

Head-to-head polymers: 33.* Bromination of *cis*-1,4-polybutadiene to head-to-head poly(vinyl bromide)

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Cis-1,4-polybutadiene (PB) in a 0.5% solution of a solvent mixture of dichloromethane and 1,2-dibromoethane or tetrahydrofuran was quantitatively brominated with elemental bromine at 0°C under careful exclusion of oxygen to head-to-head poly(vinyl bromide). Partially brominated PB has a structure of random or block sequences of butadiene units in the polymer depending on the bromination solvent but shows no stereospecificity in the -CHBr-CHBr- dyads. Partially brominated PB with block structure showed a microphase-separated morphology over a wide range of composition. Microphase separation is less pronounced for the more random structure of butadiene units. I.r and ¹³C n.m.r. spectroscopy of the partially brominated PB was used to follow the progress of the bromination.

(Keywords: head-to-head polymers; *cis*-1,4-polybutadiene; bromination; poly(vinyl bromide); micro-phase separation)

INTRODUCTION

Chlorination of 1,4-polybutadiene (PB) has been used for the preparation of head-to-head poly(vinyl chloride) (H-H PVC)¹⁻⁶. More recently, the mechanism of the chlorination was studied in greater detail⁷. It was found that the chlorination had to be carried out under careful exclusion of oxygen, at concentrations below 0.5% in the appropriate solvents and at low temperatures to prevent side reactions which result in molecular weight reduction and/or crosslinking. By careful attention to details, completely chlorinated polymers (H-H PVC) were obtained. The chlorination rate slowed down noticeably at the later stages of the reaction (>90% chlorination). From chlorination studies in the presence of known inhibitors for radical reactions and the type of solvents which were most effective for the chlorination, it was concluded that the chlorine addition was primarily an ionic addition, but that the addition was not stereospecific. ¹³C n.m.r. spectroscopy showed a nearly 1:1 ratio of threo and erythro placements of the -CHCl-CHCl- groups of the chlorinated polymer even though the starting material had a 99% *cis*-1,4-PB structure.

Bromination of PB has also been reported, but the general interest for the preparation of H-H PVB was not very high. Bromination of PB was initially carried out³ in a 0.5% solution of carbon tetrachloride or chloroform; it was found that the spectral characteristics of the bromination products of PB starting from *cis*-1,4- or *trans*-1,4-PB gave the same stereochemistry of the -CHBr-CHBr unit. Additional work on the bromination of *cis*-1,4-PB and polyisoprene was carried out at 0°C to -20°C⁸. The bromination mixture became inhomogeneous under the reaction conditions used even though the bromination was carried out only in 0.1% solution. The brominated

polymer was, however, soluble in THF⁸. It was also found⁴ that only low molecular weight *trans*-1,4-PB (<10⁴ MW) and *cis*-1,4-PB could be brominated in the usual solvents. For the bromination of crystalline high molecular weight *trans*-1,4-PB, a mixture of pyridine and CS₂ had to be used, and pyridinium perbromide was found to be a good brominating agent. The bromination was carried out at very low concentrations of polymer (0.25% solution), but the product of high bromination (from *trans*-1,4-PB) still precipitated at the end of the reaction. Brominated *trans*-1,4-PB was soluble in dimethylformamide (DMF) and cyclohexane but was essentially insoluble in methanol, THF, chloroform, benzene and pyridine. Bromination of *cis*-1,4-PB proceeded smoothly in chloroform; the final product was partially soluble in chloroform and benzene, but soluble in THF and pyridine.

Later work⁵ on the halogenation of polyalkenamers mentioned only briefly the results of the bromination of PB. It was pointed out that the bromination was carried out in solutions of less than 1% polymer and at temperatures from -20°C to +20°C. It was recommended that bromine be added in dichloromethane as a solvent to avoid local overheating during the bromination. *Trans*-1,4-PB had to be brominated in suspension or at slightly higher temperatures (30°C to 40°C) in solution; the brominated polymer was characterized by its intrinsic viscosity.

It was the objective of this work to study carefully the bromination conditions for the synthesis of H-H PVB from *cis*-1,4-PB and to prepare and characterize partially brominated PB. A careful study of the *T*_g, the morphology, and the possible separation of the phases of partially brominated PB was also an objective of this investigation.

EXPERIMENTAL

Materials

Cis-1,4-polybutadiene (PB) was obtained from SNAM Progetti, San Donato, Milan, Italy, was made with a

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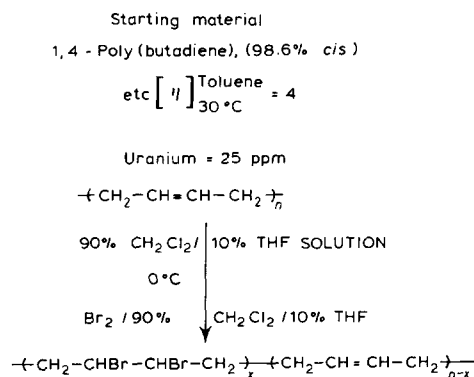
uranium catalyst and consisted of 98.6% *cis*-1,4, 1.0% *trans*-1,4, and 0.4% 1,2 linkages⁸ ($\eta_{inh} = 4.2$). It is not known if this polymer was completely linear or whether it may have had some branches, which is not uncommon for PBs made with coordination initiators. All our discussions are based on the assumption that our PB is essentially linear.

Dichloromethane, chloroform and methanol (Fisher Scientific Co.) were distilled and nitrogen was passed through them before use. Tetrahydrofuran (THF) (Fisher Scientific Co.) and 1,4-dioxane (Aldrich Chemical Co.) were distilled from lithium aluminium hydride (Ventron Alfa Products) under a nitrogen atmosphere. 1,2-Dibromoethane (Eastman Organic Chemicals) (48°C/40 mmHg) was distilled through a Vigreux column. Bromine (Mallinckrodt Chemical Works) (analytical grade) was used without further purification.

Bis(2-hydroxy-3-*t*-butyl-5-methyl phenyl)methane (Pfaltz and Bauer, Inc.) was used as a radical scavenger. Deuterated THF (98% THF-*d*₈) (Aldrich Chemical Co.) was used as solvent for the determination of ¹H n.m.r. spectra.

Preparation of partially brominated PB

PB (0.5 or 1.0 g, 9.3×10^{-3} , or 8.6×10^{-2} moles butadiene units) was dissolved in 160 ml of dichloromethane; the solution was filtered through a sintered glass filter and diluted with the co-solvent to obtain 200 ml of 0.25 or 0.5% polymer solution. Chloroform, THF, 1,4-dioxane and 1,2-dibromoethane were used as co-solvents with dichloromethane. The solution was placed in a 250 ml three-neck, round-bottom flask equipped with a stirrer and a gas inlet and exit. The bromine solution (0.1–0.5 ml bromine/1 ml solution in dichloromethane) was added to the PB solution with a syringe. The solution was kept stirring for 30 min after all of the bromine had been added. Bis(2-hydroxy-3-*t*-butyl-5-methyl phenyl)methane (0.1 wt% of polymer) was then added to the solution, which was concentrated under reduced pressure (0.1 mm) and the residual solution (60 ml) poured into 1 l of methanol. The polymer precipitated, was filtered, washed thoroughly with methanol, and dried at 0.1 mm. To prepare a uniform film, the polymer was redissolved in THF (10% polymer solution) and cast on a glass plate. All operations were carried out under exclusion of any oxygen whenever possible.



Measurements

Infra-red spectra of brominated PB were measured with a Perkin-Elmer 180-IR or 727 Infra-red spectrophotometer on cast film. ¹H n.m.r. spectra were de-

termined in deuterated THF (THF-*d*₈) at room temperature on a 60-mHz Hitachi Perkin-Elmer R-24 NMR spectrometer. The concentration of polymer in THF-*d*₈ was about 10% (w/v).

¹³C n.m.r. spectra were measured in THF at room temperature on a Varian CFT-20 spectrophotometer. The concentration of polymer solution was between 20 and 25% (w/v) and at least 9000 transients were taken.

D.s.c. measurements were carried out with a Perkin-Elmer DSC-2 calorimeter fitted with scanning autozero at a scanning rate of 20°C/min with sample sizes of 10 to 20 mg. The DSC-2 calorimeter was calibrated against cyclohexane which had two transitions (crystal transition at 186.1 K and melting at 279.7 K) in the desired temperature range. The *T*_g was taken as the temperature at which one half of the step change in heat capacity associated with the glass transition was achieved.

Elemental analyses were done by the Microanalytical Laboratory Office of Research Services, University of Massachusetts, Amherst, Massachusetts (Table 1).

RESULTS AND DISCUSSION

PB of high molecular weight and high *cis* content was partially brominated to polymers which had degrees of bromination of 20% up to complete bromination. These polymers were characterized by spectroscopic techniques and their molecular structures determined. The phase behaviour of these polymers was studied by d.s.c. measurement.

Partial bromination of PB

For the chlorination of PB, dichloromethane has been used as the solvent, and only addition to the double bonds of the polybutadiene but no substitution in the methylene group by chlorine was observed⁵⁻⁷. The chlorination proceeded in solution not only for low degrees of chlorination but also for complete chlorination.

Initial experiments on the bromination of PB in dichloromethane as the sole solvent resulted in precipitation of the polymeric bromination product soon after the bromination had started even though the reaction was carried out in 0.25% polymer solution and even though the bromination was carried out with vigorous stirring to avoid as much as possible local excess of bromine. Consequently, a possible use of some co-solvents had to be investigated in attempts to keep the brominated PB in solution and to achieve complete bromination. The maximum amount of dichloromethane was retained in the solvent mixture as it was a solvent of proper polarity, and it was suspected that in this solvent the bromine addition to the double bonds occurred through an ionic mechanism without substitution on the methylene group adjacent to the -CH=CH- unit.

1,2-Dibromoethane (20% by volume) was found to be the most efficient co-solvent with dichloromethane for the bromination of PB. A series of partially brominated PBs were prepared with this solvent system; the concentration of PB was kept below 0.5% in all the bromination reactions.

THF could also be used as a co-solvent with dichloromethane for the bromination of PB, but with some limitations. It was found that the minimum concentration of THF in dichloromethane to keep 0.5% polymer solutions homogeneous throughout the bromination was 4%; PB

Table 1 Elemental analysis of partially brominated *cis*-1,4-polybutadiene

Sample	Solvent ^a	Content (wt%)			H/C (wt/wt)	Bromination ^b (%)
		C	H	Br		
A	—	89.02	11.40	0.00	0.128	0
B	T	55.83	6.91	37.30	0.124	20
C	Br	51.03	6.51	42.74	0.128	25
D	T	39.59	4.88	54.79	0.123	41
E	T	36.82	4.62	55.84	0.125	43
F	Br	36.02	4.40	59.62	0.122	50
G	T	30.16	3.80	64.09	0.126	60
H	T	25.19	3.37	70.42	0.134	80
I	Br	24.94	3.25	72.51	0.130	89
J	Br	22.99	2.89	74.25	0.126	100 ^c

^aT: Dichloromethane/THF (96/4), Br: Dichloromethane/1,2 dibromomethane (8/2)

^bCalculated from the following equation:

$$\text{Degree of bromination} = \frac{54(\text{Br content})}{159.8 \left(1 - \frac{\text{Br content}}{100} \right)}$$

^cJudged from its ¹³C n.m.r. spectrum, J was 100% brominated PB

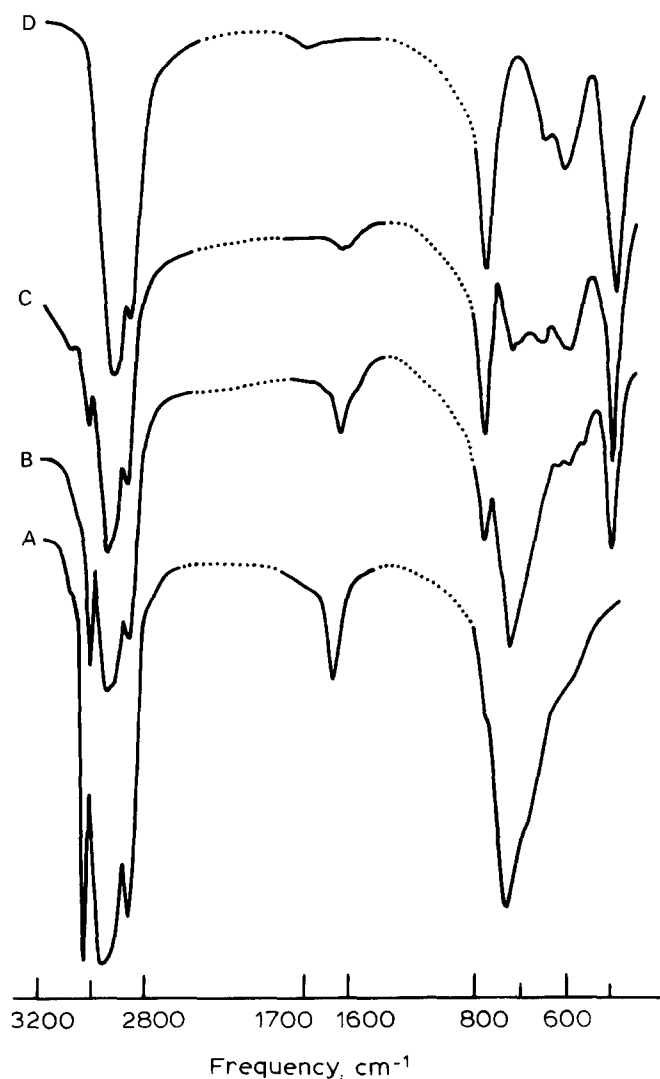


Figure 1 Infra-red spectra of partially brominated *cis*-1,4-polybutadiene: A, *cis*-1,4-polybutadiene; B, 41% bromination; C, 60% bromination; D, 100% bromination

was brominated effectively in this mixed solvent system. Although THF as a co-solvent was useful to prevent precipitation of the polymer as bromination proceeded, it was not the most effective solvent for bromination to high degrees of bromination.

The mixed solvent system of 5% of 1,4-dioxane in dichloromethane or in a chloroform/dichloromethane mixture (1:2), which was an effective solvent for the homogeneous chlorination⁶, could not be used as brominated PB precipitated early in the bromination reaction.

Partial bromination of PB was carried out at 0°C and -20°C. Since no advantage was found in conducting the reaction at the lower temperature, all subsequent brominations were carried out at 0°C. The bromine solution was added to the PB solution dropwise and was dispersed quickly in the stirred mixture; the bromine colour faded within minutes.

Complete exclusion of oxygen from the bromination reaction of PB was essential as bromine catalyses oxidation reactions. Oxidation is not catalysed by chlorine to the same degree. With this precaution, the absence of oxidation products could be demonstrated in a successfully brominated sample of PB by the investigation of the infra-red spectrum.

It is well known that under the conditions we adopted, addition of bromine to a double bond proceeds by a cationic mechanism with a bridged, positively charged bromonium ion as the intermediate. It was therefore of interest to estimate a possible contribution from a radical mechanism to the bromine addition to the double bonds of PB. Bromine addition was consequently carried out in the presence of a radical scavenger (2 wt% of polymer) and by careful exclusion of light. An amount of bromine necessary for 100% bromine addition was added, and the degree of bromination of the bromination product was 90%. It was concluded that the radical addition probably does not contribute significantly to the bromine addition as the stereochemistry of the product identified by ¹³C n.m.r. spectroscopy was not distinguishable from the product obtained without radical scavenger.

The characteristics of the infra-red spectra of *cis*-1,4-PB and its successive bromination products up to completely brominated PB are illustrated in Figure 1. The progress of the bromination of PB can be followed by the decrease of the absorption of 3005 cm⁻¹ and 1655 cm⁻¹ typical of unsaturation. With the increase in the degree of bromination, the band at 735 cm⁻¹ (C-H rocking) also decreased and the band at 545 cm⁻¹ (C-Br stretching) increased. The ratio of these two bands could be used to measure the degree of bromination. Another C-Br stretching band was observed at 625 cm⁻¹, but it was less characteristic. Other bands which increased in intensity

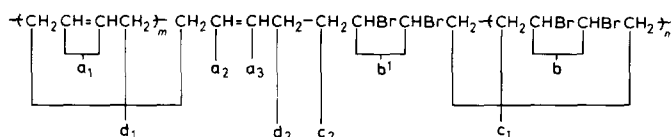
Table 2 Chemical shift data of ¹H n.m.r. spectra* of partially brominated *cis*-1,4-polybutadiene

Sample	τ (centre)		
	-CH=	-CHBr-	-CH ₂ -
<i>cis</i> -1,4-Polybutadiene	4.5-4.7(4.59)	—	7.8-8.0(7.89)
25% Brominated PB	4.4-4.8(4.59)	5.5-5.9(5.74)	7.6-8.2(7.94)
100% Brominated PB	—	5.6-5.9(5.74)	7.6-8.2(7.94)

* Obtained in 10% polymer solution of THF-d₈ at room temperature on a 60 MHz n.m.r. spectrometer

Table 3 Chemical shift data of ^{13}C n.m.r. spectra* of partially brominated *cis*-1,4-polybutadiene

Signal	Chemical shift (p.p.m. downfield from TMS)	Assignment
1	131.5	a ₃
2	130.0	a ₁
3	128.4	a ₂
4	59.8	b, b', b
5	58.9	
6	36.1	c ₂
7	35.7	
8	34.7	c ₁
9	28.0	d ₁
10	27.1	d ₂



* Obtained in 20–25% solution of THF at room temperature

with the increase in the degree of bromination were 1295 cm^{-1} (CH wagging), 1095 cm^{-1} (C–H rocking) and 780 cm^{-1} (CH rocking), while 1310 cm^{-1} (CH wagging) and 995 cm^{-1} (CH rocking) decreased with increasing degree of bromination. Drehfahl has shown earlier infrared spectra of brominated *cis*- and *trans*-1,4-PB and their stereospecific model compounds¹⁰. According to these data, the differences in specific i.r. absorption peaks between the threo and erythro isomers of the model compounds are very small. The absorption at 530 cm^{-1} seems to distinguish between the erythro and threo isomers but is partially overlapped by a band at 545 cm^{-1} ; consequently, the stereochemistry of the polymer cannot be determined on the basis of the infrared data alone.

Partially brominated polybutadiene samples were also characterized by n.m.r. spectroscopy. The ^1H n.m.r. spectra (Table 2) showed the presence of chemical shifts between 5.5 and 5.9 ppm, centring at 5.74 ppm; the value of CHBr is 7.6 to 8.3 ppm (centring at 7.94 ppm) for CH_2 protons in addition to the chemical shift of the CH protons between 4.0 and 4.8 ppm. These peaks did not give sufficient information for determining either the sequence of individual groups or their configuration. It is expected that some increase in resolution, but no dramatic improvement of the ^1H n.m.r. spectra, could be obtained by taking spectra at higher magnetic fields.

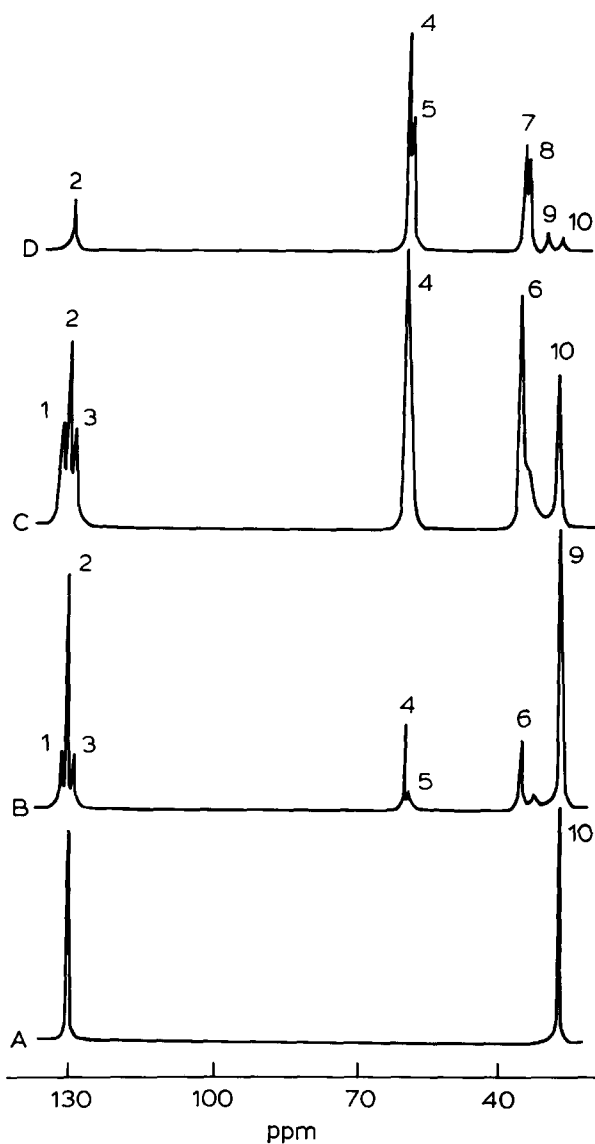
Much more information could be obtained by the study of the ^{13}C n.m.r. spectra of samples of partially brominated PB; spectra of samples obtained by bromination in dichloromethane/1,2-dibromomethane (4:1) are shown in Figure 2 and Table 3. The numbers of the carbon atoms in Table 3 refer to Figure 2. The results of this study allow us to draw conclusions about the configuration of the CHBr relative to other neighbouring groups and also give some indication about long-range order including the development of sequences of butadiene units and $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ units. For comparison the ^{13}C n.m.r. spectra of H–H PVB and H–T PVB are shown in Figure 3.

Important are the peaks (1 + 3) and peak 2 on spectra B and C in Figure 2. Peaks 1 and 3 represent the vinyl carbon atoms of butadiene units adjacent to $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ units as is the case of partially chlorinated PB⁶. Peak 2 (centre) represents vinyl carbon atoms of butadiene unit sequences, and the ratio of these

peaks represents in first approximation a measure of the block structure of the partially brominated PB chain.

If the bromination occurred statistically, as in 2% brominated polybutadiene, 33 butadiene units would be separated by one brominated unit per 100 butadiene units. Statistical bromination to a 50%-brominated polybutadiene would leave 3.7 nonbrominated butadiene units adjacent to brominated butadiene units per 100 original butadiene units. As a consequence, the peak area ratio of peaks (1 + 3) to peak 2 should be $0.79 [= 33/(100-33-25)]$ for 25%-brominated butadiene and 3.00 for 50%-brominated polybutadiene. The actual measured values for these peaks were 0.54 and 2.23 for these polymers. These data are in relatively good agreement with the values obtained for the chlorination of PB, but are 15% smaller than the statistical values⁶. It is consequently concluded that the bromination of PB in dichloromethane/1,2-dibromoethane proceeded in a more random fashion.

In addition to the question of randomness or blockiness of the polymer which describes the relationships between


Figure 2 ^{13}C n.m.r. spectra of partially brominated *cis*-1,4-polybutadiene: A, *cis*-1,4-polybutadiene; B, 25% bromination; C, 50% bromination; D, 89% bromination

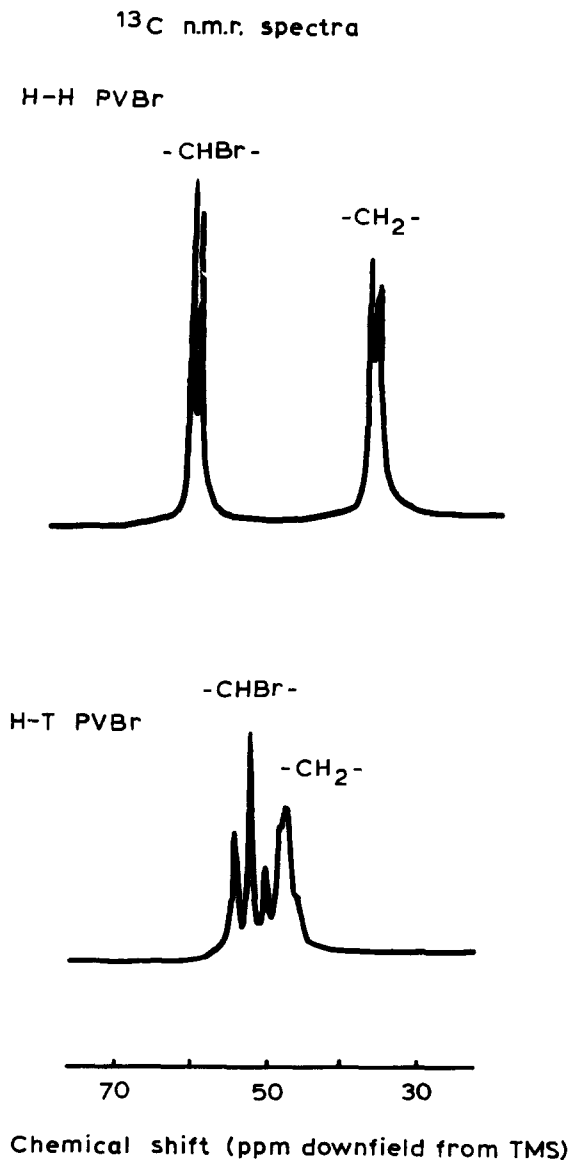


Figure 3 Comparison of ^{13}C n.m.r. spectra of head-to-head poly(vinyl bromide) and head-to-tail poly(vinyl bromide)

the butadiene units and the $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ units, the relative stereochemistry of the carbon atoms to which the bromine atoms are attached is of importance and could be determined by ^{13}C n.m.r. spectroscopy. Many cases of ionic halogenation of alkenes showed preferential *trans* addition leading to the formation of the *threo* isomer on halogenation of the *cis* isomer of the internal olefin. This stereospecificity of addition, if it occurs, is generally considered a result of the formation of an intermediate which has a bridged halogen cation structure in back of the anion which would then lead to the *trans* addition. This tendency toward the formation of the *trans* addition product is more pronounced with bromine than with chlorine since bromine is the better bridging atom¹¹.

As shown in Figure 2, the methine carbon of brominated butadiene units in 25%- and 50%-brominated PB had one ^{13}C n.m.r. peak accompanied by a very small peak or a slight shoulder on the upfield side. The relative intensity of the upfield peak to the downfield peak increased as the degree of bromination increased from 50% to 100%. In the 100%-brominated PB, the upfield

peak has almost the same intensity as the downfield peak. A similar phenomenon was also observed when the peaks of the methylene carbon of the $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ units between 34 and 36 ppm were inspected. This apparent change of the stereochemistry during the bromination is substantially different from the observation during the chlorination of PB. Two pairs of chemical shift values in chlorinated PB, in the range of 65.7 to 66.1 ppm and 32.9 to 33.6 ppm, have been observed; however, the relative intensity of these peaks remained constant throughout the chlorination. It can consequently be concluded that the chlorination of PB was not stereospecific and erythro and *threo* linkages were formed in the ratio of nearly 1:1. The change in the stereospecificity of the addition of bromine to the double bond of PB seems to occur as the bromination of PB proceeds (in the dichloromethane/1,2-dibromoethane mixture) and the initial stereospecific addition is followed by an increasing contribution of random addition most probably caused by configurational restriction of the polymer chain in solution.

If the downfield atom (peak 4, in Figure 2) is assigned to the carbon of the erythro isomers, one would have to conclude that the bromination of PB occurred by *cis* addition in the early stage, followed by *trans* addition as the preferential addition in the latter stages of the polymerization.

A second and more plausible explanation for the effect is that conformational restrictions develop in higher brominated materials, which give higher energy to the rotamer of the lowest energy, and consequently result in the contribution of the other rotamers to the total conformation which cause some change of chemical shift values in the ^{13}C n.m.r. spectrum. The energy difference between the conformations of each isomer is suspected to be small, and sizable and bulky bromine atoms can provide enough restrictions to overcome these differences. One must consider the polymer effect in the addition of bromine to a double bond in PB when bromination of low molecular weight analogues proceeds to pure geometric isomers.

The orientation of the rotamers of the two halogen atoms of the meso and racemic isomers of the 2,3-dichlorobutanes have been investigated¹². According to ^1H n.m.r. studies¹³, the most stable rotamer for erythro-2,3-dichlorobutane is the rotamer with the chlorine atoms

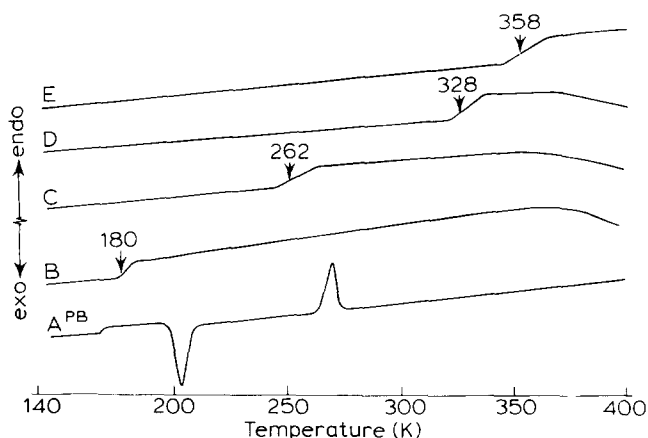


Figure 4 D.s.c. thermogram of partially brominated *cis*-1,4-polybutadiene brominated solvent: dichloroethane/1,2-dibromoethane (4:1): A, *cis*-1,4-polybutadiene; B, 25% bromination; C, 50% bromination; D, 89% bromination; E, 100% bromination

Table 4 D.s.c. data of transition temperatures^a of partially brominated *cis*-1,4-polybutadiene^b

Degree of bromination (mol %)	w ₂ (weight fraction of PVB)	T _g ^b (K)
0	0.00	165 ^c
25	0.57	180
50	0.80	262
89	0.97	328
100	1.00	358

^a Scanning rate 20°C/min^b Bromination in dichloromethane/1,2-dibromoethane (80/20) and precipitation in methanol^c Temperature of crystallization: 203 K, melting temperature: 270 K**Table 5** D.s.c. data of transition temperatures^a of partially brominated *cis*-1,4-polybutadiene^b

Degree of bromination (mol %)	w ₂	Film or precipitate	T _{gL} ^d (K)	T _{gH} ^e (K)
0 ^c	0.00	f	165	—
20 ^c	0.50	f	170	320
41	0.74	f	197	314
43	0.75	f	194	320
		p	198	323
60	0.86	f	203	323
80	0.94	f	—	331

^a Scanning rate: 20°C/min^b Bromination in dichloromethane/THF (96/4) and cast into film or precipitated in methanol^c Temperature of maximum rate of crystallization: 203 K; melting temperature: 270 K^d T_{gL} refers to the T_g observed at lower temperatures^e T_{gH} refers to the T_g observed at higher temperatures

trans, although it is proposed that all three rotamers (1 *trans* and 2 *gauche* structures) are equally populated in threo-2,3-dichlorobutane. On the other hand, it was found that the *trans* rotamer of threo-2,3-dibromobutane was most stable¹⁴. If the *trans* rotamers are the most stable configuration of the erythro- and threo-2,3-dibromobutane isomers, the methine carbon atom of each isomer would have a similar environment with respect to the bromine atoms in the *trans* position; no chemical shift difference would be expected. This situation might actually occur in brominated PB of low degree of bromination, and the conformational restrictions caused by the polymer chain could readily cause a change and restrictions in the probability of the occurrence of rotamers in highly brominated polybutadiene.

A more extensive study is, however, needed to explain all the effects and give a complete picture of the ¹³C n.m.r. assignment of the chemical shift peaks, which in turn will lead to a better understanding of the mechanism of halogenation.

Morphology of partially brominated polybutadiene

Partially chlorinated PB shows two T_g's, which indicates the existence of a microphase-separated morphology in this polymer⁶. The thermal behaviour of samples of partially brominated PB were investigated, not only to obtain information about their T_g but also to find out about their morphology. It was necessary in this study to use two sources of partially brominated PBs. One set of samples was brominated in dichloromethane/1,2-dibromoethane. Information from their ¹³C

n.m.r. spectra made it apparent that these polymers were random polymers of butadiene units and -CHBr-CHBr- units. Another series of brominated PBs were obtained in the dichloromethane/THF mixed solvent system. These polymer samples were not as extensively studied as the reaction did not proceed stoichiometrically in the latter part of the bromination.

The thermal behaviour of the samples of brominated PB obtained by addition of bromine in dichloromethane/1,2-dibromoethane mixed solvent system by d.s.c. are shown in Figure 4. PB showed a glass transition temperature of 165 K, a maximum temperature of crystallization of 203 K, and a melting temperature of 270 K. For the partially brominated PB, only one T_g, the T_g of PB, was observed up to a degree of bromination of about 50%. The T_g of samples of partially brominated PBs increased as the degree of bromination increased. We have used the Fox-Flory equation for random copolymers to estimate the composition dependence of T_g,

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where w₁ and w₂ are the weight fractions of the component polymers (in our case they are weight fractions of PB segments and -CH₂-CHBr-CHBr-CH₂- segments). T_{g1}, T_{g2} and T_g are the glass transition temperatures for the component polymers and for the copolymer, respectively. The T_{g1} and T_{g2} in our systems were 165 K and 358 K, as indicated in Table 4. In Figure 6, the T_g of the PB brominated in dichloromethane/1,2-dibromoethane were plotted together with the theoretical curve obtained from the Fox equation. Our values deviated somewhat from the theoretical curve, but data for 50% and 89% brominated PB were quite close to the theoretical curve. It was consequently assumed on the basis of the d.s.c. data that no appreciable phase separation occurred. This observation was also strengthened by the fact that no crystallization exotherm or melting endotherm was found in the d.s.c. thermogram of 25%-brominated PB, which indicated that the brominated phase probably has some miscibility with the PB phase and does not phase separate. This observation is also understandable as ¹³C n.m.r. spectroscopy has indicated a random sequential distribution of -CHBr-CHBr- units during the early period of bromine addition to PB.

D.s.c. thermograms of cast films of partially chlorinated PB had shown⁶ a tendency to display a broad exotherm at

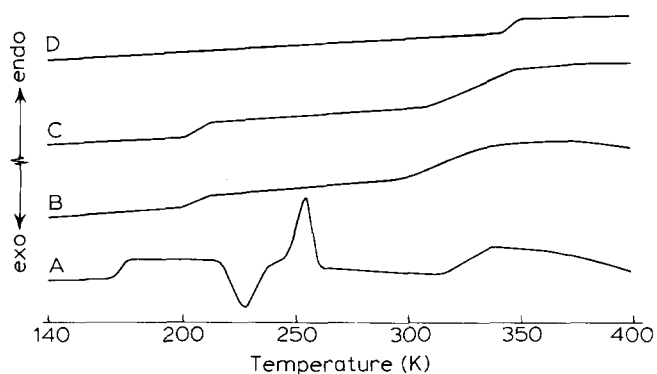


Figure 5 D.s.c. thermogram of partially brominated *cis*-1,4-polybutadiene brominated solvent: dichloromethane/THF (96/4): A, 20% bromination; B, 41% bromination; C, 60% bromination; D, 80% bromination

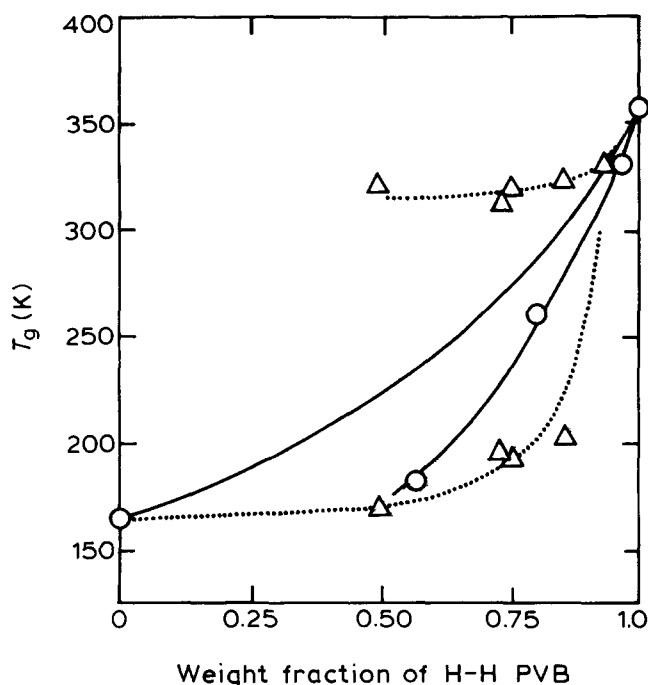


Figure 6 T_g correlation of partially brominated *cis*-1,4-polybutadiene as a function of weight fraction of poly(vinyl bromide): O, brominated in dichloromethane/1,2-dibromoethane and precipitated; ▲, brominated in dichloromethane/THF and cast; △, brominated in dichloromethane/THF and precipitated

temperatures just above the glass transition temperature. This phenomenon made it difficult to determine accurately the higher glass transition temperature which was the T_g of the chlorinated phase. As a consequence, only precipitated polymer samples were used to determine the T_g by d.s.c. of partially chlorinated PB. All the d.s.c. thermograms of partially brominated PB in Figure 4 display an even more marked exotherm behaviour above 350 K, although samples of precipitated polymer were used. The exothermic deviation from the baseline above the T_g of the polymer is believed to be caused by crystallization of the $-\text{CHBr}-\text{CHBr}-$ units; it suggests that sequences of these units may be more crystallizable than the corresponding $-\text{CHCl}-\text{CHCl}-$ units. A more accurate study could not be undertaken as significant polymer degradation above 400 K always occurred and could not be eliminated.

The thermal behaviour of another series of brominated PB prepared by bromine addition to PB in dichloromethane/THF mixed solvent solutions have been investigated and are shown in Figure 5. Samples of these polymers were either precipitated into methanol or cast into a film. Only the 20%-brominated PB exhibited crystallization and melting of the PB-rich domain. All partially brominated PB up to a degree of bromination of 80% showed clearly two T_g 's. The results are plotted on the Fox relation in Figure 6. The bromination products from this solvent system yielded results which are quite different from those observed in the bromination experiments in dichloromethane/1,2-dibromoethane. Clear evidence of the formation of a block structure of $-\text{CHBr}-\text{CHBr}-$ units is indicated and is responsible for the microphase separation. Although a sample of 40%-brominated PB showed its lower T_g on repeated d.s.c.

scanning, the samples brominated to a 61% conversion showed the low-temperature T_g which is attributed to the PB phase only in the d.s.c. thermogram of the first scanning. The dependence of the low T_g and the high T_g on the degree of bromination (or w_2 of the weight fraction of $-\text{CHBr}-\text{CHBr}-$) is small, and its dependence is similar to that of chlorinated PB.

For a sample of 43%-brominated PB, the thermal behaviour of a cast film was compared with that of a precipitated polymer. There were no appreciable differences either in the T_g value or in the extent of the endotherm at the glass transition temperature. For these types of polymers, the sample preparation or the isolation of the polymers does not seem responsible for the thermal behaviour of the samples, and, indeed, the preparation of this particular sample appears to have only a minor influence on the polymer morphology.

Judging from the numerical value of the T_g , it appears that the PB domain of the PB brominated up to a degree of bromination of 20% is essentially free of $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ rich polymer. However, samples of 41% and 60% bromination contain approximately 10 mol% of brominated units. On the other hand, in the phase-separated system of the brominated PB phase, it is estimated that 15–20% of butadiene units, at least one unit adjacent to each 5–6 brominated units, is incorporated in the $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ phase. Above a degree of bromination of 80% ($w_2=0.94$), the polymer shows only one phase in its morphological structure, the $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ phase.

The clear difference between the morphology of polymers prepared in different solvent mixtures of dichloromethane indicated that the bromination had occurred either in block or in a more random fashion and developed a different sequence of PB units and $-\text{CH}_2-\text{CHBr}-\text{CHBr}-\text{CH}_2-$ units. The formation of block structures was indicated not only in the halogenation of PB^{6,15} but also in some addition reactions on the double bonds of PB or natural rubber^{16,17}. The detailed mechanism of the bromination reaction of PB is still not completely understood.

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