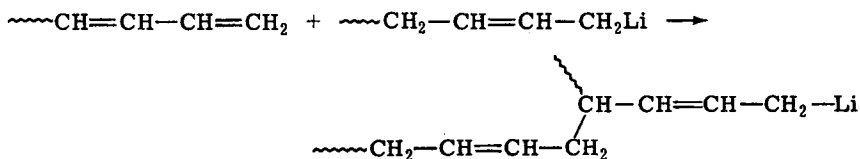
occurs when polybutadienyllithium is thermolyzed since the high molecular weight peak contained nearly 100% styrene, a result consistent with those data obtained from the block styrene determination of the degree of metalation.

DISCUSSION

These data indicate that in addition to elimination of lithium hydride, there are at least two additional thermolytic reactions of polybutadienyllithium, an addition and a metalation reaction. We do not propose that the addition reaction involves a radical process in which two polymer radicals are coupled with the formation of a polymer twice the molecular weight of the original polymer and metallic lithium since the data can be readily explained by an ionic mechanism. Since the elimination reaction of polybutadienyllithium,

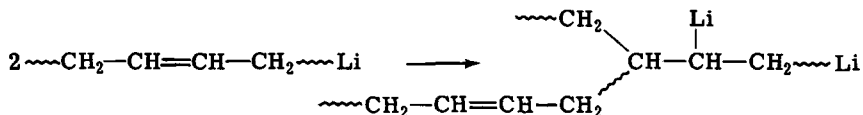


would result in the formation of a polymer chain with a terminal conjugated olefin endgroup, it seems likely that the remaining polybutadienyllithium would readily add to the conjugated double bonds to give a polymer of approximately twice the molecular weight of the base polymer:

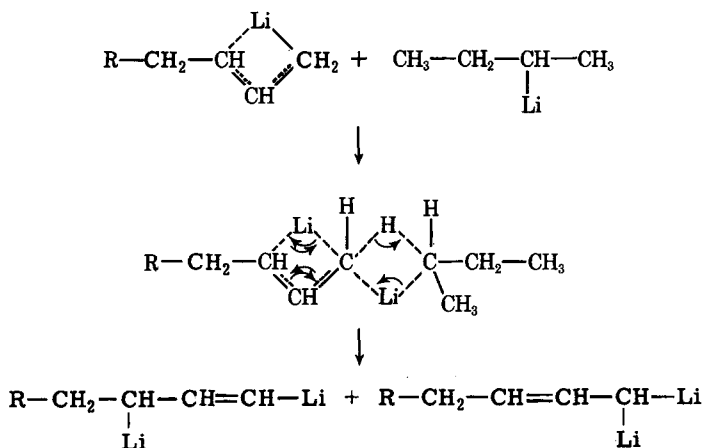


Our data would also suggest that addition also likely occurs at sites other than conjugated olefinic linkages, since we observed that up to 70% of this higher molecular weight polymer was formed when as much as 80% of the live ends were remaining. The proposed mechanism would require that the fractional loss of carbon-bound lithium equal one half or more the amount of high molecular weight polymer formed. We suggest that this could be due

to addition, particularly at the higher temperatures, of polybutadienyllithium to isolated double bonds in the polymer backbone:



The metalation reaction observed for polybutadienyllithium has not to our knowledge been previously reported. Naylor, Hsieh, and Randall⁹ have reported the metalation of the *sec*-butyllithium adduct of butadiene by *sec*-butyllithium to form a dilithium compound. The following mechanism for metalation was proposed from NMR and mass spectroscopy investigations on the deuterated derivatives:

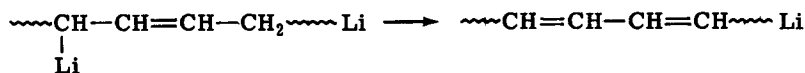


This mechanism would perhaps be applicable to the thermolytic metalation of polybutadienyllithium by another active molecule for metalation occurring exclusively on the terminal monomer unit. The observed poly-lithiation indicates that metalation of the polybutadiene backbone is also important. A previous investigation¹⁰ of the metalation of polybutadiene with a butyllithium-*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex would suggest that the most likely site for metalation is the allylic position:



From our data, we cannot conclude whether metalation occurs exclusively by this mechanism, but this seems quite improbable. The lithiation of acetylenes^{11,12} was found to promote further metalation to give poly-lithiated products. Since the terminal unit of the polymer chain may also have a carbon-bound lithium, this might be expected to facilitate further metalation on the terminal monomer unit to give metalation similar to that observed by Naylor, Hsieh, and Randall.

The elimination of lithium hydride from the metalated product would also be an expected reaction:



Repetitive elimination from the same metalated polymer chain would yield a product with multiple conjugated olefinic bonds which could also add polybutadienyllithium or metalated polybutadienyllithium. This could explain the skewing of the GPC peak for the high molecular weight species formed on heating to higher molecular weights (Fig. 1).

The addition reactions, particularly an addition reaction involving a metalated polymer chain, would be expected to result in the formation of a highly branched polymer and ultimately in gelation. We have not observed gelation in this particular investigation. We believe that this can be attributed to the initially low molecular weight of the polybutadienyllithium and to the relative rates of the elimination, addition, and metalation reactions. A fast elimination reaction relative to the addition and metalation reactions would prohibit the formation of a network. We believe that these investigations were conducted over a temperature range less than that required for gelation, since it appeared that at 120°C the addition reactions were just beginning to predominate over elimination. A continuous polymerization would perhaps gel at a lower temperature due to backmixing, and additional polymerization would relieve steric hindrance at the active lithiated sites which could further increase the rate of addition and network formation. Further investigations of the mechanism of these thermolytic reactions and the mechanism of branching and gelation are in progress.

CONCLUSIONS

In addition to the expected elimination of lithium hydride, metalation and addition reactions have been observed as competitive thermolytic reactions of polybutadienyllithium. These reactions produced measurable changes in the molecular weight and molecular weight distribution of the polymer isolated after thermolysis. The changes in macrostructure would be expected to be even larger if additional monomer were available during thermolysis. This study illustrates the importance of polymerization temperature on the macrostructure of polybutadiene and offers new information of importance on the mechanism of branching and gelation of polybutadiene.

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