Observations on the preparation of polybutadiene containing vinyl cyclopentane units

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At low monomer concentrations the use of TMEDA and THF as promoters in the n-BuLi-initiated polymerization of butadiene results in the formation of vinyl cyclopentane chain units in addition to the normal 1,4- and 1,2-microstructure. TMEDA is more effective than THF in promoting formation of the cyclic structure and with TMEDA the cyclic content of the polybutadiene can be as high as 45 wt %. Surprisingly, the use of high levels of THF in conjunction with n-BuLi and TMEDA can actually suppress the formation of cyclic units. The sodium counterion is also shown to yield the cyclic structure with the same promoters.

INTRODUCTION

The attainment of cyclic structures in polydienes has, almost without exception, been accomplished by post-polymerization reactions, e.g. via the use of Lewis acids. However, an analysis[1] of low molecular weight polybutadienes by ^1H (300 MHz) and ^{13}C n.m.r. revealed the presence of the 1,2-dialkyl-4-vinylcyclopentane ring as a chain component. These samples were not subjected to any post-polymerization treatment. These results confirmed suggestions of Aukett and Luxton[2] regarding the potential identity of the cyclic component.

The method of synthesis of these polybutadienes involved n-butyllithium and tetramethylethylene diamine in toluene solution under conditions of continuous monomer addition[3]. The relatively low concentration of monomer during the duration of polymerization was found to be a significant factor in the introduction of the cyclic component in the polybutadiene chain. Typically, the microstructure of these polybutadienes could be represented as containing about 50% 1,4; 25% 1,2; and 25% cyclic.

The formation of the 1,2-dialkyl-4-vinylcyclopentane unit results in a reduction in the level of unsaturation in the polybutadiene chain. A loss of unsaturation and formation of cyclic units has been reported[4] when tetramethylethylene diamine or a tetramethylethylene diamine/metal alkoxide promoter system has been used in conjunction with sodium metal or organo-sodium, again under monomer-starved conditions. However, the structure of the cyclic unit was not identified.

It was thus our intention to examine the influence of promoter concentration and identity, monomer flow rate (concentration), polymerization temperature, and mixed promoter systems, on the cyclic content of these polybutadienes. Some preliminary work on the influence of counterion identity is also reported.

EXPERIMENTAL

The polymerizations involving n-butyllithium (n-BuLi) were carried out at atmospheric pressure under nitrogen in a 4 l stainless steel reactor equipped with a solid CO_2–methanol condenser. Butadiene was metered into the reactor via a calibrated rotameter after passage through a type 3A molecular sieve drying column.

Either n-hexane or cyclohexane were used as the main solvents. Toluene was not used to avoid the chain transfer reaction which occurs with this solvent. The initial n-butyllithium concentration was maintained at ~0.16 mol l^{-1} and the ratio of consumed monomer weight to n-butyllithium was such that the theoretical molecular weight was $\sim 5 \times 10^3$. Final polymer concentration was ~50 wt %.

The effect of counterion was qualitatively examined by using sodium naphthalene as the initiator. These polymerizations were conducted under high vacuum conditions at 30°C.

The solvents and polar promoters tetramethylethylene diamine (TMEDA) and tetrahydrofuran (THF) were purified by distillation from calcium hydride under nitrogen. They were stored over either 3A molecular sieve or calcium hydride, under nitrogen, prior to use.

The cyclic component was evaluated by ^1H n.m.r. analysis using the Varian HR-300 spectrometer. Hexachlorobutadiene at 120°C or carbon tetrachloride at room temperature were the solvents. Hexamethyldisilane or tetramethylsilane were used as standards.

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Table 1 Polymerization parameters and microstructure characterization of polybutadienes

Sample	Molar ratio n-BuLi:TMEDA:THF	Polymerization temp. (°C)	Monomer flow rate 1/min	Reaction time (min)	Microstructure[a] 1,4	1,2	Cyclic
Flow rate							
207	1:2:–	40	3.5	185	30(22)	34(25)	36(53)
235	1:2:–	40	1.75	360	26(18)	32(23)	42(59)
238	1:2:–	40	0.85	585	28(19)	26(18)	46(63)
Polymerization temperature							
209	1:2:–	75–80	1.75	330	39(28)	24(18)	37(54)
235	1:2:–	40	1.75	360	26(18)	32(23)	42(59)
TMEDA concentration							
236	1:5:–	40	1.75	360	27(19)	31(22)	42(59)
235	1:2:–	40	1.75	360	26(18)	32(23)	42(59)
237	1:1:–	40	1.75	360	26(18)	35(26)	39(56)
Promoter identity							
208	1:–:70	40	3.5	185	18(15)	64(54)	18(31)
200	1:–:50	40	3.5	185	26(22)	54(45)	20(33)
207	1:2:–	40	3.5	185	30(22)	34(25)	36(53)
Mixed promoter temperature effect							
219	1:2:25	60	1.75	335	30(25)	47(39)	22(36)
223	1:2:25	30–35	1.75	340	17(14)	59(48)	24(38)
THF concentration							
219	1:2:25	60	1.75	335	30(25)	47(39)	22(36)
218	1:2:5	60	1.75	325	32(22)	25(17)	43(60)
223	1:2:25	30–35	1.75	340	17(14)	59(48)	24(38)
239	1:2:25	40	1.75	360	28(21)	37(27)	35(52)
235	1:2:–	40	1.75	360	26(18)	32(23)	42(59)

[a] Values in brackets denote the weight percent of butadiene incorporated into the chain. All values are rounded off to the nearest whole number

The microstructure was determined from the peaks appearing at 5.32–5.37 ppm (=CH–1,4 polybutadiene), 5.55 ppm (=CH–1,2-polybutadiene) and 5.7 ppm (=CH vinylcyclopentane)[1]. The signal appearing at 5.7 ppm has previously been shown[1], using ^{13}C n.m.r. to be caused by the vinyl group on the 1,2,4-substituted cyclopentane ring.

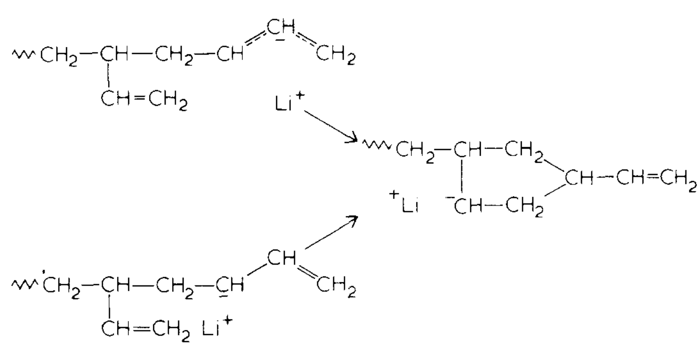
Comparison of the molecular weight and molecular weight distribution (*MWD*) of the polymers prepared with n-butyllithium was made using a Waters ALC 202 liquid chromatograph fitted with four Styragel columns of nominal porosities $10^5/10^4/10^3/500$ Å. The carrier solvent was THF at ambient temperature and the polymer concentration was 1–1.5 wt %. Calibration of the column system with both polystyrene and low molecular weight polybutadiene standards gave a linear log(molecular weight) vs. elution volume plot over the range of interest. The microstructure of the polybutadiene standards was ~80% total 1,4 (mixed *cis* and *trans*) and molecular weights quoted are on the basis of this microstructure. No corrections were made for the high levels of vinyl 1,2 or cyclic structures in the polymers studied, or for column broadening effects.

RESULTS AND DISCUSSION

The combined data for the polymerizations conducted with the lithium counterion are shown in *Table 1* while *Figure 1* shows a typical ^1H n.m.r. spectrum. The results in *Table 1* are arranged to illustrate the effects of monomer flow rate, polymerization temperature, TMEDA concentration, promoter identity (TMEDA or THF), mixed promoters (TMEDA and THF) and polymerization temperature on mixed promoter systems.

A decrease in monomer flow rate, e.g. monomer concentration, leads to an increase in the cyclic content, (from 36 to 46%) for the case of constant temperature and n-butyllithium:TMEDA ratio. This is the anticipated result, particularly in view of the fact that no cyclic component can be found when these polymerizations are conducted under conditions where all of the monomer is present at the outset of the reaction.

The mechanism proposed[1] to explain the mode of cyclic component formation is as follows:



In the interest of simplicity, the presence of TMEDA is omitted. It must also be noted that the use of the delocalized and 1,2-localized structures is not designed to imply that the primary allylic chain end does not exist in this system. Our use of the delocalized and localized structures is motivated by convenience and is not to be

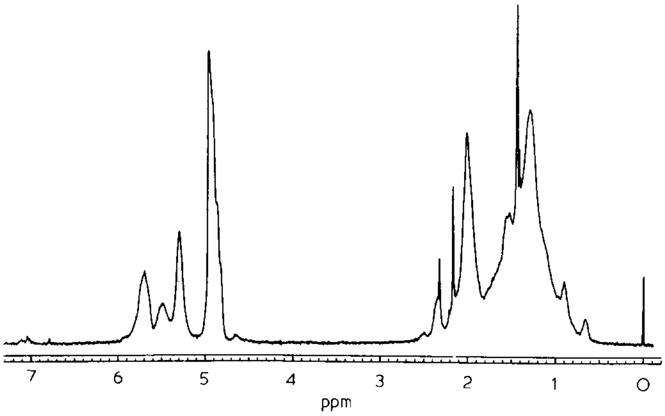


Figure 1 ^{1}H-n.m.r. spectrum of polybutadiene

interpreted as a claim or implication that these are the majority structures for the active chain ends. It should be noted, though, that the existence of the delocalized and 1,2-localized structures in anionic systems involving dienes is well established[5–14].

Clearly, in the presence of monomer, reaction at the α or γ carbon will yield respectively the 1,4 or 1,2 structure as the penultimate unit. However, in the absence of monomer (or at low monomer concentrations) the potential exists for reaction with the penultimate vinyl unit leading to the vinyl cyclopentane ring. There exists considerable precedence in the literature[15–26] which demonstrates that when anionic species (Grignard or organo-lithium reagents) undergo cyclization reactions, the cyclopentane ring is the favoured structure. Logically, this intramolecular cyclization step, involving reaction with an alkyl-substituted ethylene unit, would be expected to have a higher energy of activation than the propagation step involving monomer. Thus, the observed increase in cyclic content at the lower flow rate is consistent with the relative activation energies of the two competitive processes.

Two further comments can be made regarding the above mechanism. It is apparent that the cyclization reaction as we have presented it is dependent upon the presence of a 1,2 unit in the penultimate position. Hence, it is important to note that the 1,4-content in samples 207, 235 and 238 remains essentially unchanged. Thus, the increase in cyclic content can be directly related to the decrease in monomer flow rate. Secondly, the argument could be raised that the formation of the secondary carbanion in the cyclization reaction is energetically unfavourable since this species represents a more unstable species than the delocalized structure or, for that matter, the primary allylic chain end. Suffice it to mention that the elimination of either of these structures by the cyclization step is accompanied by the formation of the carbon–carbon single bond. Thus, taken on the whole, the formation of the secondary carbanion on the vinyl cyclopentane ring does not represent an improbable event from an energetic standpoint.

The influence of polymerization temperature on the cyclic content can also be used to substantiate some of the above conclusions. Runs 209 and 235 show that the cyclic content undergoes a slight decrease at the higher reaction temperature. However, this must be balanced against the larger increase seen for the 1,4 content.

The increase in 1,4 content of polybutadiene with increasing reaction temperature when polymerized in the presence of a polar promoter, e.g. THF, has been previously observed[27,28]. This general effect is shown[29] in *Figure 2*. For example, at a THF concentration of 0.05 mol l^{-1} (THF:BuLi = 50), the 1,4 microstructure increases from 21%, at −10°C, to 62%, at 60°C. This effect is rationalized as follows:

$$\sim\!\sim CH_2CHCHCH_2Li + x\,THF \rightleftharpoons \sim\!\sim CH_2CHCHCH_2Li \cdot (THF)_x$$

where the complexed chain end yields a decreased mode, relative to the uncomplexed species, of 1,4 monomer addition. An increase in temperature would shift the above equilibrium to the left and thus generate an increase in the 1,4 content[27].

However, the appropriate data in *Table 1* show that the decrease in cyclic content is less than the increase in 1,4 content. Thus, as temperature is increased, the temperature increase can be seen to favour the cyclization reaction since the increase in 1,4 content outweighs the decrease in cyclic units. This is consistent with the observation that the intermolecular cyclization step is dependent upon the presence of the vinyl penultimate unit, and the expected high activation energy relative to propagation, of this step.

Parenthetically, an additional comment can be made regarding the data of *Figure 2*. The observations[27,30] have been made that irrespective of the total 1,4 content, the *trans:cis* ratio can be given as about 5:4 for polymerizations carried out at >0°C in hydrocarbons and hydrocarbon:ether mixtures. However, the low temperature (−10°C) results show that the *cis* content in polybutadiene can surpass that of the *trans* mode, when the THF:chain-end ratio is greater than about 1:1[31]. This behaviour is contrary to that predicted from Uraneck's work[27].

The concentration of promoter, TMEDA, was found to exert little influence, at 40°C, on the cyclic content of the polybutadiene once the TMEDA:n-BuLi ratio exceeds one. This indicates that TMEDA is a most effective complexing agent insofar as the butadienyllithium chain ends are concerned. These results can be contrasted with those (200 and 208) which show that THF is certainly less effective than TMEDA in promoting the formation of the cyclic structure.

However, the mixed promoter systems show that THF, when present at a 25:2 THF:TMEDA ratio tends to decrease the cyclic component in the polybutadiene. This effect can be rationalized by the assumption that the excess THF can lead to a displacement of the TMEDA from the active centre, and thus cause the measured decrease in the cyclic component.

Still unclear is the mechanism by which TMEDA can lead to the formation of the vinyl cyclopentane unit, i.e. the structure of the TMEDA-modified active centre is unknown under the conditions used in these polymerizations. Nonetheless, several trends are clear from the foregoing results. These are as follows:

(a) the cyclic content is dependent upon monomer flow rate (concentration); decreasing with increasing flow rate;

(b) the formation of the vinyl cyclopentane unit is favoured by an increase in temperature; this indicates that higher cyclic contents than we have reported could be achieved if a promoter is found which will suppress the 1,4 mode of monomer addition; and

(c) the use of cyclic ether, THF, does not lead to particularly high yields of the vinyl cyclopentane unit

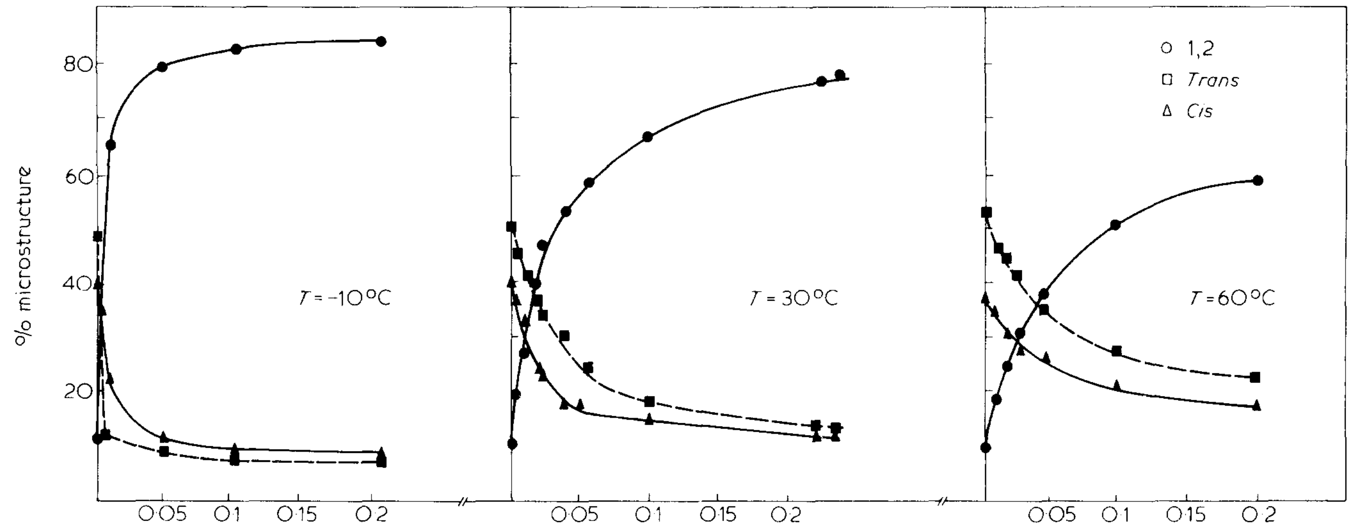


Figure 2 Effect of temperature and THF concentration on polybutadiene microstructure (via ^{13}C n.m.r.). Solvent: n-heptane; [M] = 2 Ml^{-1}; [BuLi] = 1 x 10^{-3} Ml^{-1}

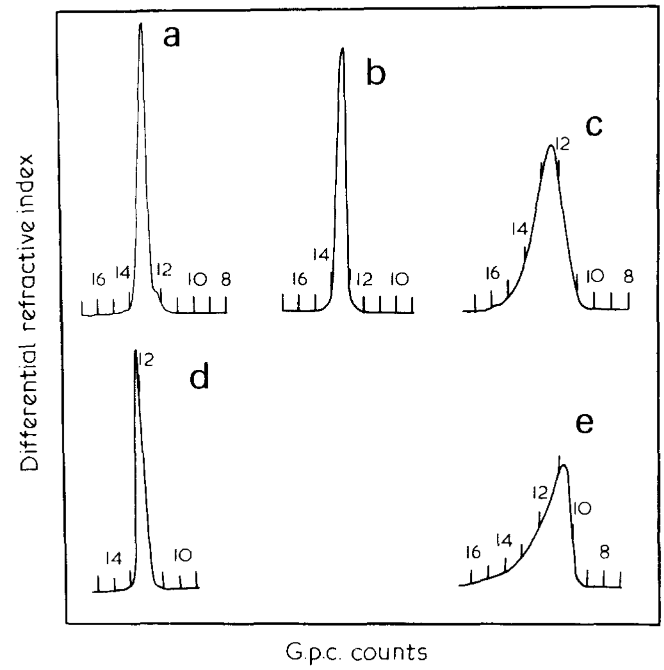


Figure 3 Gel permeation chromatograms of polybutadienes prepared with n-BuLi. (a) 207, M_p = 3300; (b) 238, M_p = 2900; (c) 209, M_p = 5000; (d) 223, M_p = 6000; (e) 219, M_p = 15 000. M_p is molecular weight of peak maximum

even when present in moderately high concentrations. In fact, when mixed with TMEDA, the presence of THF causes a suppression in the amount of cyclic units.

These findings can be accounted for by the proposed relative activation energies of the propagation and cyclization events and the apparent relative complexing efficiencies of TMEDA and THF with the butadienyllithium active centres. The indirect evidence for the displacement of TMEDA by THF at high ratios of THF:TMEDA is of interest.

Some typical gel permeation chromatograms of the cyclic polybutadienes prepared with n-butyllithium as initiator are shown in *Figure 3*. At polymerization temperatures of 35–40°C the *MWD* of the polymers prepared using either TMEDA, or a TMEDA:THF promoter combination, were narrow with a weight- to number-average molecular weight ratio less than 1.1. This was the case even at the lowest rate of butadiene addition (238 – *Figure 3b*). Hence, the active centre remained stable with respect to polymerization.

Table 2 Polymerizations with sodium counterion in THF

Sample^a	Molar ratio Na:TMEDA	Polymerization temp. (°C)	Microstructure 1,4	Microstructure 1,2	Microstructure Cyclic
AU-1	1:3	30	24	60	16
AU-2	1:0	30	25	60	15

^{a} Flow rate of ~2 ml min^{-1} was maintained. Reaction times of about 30 min were used

At polymerization temperatures of 60°C or higher the products exhibited a noticeable broadening of the *MWD* and a corresponding increase in molecular weight (209 – *Figure 3c*; 219 – *Figure 3e*). The broadening was evident on both the low and high molecular weight side of the peak maximum. The combination of organolithium and TMEDA promoter is a system well known for metallation of polydienes. Therefore, at the higher temperatures and under monomer starved conditions, the observed broadening probably results from intermolecular metallation reactions involving the attack of active centres on other polybutadiene chains. The broadening on the low molecular weight side of the peak maximum could be accentuated by an instability of the allylic–lithium chain end in a manner similar to that observed with a sodium counterion[32] and by reaction of the active centre with the promoters, particularly when THF is used[33].

The influence of the alkali matal was examined by the use of the sodium counterion in THF as solvent. The data given in *Table 2* shows only low levels of the vinyl cyclopentane unit in the products of these polymerizations. These results are perhaps not too surprising when consideration is given to the observed effect of high levels of THF on the Li/TMEDA systems.

In attempting to compare the results with the lithium and sodium counterions it should be noted that the rates of butadiene addition were different for the two series of polymerizations. Calculation of the rates of butadiene addition yields approximately 1×10^4 g monomer/mol Na/h for the polymerizations with the sodium counterion. The rate of butadiene addition for the Li/TMEDA systems ranged from 400–1600 g monomer/mol Li/h. These calculations would indicate a higher average monomer concentration in the sodium polymerizations. However, this has to be balanced against the observation that the sodium counterion in THF has been shown[34] to yield a higher apparent k_p than lithium in THF under equivalent conditions ($\sim 2\,\mathrm{l\,mol^{-1}\,s^{-1}}$ vs. $0.1\,\mathrm{l\,mol^{-1}\,s^{-1}}$ at 0°C).

Proni and coworkers[35] found no evidence of the cyclic structure in their polybutadienes prepared using the sodium counterion. However, the rate of monomer addition was not specified in their work.

In conclusion, our data is insufficient to allow any direct comparison regarding the relative effectiveness of the lithium and sodium counterions in generating the cyclic component in polybutadienes. Nevertheless, our results do show the sodium counterion can yield the vinyl cyclopentane structure under conditions of low monomer concentration.

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