The Nuclear Magnetic Resonance Characterization of a Cyclic Structure in Anionically Prepared Polybutadiene

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ABSTRACT: The structure of polybutadiene, polymerized by the lithium counterion with tetramethylethylene diamine present, has been examined by ^{1}H- and ^{13}C-NMR spectroscopy. A new type of cyclic structure for polybutadiene, a substituted cyclopentane, was found. The occurrence of this structure is apparently due to an intramolecular cyclization step which takes place during the propagation step under conditions of low monomer concentration.

The study of cyclic structures in polydienes has been the subject of analyses via IR and ^{1}H-NMR spectroscopy. These cyclic structures have been prepared by ultraviolet radiation,[1] thermal treatment,[2,3] and by reactions involving Lewis acid catalysts.[4–14] These reactions are united by a common feature, to wit, they take place following the formation of the polydiene chain. The claim has been advanced,[15] based on IR and ^{1}H-NMR analyses, that cyclic structures were formed during the polymerization of butadiene and isoprene by certain Ziegler type catalysts. However, Chen[16] demonstrated that this interpretation was in error and that no cyclic structures were present. Thus, the available evidence demonstrates that although cyclic structures can be formed in polydienes, these cyclic structures are the product of postpolymerization reactions which lead to the formation of ladder-like segments.

In this paper we report on the ^{1}H-NMR and ^{13}C-NMR analyses of polybutadienes which have been synthesized by anionic polymerization involving the lithium counterion and tetramethylethylene diamine (TMEDA). The microstructure of this polybutadiene was found to consist of the 1,4 and 1,2 forms in addition to a substituted cyclopentane. This cyclic structure is formed during chain propagation by an intramolecular cyclization reaction and is not the result of a postpolymerization process.

Experimental Section

The low molecular weight polybutadienes, I and II, were obtained from the Lithium Corp. of America and Revertex, Ltd. Polybutadiene II was prepared at a temperature of about 84 °C under conditions of continuous monomer addition.[17] The initiator was an organolithium with toluene used as the solvent. Under certain conditions toluene will also act as a chain transfer agent in polymerizations involving alkali metal counterions.[17–26] Chain transfer was promoted by the presence of the bidendate diamine tetramethylethylenediamine (RLi/TMEDA $\simeq$ 1).[17] As will be shown, the presence of this diamine promotes the formation of the cyclic structure. Hence, polybutadiene II possesses a polydisperse molecular weight distribution. Two polybutadiene II samples were examined by NMR spectroscopy and had $\overline{M}_w/\overline{M}_n$ ratios of about 2.1, as determined by gel permeation chromatography, and $\overline{M}_n$ values, from vapor pressure osmometry, of 1.7 and 1.9 $\times$ 10^3 g mol^{-1}. Both polybutadiene samples possessed symmetrical molecular weight distributions.

Polybutadiene I was prepared in toluene using *n*-butyllithium under conditions where chain transfer was minimal. Hence this sample had an $\overline{M}_w/\overline{M}_n$ of less than 1.1. The $\overline{M}_n$ of this sample was 4.9 $\times$ 10^3 g mol^{-1}. Triethylamine was used in the preparation of polybutadiene I. This amine served to increase the rate of initiation and the vinyl content over what is usually obtained in hydrocarbon solvents.

The other low molecular weight polybutadienes examined in this work are listed in the text. The "model" compounds vinylcyclopentane, 1,1-*cis*-3-*cis*-4-tetramethylcyclopentane, and 1,1-*cis*-3-*trans*-4-tetramethylcyclopentane were obtained from Chemical Samples, Inc.

The proton decoupled and proton coupled FT-NMR spectra were recorded on a Varian CFT-20 instrument at room temperature with $CDCl_3$ as the solvent. The relatively low viscosity of polybutadiene I permitted the use of only a small amount of $CDCl_3$. For this reason the characteristic bands (75–80 ppm) of $CDCl_3$ are attenuated in the spectrum of the polybutadiene I sample. The ^{1}H-NMR spectra were recorded on a Varian HR-300 spectrometer in hexachlorobutadiene at 120 °C. Tetramethylsilane and hexamethyldisilane were used as the internal standards.

Results and Discussion

Figure 1 shows the ^{1}H-NMR spectrum of polybutadiene II in comparison with the sprectum of sample I which has approximately the same cis-1,4, trans-1,4, and 1,2 content. The peaks due to the presence of the phenyl group at the end of the majority of the polybutadiene II chains are marked by an asterisk.

In addition to the poorly resolved peaks in the aliphatic region of the polybutadiene II spectrum there is a new signal at 5.7 ppm which to our knowledge does not occur in the spectra of polybutadienes reported thus far in the literature. This signal in the spectrum of the polybutadiene II must be due to a double bond which is neither that found in the 1,4 nor vinyl modes of addition.

Figure 2 shows the ^{13}C-NMR spectra of the polybutadienes shown in Figure 1. Again the aliphatic region for sample II is uninformative due to poor resolution caused by numerous peak overlappings. However, in the resonance region of the carbon–carbon double bond (Figure 3) some new signals are to be seen in the spectrum of the polybutadiene II material.

The ^{13}C-NMR spectra of polybutadienes polymerized by anionic initiators have been presented and discussed elsewhere.[27,28] The signals in the spectra of 1,2-polybutadienes have been assigned based on their tacticities[27] and the signals in the resonance region of the carbon double bond of the 1,4 units have been assigned to different sequential structures in polybutadienes.[28]

Figure 3 shows new signals in the resonance regions of the two vinyl carbon atoms. At 111.8 and 112.7 ppm there are two new signals which do not overlap. The signals of conventional 1,2-polybutadiene occur at about 114 ppm. These two new signals have approximately the same intensity and represent in this spectrum 46% of the area between 110 and 115 ppm. The new signals at about 143 ppm partially overlap the signals of the $=$CH— atom of the 1,2-butadiene unit. These signals in the ^{13}C-NMR spectrum as well as the peak at 5.7 ppm in the ^{1}H-NMR spectrum have never been observed in the spectra of other polybutadienes, including isotactic, syndiotactic, and atactic 1,2-polybutadiene.[29] It will be shown that these new signals are the result of a cyclic component in this polybutadiene.

Keeping in mind the fact that chain growth occurs under conditions of low monomer concentration, the following intramolecular cyclization mechanism involving either the α or γ carbanion can yield the cyclic structures 1,2-dialkyl-4-vin-

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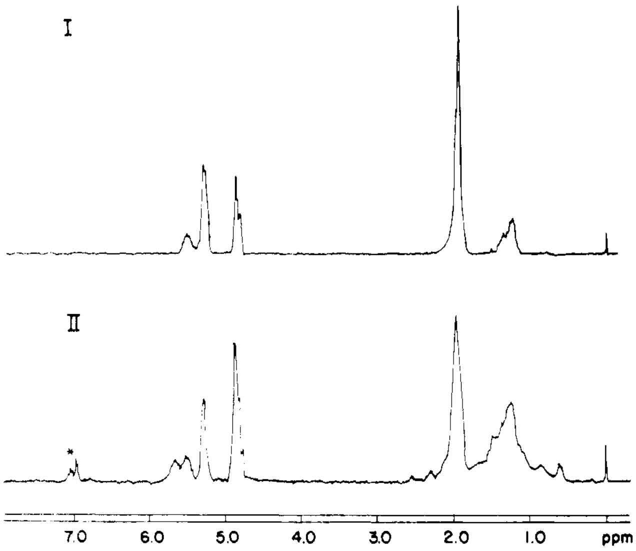
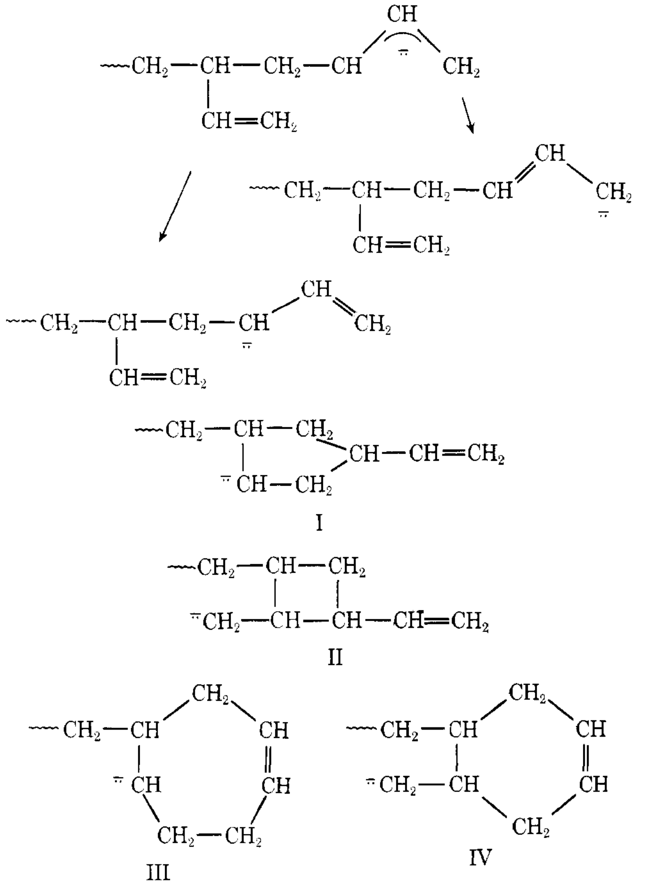


Figure 1. ^{1}H NMR spectra of polybutadienes I and II. Microstructure: I, 59% 1,4 and 41% 1,2; II, 51% 1.4, 25% 1,2, and 23% vinyl cyclopentane

ylcyclopentane (I), 1,2-dialkyl-3-vinylcyclobutane (II), 4,5-dialkylcycloheptene (III), and 4,5-dialkylcyclohexene (IV).



An intramolecular cyclization reaction has been previously invoked[30] to explain the presence of the five-membered ring, 1,2-dialkyl-2-phenyl-4-phenyl-2-vinylcyclopentane, found in poly(2-phenylbutadiene) prepared by the lithium counterion. It should be noted that the active chain ends in the structure are not meant to imply the existence of free ions, although the existence of some free ions cannot be ruled out in the presence of the polar chelating tetramethylethylene diamine.

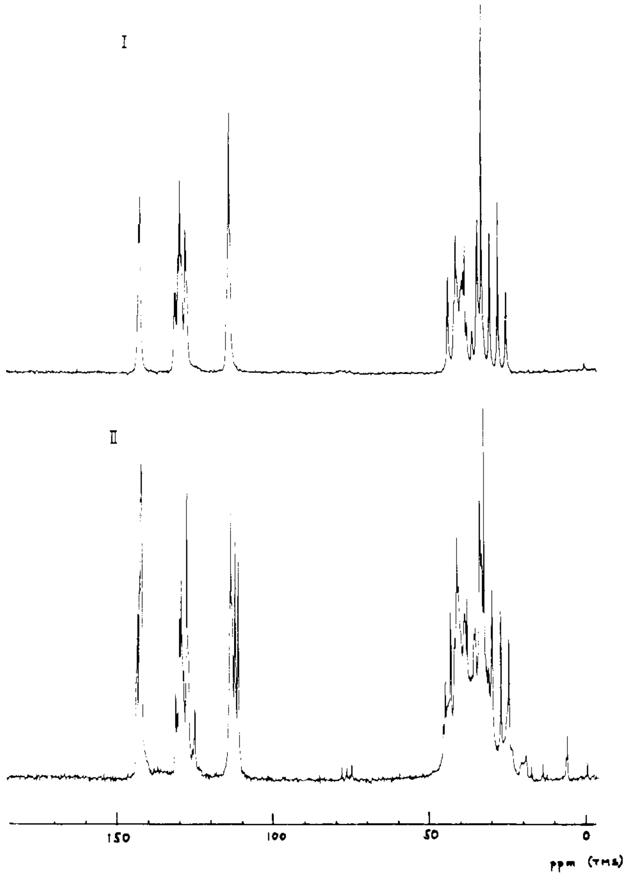


Figure 2. ^{13}C NMR spectra of polybutadienes I and II.

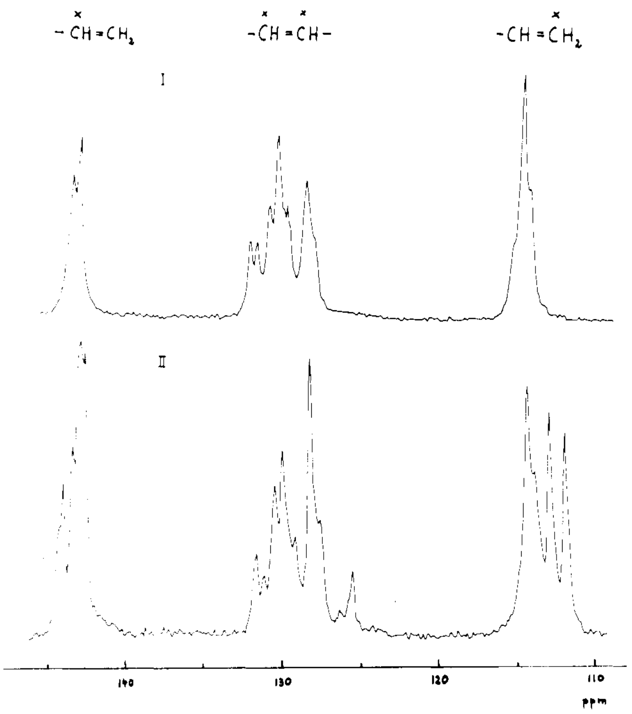


Figure 3. Enlarged ^{13}C-NMR spectra of polybutadienes I and II. The signals between 125 and 126 ppm in II are due to the presence of the terminal phenyl groups.

The existence of delocalized, i.e., π bonded, structures in anionic systems, including those derived from butadiene, involving the lithium counterion is well-established.[31-40] Hence, for the butadiene system under conditions of low monomer concentration with a 1,2 unit as the penultimate structure in the chain, attack by the allylic chain end on the penultimate

Table I
^{1}H-NMR Analysis of Polybutadiene II[a]

Chemical shift, ppm	Assignment	Exptl rel intensity, %
5.7	=CH— vinylcyclopentane	12
5.55	=CH— 1,2-polybutadiene	13
5.37–5.32	=CH— 1,4-polybutadiene	26
4.91–4.87	=CH$_2$ 1,2-polybutadiene + vinylcyclopentane	50
2.0	>CH— 1,2-polybutadiene —CH$_2$— 1,4-polybutadiene	39[b]
1.0–1.7	—CH$_2$— 1,2-polybutadiene + vinylcyclopentane	61[c]

[a] These data were from the sample provided by the Lithium Corp. of America. Nearly identical data were obtained from the Revertex, Ltd. sample. Both samples were from commercial batches. [b] Calculated intensity from olefinic region equal to 39%. [c] Calculated intensity from olefinic region equal to 61%.

1,2 unit is apparently possible. This could then result in the cyclic structures shown above, depending on whether the α or the γ carbon atom reacts with the methylene or methine carbon of the vinyl unit.

Neither the cyclohexene nor the cycloheptene structures (III and IV) seem to occur in detectable amounts. For the cycloheptene structure there should be two equally intense signals for the two carbon–carbon double bond atoms, with a calculated[41] chemical shift difference of 2.2 ppm. This chemical shift difference results from the differenct environments of the pair of double bonded carbon atoms. In the ^{13}C-NMR spectra (Figure 3) of polybutadienes I and II it can be seen that the spectrum of the latter polybutadiene contains a signal at 128.1 ppm and that this signal is much smaller in the spectrum of the polybutadiene I. This signal could be due to the cyclohexene double bond carbons, but it is, as will be shown later, due to the unequal distribution of 1,4–1,2 and 1,2–1,4 sequences in the polymer. The quantitative analysis of the ^{1}H-NMR spectrum of sample II indicates that the in-chain and ring vinyl groups are present in a near 1:1 ratio. The chemical shifts and their assignments in the ^{1}H-NMR spectrum of sample II are shown in Table I for polybutadiene II. The second polybutadiene II sample examined in this work showed relative intensities virtually identical to the data reported in Table I.

Parenthetically, it should be noted that our results are at variance with those where cyclic structures containing 6 to 18 carbon atoms were claimed[42] for polybutadienes polymerized anionically under conditions of low monomer concentrations with tetramethylethylenediamine present. In our opinion the formation of cyclic structures, via an intramolecular reaction, containing more than 7 carbon atoms is implausible. From a mechanistic standpoint, the close proximity of the α and γ carbanions and the penultimate 1,2 unit would seem to indicate that if ring closure is to occur, then the cycloheptene structure would be the largest structure formed. Our results also indirectly indicate that if the penultimate unit is present in the 1,4 form then ring closure does not occur.

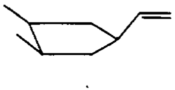
The NMR data show that the predominant cyclic structure present in sample II is the vinyl cyclopentane structure. The existence of this cyclic structure is fortified by the signals of the vinyl group in vinyl cyclopentane which occur in 143.4 ppm (=CH—) and 112.3 ppm (=CH$_2$); values which are comparable to those signals, 143–144 ppm (=CH—) and 111.8 ppm and 112.7 ppm (=CH$_2$), observed for the vinyl group of the substituted cyclopentane unit in the polybutadiene chain. The ^{1}H spectrum of vinyl cyclopentane showed, among others, bands at 2.3, 4.9, and 5.7 ppm; these are bands which are seen in the polybutadiene spectrum. The band at 2.6 ppm seen for polybutadiene II is apparently due to end groups since its intensity has been seen in other polybutadienes (the Lithenes in Table II) to vary inversely with molecular weight. However, the 0.6 ppm band in the ^{1}H-NMR spectrum and 5–20 ppm bands in the ^{13}C-NMR spectrum remain unassigned although they may be due to other end groups formed in this chain transfer system. These bands have been found only for the polybutadiene II samples. They are absent in the polybutadienes listed in Table II. It is of interest to note, though, that an unassigned signal at about 0.6 ppm has been recorded[38] in the 60-MHz ^{1}H-NMR spectrum of the proton terminated 1/1 adduct of *tert*-butyllithium and butadiene prepared in benzene.

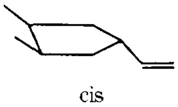
Table II
Low Molecular Weight Polybutadienes Examined by the ^{1}H-300 NMR Spectrometer

Sample	Polymerization mechanism	Source
Plastikator 32	Anionic	Chemische Werke Buna
Lithenes, P, P-4, Q and Y	Anionic	Lithium Corp. of America and Revertex, Ltd.
Butarez CTL	Anionic	Phillips Petroleum Co.
Butarez HTS	Anionic	Phillips Petroleum Co.
Ricon 100 and 150	Anionic	Colorado Chemicals and Specialties Co.
HYSTL G	Anionic	Dynachem Corp.
R-45M and R-45HT	Radical	ARCO Chemicals Co.
Budium	Cationic	E.I. du Pont de Nemours and Co.
Polyol 110 and 130	Ziegler-Natta	Chemische Werke Hüls AG

The NMR results of, for example, Morton[36] and Glaze[37] for polybutadienyllithium in ether solvents seemingly show that the 1,2-localized species can be formed from the delocalized structure. Thus it can be suggested in a speculative fashion that the cyclic structure may be the result of an attack by the 1,2-delocalized carbanion on the methylene carbon of the penultimate 1,2 unit. The carbanion product of this step is a secondary species, which is less stable than the primary carbanion which would result from the attack of the γ carbanion on the methine carbon of the penultimate 1,2 unit. However, this latter reaction would logically be expected to be infrequent since the strain energy of the resultant cyclobutane structure is considerably higher than that of the cyclopentane structure. It should also be noted that our results are in accordance with the suggestion[43] that the vinyl cyclopentane ring may be present in this low molecular weight polybutadiene.

For a trisubstituted cyclopentane, such as exists in polybutadiene II, there is a possibility of stereoisomers, i.e.,


cis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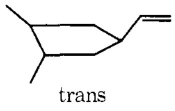
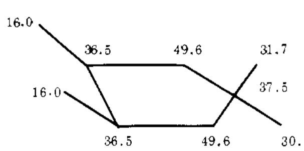
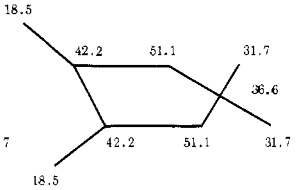

trans

These different isomeric structures can result in different signals in the NMR spectrum. In order to examine the influence of the steric arrangement of the substituents in cyclopentanes we studied the ^{13}C-NMR spectra of 1,1-*cis*-3-*cis*-4-tetramethylcyclopentane and 1,1-*cis*-3-*trans*-4-tetramethylcyclopentane, which have methyl groups instead of the vinyl substituent in position 1. The structures, V and VI, give the chemical shifts of the carbon atoms of these compounds. The assignment of the peaks in the ^{13}C-NMR spectra was possible with the help of the proton-coupled ^{13}C-NMR spectra.



V



VI

The chemical shift of the methyl groups in position 1 of V is 30.7 and 31.7 ppm, respectively. The difference in cis or trans configuration relative to the other substituents in position 3 and 4 results in a chemical shift difference of 1 ppm. The two methyl groups in position 1 of VI show only one signal at 31.7 ppm, which is exactly the same chemical shift as that of one of the 1 methyl groups of V. This indicates that within these model compounds, the methyl group as a substituent in position 1 of the cyclopentane ring detects only whether there is at least one other substituent in positions 3 and 4 in cis configuration or not. The results from these model compounds indicate that the steric arrangment in trisubstituted cyclopentane rings is the reason that in the ^{13}C-NMR spectrum of sample II, two distinct resonance signals at 111.8 and 112.7 ppm are observed for the $=CH_2$ atom of the vinyl group connected to the cyclopentane structure.

According to the proposed mechanisms there should no longer be an equal distribution of 1,2–1,4 and 1,4–1,2 sequences, i.e., the 1,4–1,2 diad will be found less frequently than the 1,2–1,4 diad. This is due to the fact that the penultimate 1,2 units can be used in the intramolecular cyclization reaction. The quantitative analysis of the signals in the resonance region between 127 and 132 ppm is not feasible due to the lack of resolution. However, it can readily be seen that the intensity of the signals in the resonance region between 127 and 128 ppm is higher than those of the signals above 130 ppm. According to the assignments in ref 27, the signals for the 1,4–1,2 sequences occur downfield from the 1,2–1,4 diads. This is due to the $-CH_2-$ group which separates the 1,4 double bond from the vinyl group.

In addition to samples I and II, other low molecular weight polybutadienes were examined by ^{1}H-NMR spectroscopy. These are listed in Table II. None of these polybutadienes showed a signal at 5.7 ppm. The microstructure of these polybutadienes ranged from high cis (Polyol 110 and 130) to high 1,2 (HYSTL) to high trans (Budium). Also, these samples failed to show characteristics in their ^{1}H-NMR spectra that could not be accommodated following the results of Santee, Malotky, and Morton.[44]

It is germane to note that Lithene polybutadienes listed in Table II are made by the process of continuous monomer addition but without the presence of tetramethylethylenediamine.[18–20] The ^{1}H-NMR and ^{13}C-NMR spectra of a polybutadiene prepared by a batch process[45] in tetrahydrofuran/TMEDA (92/2 v/v) at 0 °C showed no evidence of cyclic structures present, even though the vinyl content was nearly 90%. These two observations indicate that both a low monomer concentration and the presence of a strong polar component are prerequisites for the formation of the vinyl cyclopentane structure in butadiene polymerizations involving the lithium counterion. It is also appropriate to mention that it has been reported that strong bases,[46] e.g., *n*-butyllithium modified by tetramethylene diamine,[47,48] can bring about the formation of conjugated structures, by an isomerization reaction, in polybutadiene. However, our NMR results show that this apparently does not occur in polybutadiene II and this is not a complicating feature of the ^{1}H- and ^{13}C-NMR spectra of this sample.

Facile intramolecular cyclization reactions, similar to our suggested mechanism, have been observed for alkenyl and allenic Grignard reagents[49–53] and alkenyl species containing alkali metals.[53–60] In particular[57,58] 5-hexenyllithium was found to yield, after hydrolysis, methylcyclopentane. It would appear that the established[61,62] intramolecular lithium–olefin association is intimately related to this cyclization reaction[57,58] and, by analogy, may play a role in our proposed reaction. It is also germane to note that 3-butenyl-, 4-pentenyl-, and 6-heptenyllithium failed to cyclize nor did the 5-hexenyllithium undergo an intermolecular reaction.[57,58] These findings can be taken as an indication that the cyclopentane ring is favored and that chain branching does not occur to a significant extent in the system we have studied.

The opinion has been expressed[63] that the cyclic structure formed in polybutadienes prepared by the *n*-butyllithium/TMEDA system is a divinyl-substituted decalin preceded by the formation of the 1,2-dialkyl-3,5-divinylcyclohexane ring. This intermediate structure was presumed to add one monomer unit and then *always* undergo a subsequent cyclization step to yield the tetra-substituted decalin fused ring. However, since the quantitative ^{1}H-NMR data, and other NMR and infrared results,[63] show a near 1:1 relation between in-chain and ring vinyl groups, this proposed[63] mechanism does not allow for the presence of the divinyl-substituted cyclohexane structure, since, of course, the presence of this structure would nullify the observed near 1:1 ratio of in-chain and ring vinyl groups. Furthermore, our ^{13}C-NMR results do not indicate the presence of appreciable amounts of either the substituted cyclohexane or decalin ring structures. Thus, it is our conclusion that the predominate ring structure in the polybutadiene examined in this work is 1,2-dialkyl-4-vinylcyclopentane.

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Stabilization of Poly(vinyl chloride) by Thiols. A Mechanistic Study

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ABSTRACT: Large amounts of aliphatic or aromatic thiols will prevent the discoloration of poly(vinyl chloride) when solutions of the polymer in *o*-dichlorobenzene or benzophenone are heated in the absence of oxygen at ~160–185 °C. Polymers pretreated with thiols in this way contain very small amounts of sulfur, but their chemical stabilities (as measured by rates of nonoxidative thermal dehydrochlorination) are found to be greatly enhanced. Kinetic and structural studies show that under the pretreatment conditions, a remarkable reductive dehalogenation reaction occurs which probably has the following stoichiometry: $-CH_2CHCl- + 2RSH \rightarrow -CH_2CH_2- + RSSR + HCl$ (R = alkyl, aryl, etc.). The possible relationship of this reaction to stabilization is discussed, and it is argued that both color stability and chemical stability after thiol pretreatment must result, at least in part, from the deactivation of labile polymer defect structures, either by reductive dehalogenation or by very selective alternative routes that lead to the incorporation of only a few mercaptide groups. Possible mechanisms for the reductive dehalogenation process are considered.

The interaction of poly(vinyl chloride) (PVC) with thiols under conditions conducive to degradation of the polymer has been the object of some research and much speculation over a period of many years. Technological considerations have provided the stimuli for a major part of this attention; for example, thiols are known to be formed in situ from organotin mercaptide stabilizers for PVC, via reaction of these stabilizers with the HCl evolved from the degrading polymer.[1] Furthermore, various compounds containing the free SH group have been suggested for practical use in PVC stabilizer blends[2] and, in some cases, for use as primary stabilizers requiring no auxiliary components.[3] However, the reaction of thiols with PVC is also of interest from the standpoint of basic research, since there are reasons for believing that a detailed knowledge of this process might contribute to an understanding of the mechanism(s) of PVC degradation. Thiols are excellent radical scavengers due to the weakness of the S–H bond;[4] thus they might be expected to reduce the rate of the nonoxidative thermal degradation of PVC if radicals were involved therein.[1a,5] Alternatively, thiols could simply act as chain-transfer agents during radical–chain dehydrochlorination, thereby decreasing the average length of the chromophoric polyenes being formed and thus preventing or retarding the appearance of color without affecting the overall degradation rate.[6] Thiols have also been suggested to act as PVC stabilizers by deactivating heavy-metal dehydrochlorination catalysts,[5a] and antioxidant effects in PVC (peroxide decomposition, trapping of oxygenated radicals) due to thiols[1a,5b,c,7] and potential thiol precursors[8] have been postulated by several workers. Color stabilization of the polymer could involve the destruction of polyene chromophores rather than the prevention of their formation; such an effect might be accomplished by the homolytic or heterolytic addition of thiols to polyene double bonds.[1a,3b,5e,7b,d,9] Finally, replacement of allylic halogen by mercaptide groups derived from thiols[9g,10] could prevent color by preventing polyene elongation,[10] and it is clear that both this process and the process of C=C destruction by thiol addition might also reduce the rate of dehydrochlorination and thus cause true chemical stabilization[11] as well.

Theories of the stabilization of PVC by thiols therefore exist

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