Head-to-head polymers:
19*. Chlorination of *cis*-1,4-polybutadiene

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Chlorination of *cis*-1,4-polybutadiene (PB) has been studied in detail. It was found that chlorination must be carried out in an oxygen free atmosphere at polymer concentrations below 0.5%, and at temperatures below room temperature in mixed solvents with dichloromethane as the major component. In the initial stage of chlorine addition to the double bonds of *cis*-1,4-polybutadiene, block structures of chlorinated segments are formed. The chlorine addition to the *cis*-butadiene units was not stereospecific and the final chlorination product had nearly a 1:1 ratio of the threo- and erythro structure of the –CHCl–CHCl-units. Microphase separation in partially chlorinated PB was observed by d.s.c., dynamic–mechanical measurement, and transmission electron microscopy. It was concluded that partially chlorinated PB, whose degree of chlorination was lower than 65 mole %, was composed of almost pure *cis*-1,4-PB domains and a separate phase which consists of $-CH_2-CHCl-CHCl-CH_2-$ units with perhaps as much as 10% of *cis*-1,4-PB units incorporated in this phase. If the degree of chlorination is more than 90 mole % one phase exists.

Keywords Head-to-head poly(vinyl chloride); polybutadiene chlorination; polybutadiene partial chlorination; poly(vinyl chloride) stereochemistry; chlorinated polybutadiene glass transition temperature

INTRODUCTION

Head-to-head poly(vinyl chloride) (H–H PVC) is equivalent to a product where all the double bonds in 1,4 polybutadiene (PB) are completely chlorinated. If the starting 1,4-PB[1] was stereochemically pure, and the chlorination proceeded stereospecifically, the final polymer could be a stereoregular polymer of H–H PVC.

Chlorination of emulsion polymerized butadiene rubber was investigated in the 1950's[1]. The chlorination was carried out with PCl_5, but the final polymer had a complicated structure since the PB used for the chlorination had 1,2 and 1,4 linkages, along with the geometric isomers of 1,4-PB. Chlorination performed under these conditions caused not only chlorine addition to the double bonds, but also substitution by chlorine in the α-position to the double bond, cyclization and crosslinking. Depending upon the chlorination conditions, 80 to 110% of the theoretical chlorine uptake was registered. Consequently, the chlorination of the PB prepared by emulsion polymerization did not give a well defined product.

The first attempt to prepare H–H PVC[2] was made by chlorinating a 95–98% *cis*-1,4-PB at low temperature and in the presence of a $FeCl_3$ catalyst to prevent radical chlorination which was believed to be the cause of chlorine substitution and crosslinking[3]. In a parallel experiment, *trans*-1,4-PB was chlorinated at room temperature and the structure of the chlorinated PB was evaluated by inspection of the i.r. spectrum between 600 and 800 cm^{-1}. It was observed that chlorination of both *cis* and *trans* 1,4-PB (0.5% chloroform solution) proceeded rapidly to an uptake of about 50% chlorine and then the reaction slowed down. Chlorination of *cis* and *trans*-1,4-PB in 1% chloroform solution gave chlorination products with slightly lower chlorine content, (according to chlorine analysis) but solution properties[4] of these polymers were still studied. The i.r. spectra of chlorinated PBs (H–H PVC) were also studied and compared with oligomeric model compounds (dimers and trimers) of known stereochemistry[5,6].

In subsequent investigations[7–9], chlorination of predominantly *cis*-1,4-PB (*cis-trans* ratio 92/4 with 4% 1,2 units) and *trans*-1,4-PB (*cis-trans* ratio 1/99) was studied. This was part of a general study of the halogenation of polyalkenamers and many of the broad generalizations about chlorinations were based on work on polypentenamers. It was suggested that chlorination of polypentenamers occurred in blocks with long chlorinated segments alternating with substantially unchlorinated segments. Chlorinated block structures rather than random structures in partially chlorinated products were observed as the chlorination temperature was lowered. The chlorination of poly'butenamer' (PB) was only briefly investigated. It was postulated[8] that the chlorination of the PB's proceeded by a succession of *trans* additions with no random isomerization of the double bonds. On the basis of this proposal, *cis*-1,4-PB was expected to give poly(threo-1,2-dichlorobutane) and *trans*-1,4-PB poly(erythro-1,2-dichlorobutane).

For the chlorinations of PB's in this work[8], the recommended reaction conditions were: dichloromethane as the solvent, and 0.2–1% polymer solutions at temperatures between −20°C and +20°C (crystalline, high molecular weight *trans*-1,4-PB had to be chlorinated at slightly higher temperatures, at 30°–40°C, because of lower solubility).

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In the chlorination studies of PB in the past, the progress and completeness of chlorination was often followed by chlorine elemental analyses only, although chlorine analyses at more than 50% of chlorine content are known to be often 1–2% lower than the theoretical value.

Some physical measurements of the solid state properties of completely chlorinated PB's such as the T_g and the X-ray structure of the polymers were determined[10]. It was mentioned that a sequence of 10 monomer units of –CHCl–CHCl– units was sufficient to display crystallinity. Interpretation of the fibre diagram of these polymers allowed the calculation of a polymer structure which led to the proposal of structures of H–H erthro PVC and H–H threo PVC.

It was the purpose of this work to study the progress of the chlorination of high molecular weight PB with high *cis*-1,4 content. The chlorinated products were to be identified by ^{1}H n.m.r., ^{13}C n.m.r. and i.r. spectroscopy and by elemental analysis. Furthermore, the T_g of the chlorinated phase and the morphology of the polymers were to be determined as the degree of chlorination increased.

EXPERIMENTAL

Materials

Cis-1,4-polybutadiene (PB) was supplied by Snam Progetti Co., San Donato, Milano, Italy. The polymer was prepared by polymerization of butadiene with UO_2 (allyl)$_3$ as initiator[11] and consisted of 98.6% *cis*, 1.0% *trans* and 0.4% 1,2 structure.

The inherent viscosity of *cis*-1,4-PB in toluene at 30°C was 4.0 dL/g. *Cis*-1,4-PB solutions in dichloromethane were prepared and filtered through a sintered glass filter in a nitrogen atmosphere prior to use even though no precipitate was ever detected. Dichloromethane, chloroform, and methanol (all from Fisher Scientific Co.) were distilled at 760 mm. The solvents were deoxygenated by passing oxygen free dry nitrogen gas through the solutions before use.

Tetrahydrofuran (Fisher Scientific Co.) (THF) was distilled from lithium aluminum hydride (Ventron Alfa Products (LAH)) in a nitrogen atmosphere.

Chlorine gas (Union Carbide Co.) was passed through distilled water and dried by passing it through 96% sulphuric acid.

Bis(2-hydroxy-3-tert-butyl-5-methyl-phenyl) methane (Pfaltz and Bauer, Inc.), the antioxidant, was used as received.

For ^{1}H n.m.r. work deuterated THF (Aldrich Chemical Co.) was used.

Measurements

The infra-red (i.r.) spectra of chlorinated PB were taken as cast films. A Perkin–Elmer 283 or 727 spectrophotometer was used. ^{1}H n.m.r. spectra were measured in deuterated THF at room temperature on a 60 MHz Hitachi Perkin–Elmer R-24, or at elevated temperature (80°C) on a 90 MHz Perkin–Elmer R-32 spectrophotometer. ^{13}C n.m.r. spectra were recorded in 25% THF solution at room temperature with more than 10 000 transients on a Varian CFT-20 spectrophotometer. Pulse interval, pulse width and the number of data points were 1.023 s, 15 ms and 8192, respectively, for all ^{13}C n.m.r. spectra.

A Perkin–Elmer differential scanning calorimeter (DSC-2) fitted with Scanning Autozero (SAZ), was used for the determination of the glass transition temperature (T_g) and the thermal behaviour of the polymers. D.s.c. scans were obtained at a heating rate of 20°C/min with sample sizes from 10 to 20 mg. The temperature at one half of the ΔC_p of transition was taken as the T_g.

Dynamic mechanical characterization was carried out with a Rheovibron Dynamic Viscoelastometer Model DDV II (Toyo Measuring Instrument Co., Tokyo, Japan) in the temperature range of 130K to 370K at a frequency of 110 Hz and at a heating rate of approximately 1°C/min.

The morphology of films of partially chlorinated PB was examined with a JEOL 1000 CX scanning transmission electron microscope equipped with a tungsten hairpin filament and operated at 100 KV in transmission mode. Thin films of 53% chlorinated PB were prepared by casting a 0.5% solution of the polymer in THF onto mica and allowing it to evaporate into a nearly saturated THF atmosphere. For comparison, a solution of 47% PVC and 53% PB in THF was prepared and films were cast similarly. Some of the films were stained by exposing them to osmium tetroxide vapour for one hour.

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

Preparation (partial chlorination)

Cis-1,4-PB (1.0 g, 18.6 mmole butene units) was dissolved in 200 ml of dichloromethane. When a high degree of chlorination of *cis*-1,4-PB was desired, a mixed solvent of chloroform (65 ml) and dichloromethane (135 ml) for 1.0 g of *cis*-1,-PB was used to keep the reaction system homogeneous in the later stages of the reaction. The *cis*-1,4-PB solution was placed in a 250 ml three-neck round-bottom flask equipped with a stirrer and nitrogen inlet and exit tubes. To measure the volume accurately, chlorine was condensed in a graduated cylinder; it was then vapourized and passed into the solution of *cis*-1,4-PB at 0°C at the rate of 0.02 ml min^{-1} (equation (1)). The polymer solution was stirred for an additional 30 minutes after the chlorine addition was completed, and the antioxidant (0.1 wt% with respect to polymer) was added to the solution. The solution was concentrated under reduced pressure (0.1 mm) to a volume of 60 ml and then poured into methanol (one litre) to precipitate the polymer. The polymer was filtered, washed with methanol, and dried for one day at 0.1 mm.

Occasionally chlorinated PB samples were cast directly without isolation of the polymer after the chlorination was completed, but casting of the polymers was usually done from THF solutions of the precipitated polymer.

Oxygen must be completely excluded from all procedures, otherwise oxidation and/or crosslinking occurs, especially when products with a higher degree of chlorination are investigated.

RESULTS AND DISCUSSION

Cis-1,4-PB of high molecular weight which contained only about 0.4% 1,2- and 1.0% *trans*-1,4-PB linkages, was chlorinated to give polymers with various degrees of chlorination including completely chlorinated PB, which

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

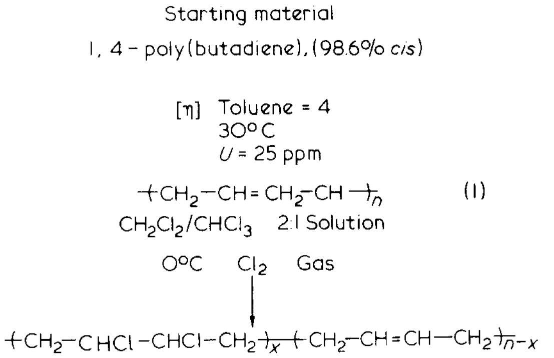
Sample	Content (wt %) C	H	Cl	H/C ratio (wt/wt)	Degree of[a] chlorination %
A	89.02	11.40	0.00	0.128	0
B	67.77	8.77	22.47	0.129	22
C[b]	56.18	7.26	34.69	0.129	40
D	56.56	7.13	35.73	0.126	42
E[b]	55.29	6.67	37.69	0.121	45
F[b]	52.10	6.60	40.38	0.127	52
G[b]	49.86	6.45	42.84	0.129	57
H	48.05	6.01	46.27	0.125	65
I[b]	41.57	5.42	50.55	0.130	78
J[b]	42.43	5.46	51.49	0.129	81
K[b]	41.05	5.27	52.77	0.128	85
L[b]	37.91	4.79	57.20	0.126	100
M[b,c]	51.56	6.49	42.07	0.126	55

[a] Calculated from the following equation:

$$\text{Degree of chlorination} = \frac{54\ (\text{Cl content})}{71\left(1 - \dfrac{\text{Cl content}}{100}\right)}$$

[b] Chlorinated in mixed solvent

[c] Chlorinated in the presence of potential radical scavenger



is equivalent to H-H PVC (equation (1)). The progress of chlorination was followed by i.r., and ^{13}C n.m.r. spectroscopy and by elemental analysis (see *Table 1*). Partially chlorinated *cis*-1,4-PB has interesting physical and mechanical properties. The glass transition temperature (T_g), and dynamic mechanical properties of several partially chlorinated polymers were measured. The chlorination products of *cis*-1,4-PB were also characterized by *TEM*.

Partial chlorination of cis-*1,4-PB*

The chlorination of *cis*-1,4-PB was carried out in a 0.5% solution in dichloromethane. When attempts were made to produce polymers with degrees of chlorination higher than 65%, the reaction mixture became inhomogeneous. A mixture of dichloromethane and chloroform in a volume ratio of 2:1 was necessary to keep more highly chlorinated PB in solution. This limited solubility of chlorinated PB had not been observed in previous investigations[8-11]. Apparently these investigators used PB of low molecular weights which remained in solution, even at high degrees of chlorination. The chlorination of *cis*-1,4-PB with chlorine gas proceeded rapidly and complete chlorination was achieved within 50 minutes. The degree of chlorination was found to be proportional to the amount of chlorine charged up to 85% chlorination (*Figure 1*). Above this level the reaction became slower and complete chlorination was only possible with an excess of chlorine. The reaction was carried out either at 0° or −20°C but this temperature difference did not influence the chlorine uptake or the structure of product obtained. As a matter of convenience, all chlorinations were subsequently carried out at 0°C.

Earlier workers suggested that chlorine addition to the double bond is not the sole reaction, but that chlorine substitution also played a role at higher degrees of chlorination. Some investigators[8,12] claimed to have noticed chlorine substitution, when the reaction was carried out in chloroform solution. We have no indication that this was the case in our chlorination reactions. Nevertheless, in our experiments we have kept the amount of chloroform to a minimum in the solution mixtures.

One of the important aspects of the chlorination is the extent to which it occurs on individual molecules as opposed to the polymer as a whole. To answer this question, a polymer with an overall chlorine content of 38% was fractionated. To obtain the first fraction, a 0.5% solution was concentrated to a 2% solution, causing higher chlorinated molecules of *cis*-1,4-PB to precipitate since they have a lower solubility in dichloromethane (Fraction 1, 41% of the total polymer). The filtrate was poured into acetone which precipitated 53% of the total polymer (Fraction 2). A small amount (6% of the total polymer, Fraction 3) was left in the filtrate and was isolated by evaporation. The degree of chlorination of Fraction 1 was 48%, that of Fraction 2 was 31% and Fraction 3 had a chlorine content of less than 20%.

It is important to realize that dichloromethane has a dielectric constant of about 10 and most cationic polymerizations are carried out in this solvent. To check the possibility of radical reactions in this solvent at 0°C, chlorination of *cis*-1,4-PB was carried out in the presence of a radical scavenger (10 weight % of the polymer). Although the calculated amount of chlorine for 85% chlorination of PB was added, the reaction was retarded by the radical scavenger and only a 55% degree of chlorination was achieved. This result is inconclusive and cannot help to explain the actual mechanism of the chlorination of PB since the radical scavenger (DHPH)

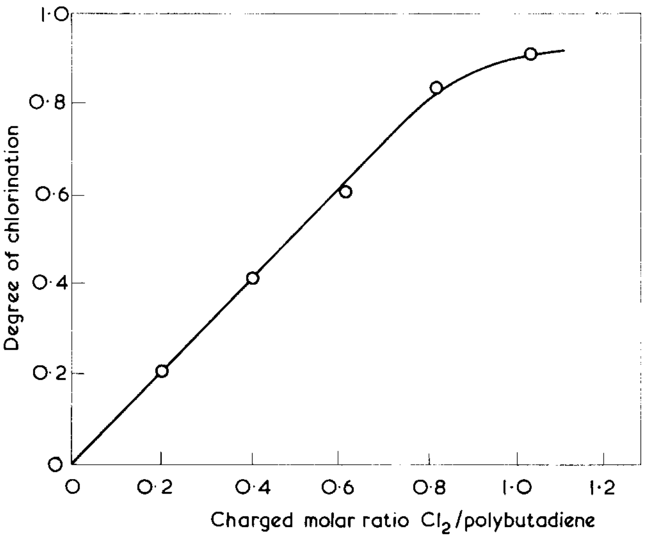


Figure 1 Chlorination of *cis*-1,4-polybutadiene

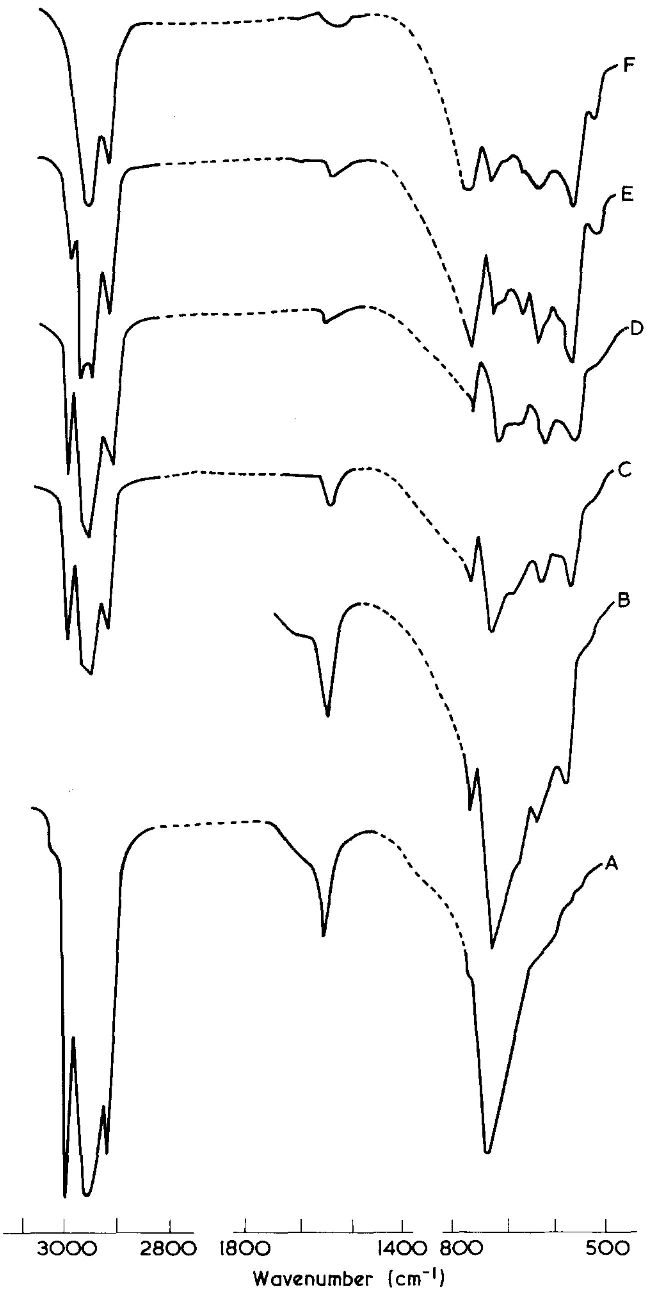


Figure 2 Infra-red spectra of partially chlorinated *cis*-1,4-polybutadiene: A, *cis*-1,4-polybutadiene; B, 22% chlorination; C, 42% chlorination; D, 65% chlorination; E, 81% chlorination; F, 100% chlorination

has a basic function in the molecule which could interfere with an electrophilic chlorination.

The infra-red spectra of selected samples of partially chlorinated PB are shown in *Figure 2*. The *cis*-1,4-PB spectrum is also shown as a reference. It can be seen that both the carbon–hydrogen alkene stretching band at 3005 cm^{-1} and the carbon–carbon stretching band at 1650 cm^{-1} decrease as the degree of chlorination increases. In turn, the carbon–chlorine stretching bands at 590 cm^{-1} and 645 cm^{-1} increased with increasing degree of chlorination. The change of the relative intensity of these bands is very easy to follow and the progress of chlorination can be observed from the change of the infra-red spectrum of the chlorinated polymers. The spectra of partially chlorinated PB samples were compared with spectra of meso- and racemic 3,4-dichlorohexane[13] which had been measured earlier. The spectrum of highly chlorinated PB is more similar to that of the racemic model compound but it also has absorption bands characteristic of the meso isomer.

The ^{1}H n.m.r. spectrum of chlorinated PB in deuterated THF was measured (10 weight % polymer solution) at room temperature on a 60 MHz instrument and gave only limited information, as seen in *Figure 3* and *Table 2*. The difference in the chemical shift of the methylene protons of *cis*-1,4-PB and chlorinated PB was not as significant as described earlier[11]. Partially chlorinated PB showed one broad methylene proton resonance without any significant shoulders.

Much more informative was the ^{13}C n.m.r. spectrum of 30% chlorinated PB, which is shown in *Figure 4* and *Table 3*, and is compared with 100% chlorinated PB (H–H PVC) and *cis*-1,4-PB. The spectrum of our starting *cis*-1,4-PB is free of carbon resonances of both the *trans*-1,4-isomer (α carbon = 130.2 ppm, β carbon = 32.9 ppm downfield from TMS)[14], and also the 1,2-isomer (C-1, 144 ppm; C-2, 114 ppm; C-3, 41 ppm; C-4, 39.5 ppm)[15] Three signals at 131.4, 130.0 and 128.8 ppm in the spectrum of 45% chlorinated

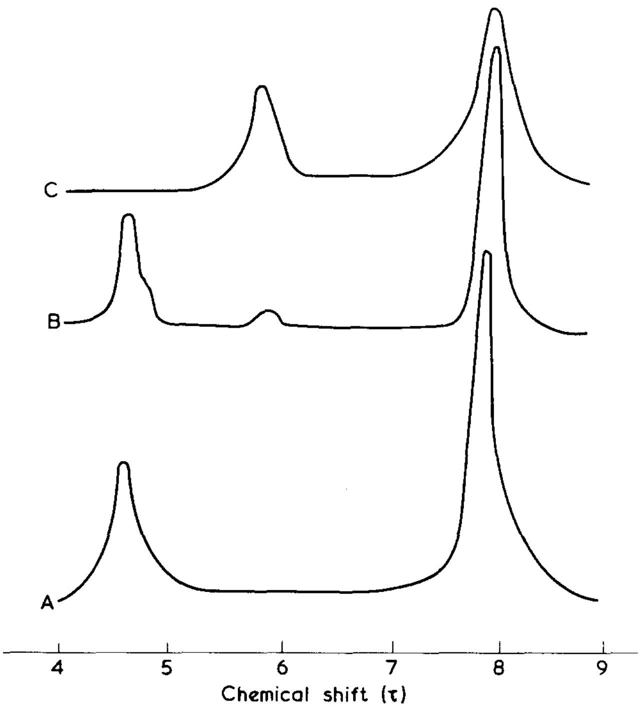


Figure 3 ^{1}H n.m.r. spectra of partially chlorinated *cis*-1,4-polybutadiene: A, *cis*-1,4-polybutadiene; B, 30% chlorination; C, 100% chlorination

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

	τ(centre)		
Sample	–CH=	–CHCl–	–CH$_2$–
Cis-1,4-polybutadiene	4.5–4.7 (4.59)	–	7.8–8.0 (7.89)
22% Chlorinated PB	4.5–4.8 (4.60)	5.9–6.0 (5.95)	7.9–8.1 (7.98)
100% Chlorinated PB	–	5.5–6.0 (5.80)	7.6–8.4 (8.00)

* Obtained at 10% polymer solution in deuterated THF at room temperature on a 60 MHz instrument

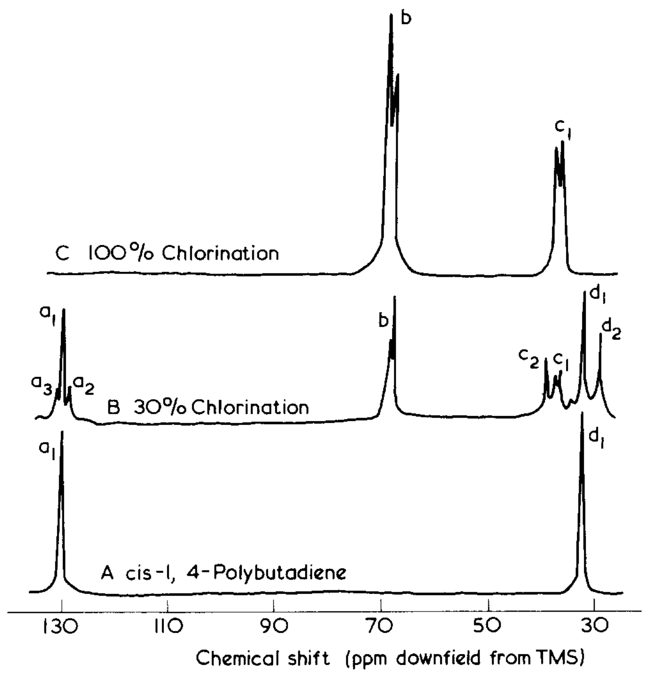
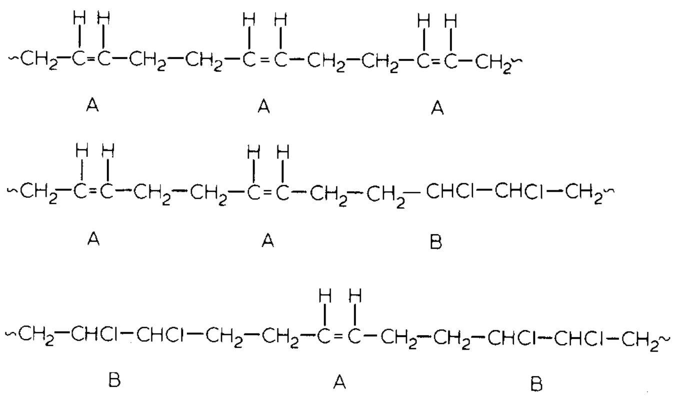


Figure 4 ^{13}C n.m.r. spectra of partially chlorinated *cis*-1,4-polybutadiene: A, *cis*-1,4-polybutadiene; B, 30% chlorination; C, 100% chlorination



$$\sim CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2\sim$$

A A A

$$\sim CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-CH_2-CHCl-CHCl-CH_2\sim$$

A A B

$$\sim CH_2-CHCl-CHCl-CH_2-CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-CH_2-CHCl-CHCl-CH_2\sim$$

B A B

$$\begin{aligned} &A\text{-}A\text{-}A \xrightarrow{k_1} A\text{-}B\text{-}A \\ &A\text{-}A\text{-}B \xrightarrow{k_2} A\text{-}B\text{-}B \\ &B\text{-}A\text{-}B \xrightarrow{k_3} B\text{-}B\text{-}B \end{aligned} \qquad (2)$$

PB are assigned to the alkene carbon atoms. The two peaks on either side of the central peak are assigned to the alkene carbon of a butadiene unit flanked by one chlorinated and one butadiene unit. These resonances were of comparable height and remained present even after the central peak had disappeared from the spectra of highly chlorinated PB. The spectra indicate one of two possibilities: either the concentration of isolated unchlorinated units is negligible, even in polymers of more than 90% chlorination, or the alkene carbon peak of the isolated units is overlapped by either the a_2 or a_3 peak, and the concentration of isolated units is so low that it cannot be detected.

Assuming that chlorine addition occurred statistically, a chlorinated PB containing 45% chlorinated units should be composed of 11.1 isolated unchlorinated units, 6.1 diad sequences of unchlorinated unit, 3.4 unchlorinated triads, 1.9 unchlorinated tetrads and 1.0 unchlorinated pentad, and should have 24.8 totally unchlorinated sequences per 100 butadiene units. The total number of end units of unchlorinated sequences should be $(2\times24.8)-11.1=38.5$ per 100 butadiene units. In this case, the area ratio of signal 2 to all signals in the range of 128 to 132 ppm should be $(55-38.5)/55=0.30$. The measured ratio however is 0.71, which implies that chlorination did not occur in a statistical manner, but rather in a manner highly favouring the formation of block structures. Clearly however the ratio is not large enough to indicate that chlorination occurred by formation of blocks of chlorinated segments. In equation (2) the progress of the chlorination of various $-CH=CH-$ triads is indicated. This reaction is very similar to substitution reactions on polymer chains with reactive side groups[16]. The formation of blocks of $-CH_2-CHCl-CHCl-CH_2-$ is favoured because the reaction rate k_2 of chlorine additions to the double bond seems to be the fastest reaction. The origin of the effect of adjacent groups on the chlorine additions will be discussed later.

The long range stereochemistry of H–H polymers has been studied with H–H polystyrene and H–H poly(vinyl cyclohexane) as examples. It was clearly shown that ^{13}C n.m.r. spectroscopy is capable of detecting long range order[17] (long range stereochemistry beyond the normal threo and erythro placements).

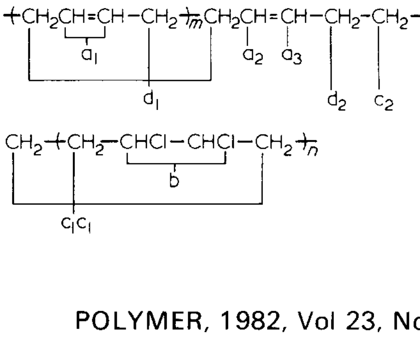
The chemical shift of chlorinated carbon atoms in adjacent positions has been studied previously[15,18] in order to determine H–H sequences in H–T PVC. Meso and racemic 2,3-dichlorobutane were used as model compounds. (Chemical shifts of methine and methyl carbon atoms in meso and racemic 2,3-dichlorobutane are 61.3 and 21.8, and 60.2 and 19.7 ppm, respectively.) In partially chlorinated PB two peaks were observed for $-CHCl-$ carbon atoms at 66.1 and 65.7 ppm (*Table 3*). This splitting was observed even in the spectrum of completely chlorinated PB and it was concluded that these two peaks resulted from threo and erythro placement. Based on the chemical shift values of the corresponding carbon atoms

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

Signal	Chemical shift (ppm downfield from TMS)	Assignment	
1	131.4	a_3	
2	130.0	a_1	
3	128.8	a_2	
4	66.1	b	erythro
5	65.7		threo
6	35.5	c_2	
7	33.6	c_1	erythro-erythro
8	33.3		erythro-threo
9	32.9		threo-threo
10	28.0	d_1	
11	24.9	d_1	

Insert chem. form. C

* Obtained at 25% polymer solution in THF at room temperature on a 20 MHz instrument



$$+CH_2CH=CH-CH_2+_m CH_2CH=CH-CH_2-CH_2-CHCl-CHCl-$$

$$CH_2+CH_2-CHCl-CHCl-CH_2+_n$$

in the pure model compounds we have assigned the peak at 66.1 ppm to the carbon atom of the meso (erythro) isomer and the other one to the racemic (threo) isomer. Triplets at 33.6, 33.3 and 32.9 ppm were assigned to methylene carbon atoms in mm, mr and rr dyad sequences of chlorinated butadiene units, although the peak at 33.3 ppm could not always be detected. The intensity of the meso and racemic peak is comparable in the methine and methylene carbon atom chemical shift. Most previous investigators[4,7,9] concluded from measurements of solution properties of halogenated PB, or from X-ray analysis of the crystalline fractions of the polymer, that it had exclusive threo structure. This was assumed to be the result of *trans* addition of halogen atoms to the *cis* double bond of the butadiene units in the polymer. Indeed, there are many examples which show that the chlorination in linear low molecular weight alkenes occurs with high *trans* stereospecificity. It has been suggested that free rotation of the carbon–carbon bond of the intermediate cation is prevented during electrophilic chlorination because of the stable three-centred cation and as a consequence, stereospecific chlorination occurs. Only a few exceptions to stereospecific *trans*-chlorination *via* a chloronium salt have been found. These can be expected to occur if the intermediate ion can rearrange to a more stable form before proceeding to the product[18].

Using ^{13}C n.m.r. spectroscopic analysis, we were able to analyse the sequence structure of the whole polymer more effectively than previously done by measurements of solution properties or by X-ray analysis. These results also showed that no formation of *trans* double bonds occurred, which indicates that no isomerization took place and that the *cis* double bond of the original PB was retained throughout the chlorination reaction.

Morphology of partially chlorinated PB's

Investigation of chlorination products of PB by d.s.c. revealed that over a relatively large range of compositions partially chlorinated butadiene is an amorphous microphase-separated system in which chlorine-containing phases and PB phases have their own glass transition temperatures. The domain structure and the interfaces of these polymeric systems depend on the type of chlorination used in their preparation, and on the thermal history of the samples. It was most convenient to compare polymer samples obtained by precipitation from solution. As samples were scanned and rescanned in the d.s.c apparatus, substantial changes occurred. *Figure 5* shows the thermal behaviour of various samples of chlorinated PB's of various compositions. *Cis*-1,4-PB exhibited three transitions, a T_g at 165K[20], a crystallization peak at 203K and a T_m at 270K[21]. As the degree of chlorination increased, up to high degrees the T_g of the *cis*-1,4-PB phase remained essentially the same, the crystallization peak remained between 203–209K, and the melting peak shifted to 266K. As polymer samples of increasing degree of chlorination were studied, one more transition peak was noticed between 320 and 350K which depended upon the degree of chlorination. A 42% chlorinated PB has a second, higher, T_g at 322K. The T_g of 65% chlorinated PB was similar to that of the 42% chlorinated PB. A sample of 81% chlorinated PB had a simple d.s.c. curve which exhibited two glass transitions, one at 207K and one at 329K, with no peaks of an exothermic and endothermic nature which would indicate the crystallization and melting of a PB phase. 100% Chlorinated PB has only one T_g at 347K, and no other lower thermal transitions.

The existence of two T_g's in chlorinated PB's with degrees of chlorination from 40 to 80%, supports the initial supposition that chlorination of *cis*-1,4-PB occurred in blocks and, more importantly, that the bulk polymer phase is then separated into two domains, a domain of the PB phase and one of the chlorinated phase. Chlorinated PB up to a degree of chlorination of 65% clearly showed the low temperature T_g, indicative of the PB phase. It also showed exothermic and endothermic peaks resulting from the crystallization and melting of the PB phase. Above a degree of chlorination of 85%, chlorinated PB showed only one T_g. This behaviour indicated that highly chlorinated PB is apparently homogeneous in its morphology, and that the unreacted butadiene units are incorporated in the chlorinated phase and act as plasticizers in the H–H PVC matrix.

This proposal was checked by the Fox equation (equation (3))[22], which is generally used to explain the T_gs of compatible systems of two kinds of homopolymers

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{3}$$

where w_1 and w_2 are the weight fractions of the homopolymers. In our case, they represent the weight fractions of the butadiene and H–H PVC segments. T_{g_1}, T_{g_2} and T_g are the glass transition temperatures for the two homopolymers and for mixed polymer, respectively. The T_{g_1} and T_{g_2} for *cis*-1,4-PB and H–H PVC were 165K and 347K (*Table 4*). As shown in *Figure 6*, the curve which connects the higher T_g meets with the theoretical Fox curve at $w_2 = 0.95$ or a degree of chlorination of 89%. This is in excellent agreement with the intercept of the change in slope of the curve where the degree of chlorination is plotted against the amount of chlorine gas charged (*Figure 1*) which is at about 85% chlorination. As a consequence, chlorination to degrees higher than 89%

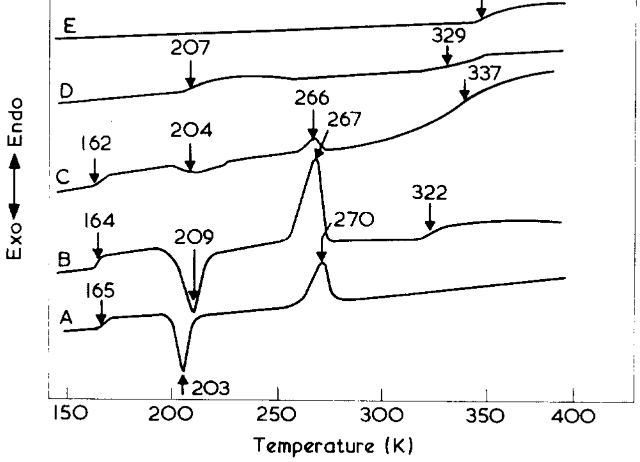


Figure 5 D.s.c. scans of partially chlorinated *cis*-1,4-polybutadiene: A, *cis*-1,4-polybutadiene; B, 42% chlorination; C, 65% chlorination; D, 81% chlorination; E, 100% chlorination

Table 4 D.s.c. data of transition temperatures of partially chlorinated *cis*-1,4-polybutadiene

Degree of chlorination	Weight % of $-CH_2-CHCl-CHCl-CH_2-$ units	Precipitated polymers T_g (low)	T_{cr} (low)[a] (K)	T_m (low)[b]	T_g (high)	Polymer films T_g (low)	T_{cr} (low) (K)	T_m (low)	T_g (high)
0	0	165	203	270	–				
22	0.40					166	201	267	[d]
40[c]	0.61	165	202	266	324				
42	0.63	164	209	267	322	164	200	266	[d]
52[c]	0.72	166	201	266	314				
65	0.81	162	204	266	337	164	203	262	[d]
78[c]	0.89	–	–	–	324				
81	0.91	207	–	–	329				
85[c]	0.93	–	–	–	326				
100	1.00	–	–	–	347				

[a] T_{cr} (low), crystallization temperature of PB domain

[b] T_m (low), melting temperature of PB domain

[c] Chlorinated in mixed solvent

[d] Deviation to exothermic side interfered with exact determination of T_g (high)

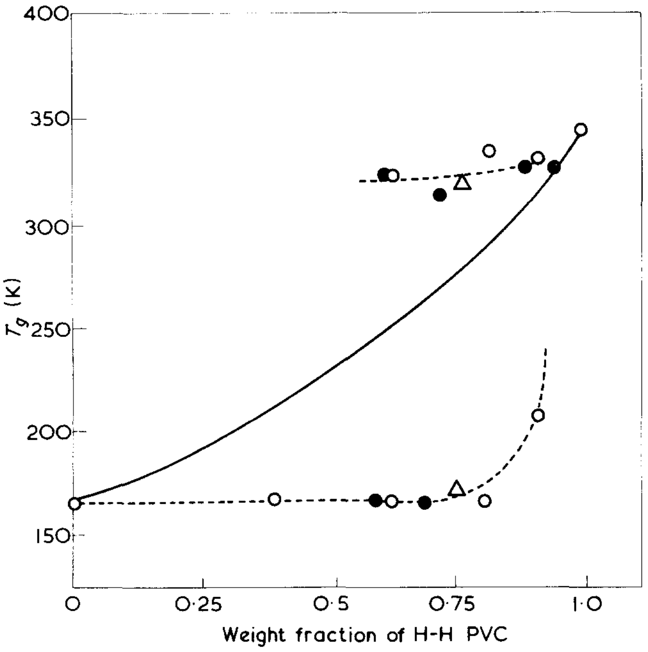


Figure 6 T_g correlation of two phases of partially chlorinated *cis*-1,4-polybutadiene as a function of weight fraction of PVC: (○) chlorinated in dichloromethane (d.s.c. data); (●) chlorinated in mixed solvent (d.s.c. data); (△) chlorinated in mixed solvent (Rheovibron data)

occurs by chlorinating single units of butadiene between blocks of –CHCl–CHCl– units with an average length of about 10 units.

It would also have been desirable to study the higher T_g of chlorinated PB with a low degree of chlorination. This however, was very difficult because the glass transition temperature is of relatively small magnitude, and is in the area of the endothermic and exothermic peaks of the PB crystallization and melting, as shown in *Figure 7*.

It appears that some incorporation of the PB phase into the chlorinated phase is possible, but apparently there is no incorporation of a chlorinated phase into the PB phase as the T_g of PB does not change, even at degrees of chlorination up to 80%.

Details of the behaviour of chlorinated PBs depend on the thermal history of the individual sample. The effects of the cooling rate of a sample on its d.s.c. scan is shown in

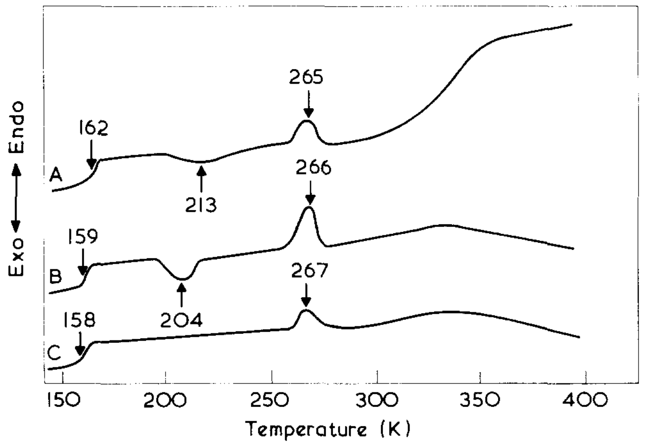


Figure 7 Effects of thermal history of precipitated 65% chlorinated *cis*-1,4-polybutadiene on thermal behaviour (d.s.c.): A, first scan; B, rescan after quenching from 400K to 140K; C, rescan after cooling from 400K to 140K at a cooling rate of 10°/min

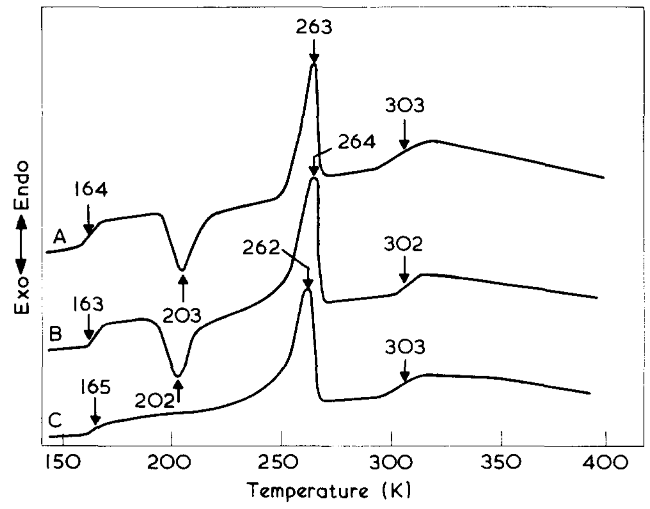


Figure 8 Effects of thermal history of solution cast (4% solution) of 65% chlorinated *cis*-1,4-polybutadiene on thermal behaviour (d.s.c.): A, first scan; B, rescan after quenching from 400K to 140K; C, rescan after cooling from 400K to 140K at a cooling rate of 10°/min

Table 5 Dynamic mechanical data (Rheovibron) of cast film of partially chlorinated *cis*-1,4-polybutadiene

Degree of chlorination (%)	β low (K)			α low (K)			β (high (K)		
	E'	E''	tan δ	E'	E''	tan δ	E'	E''	tan δ
40	–	176	178	–	276	275	–	321	344
58	–	173	173	–	294	294	–	324	348

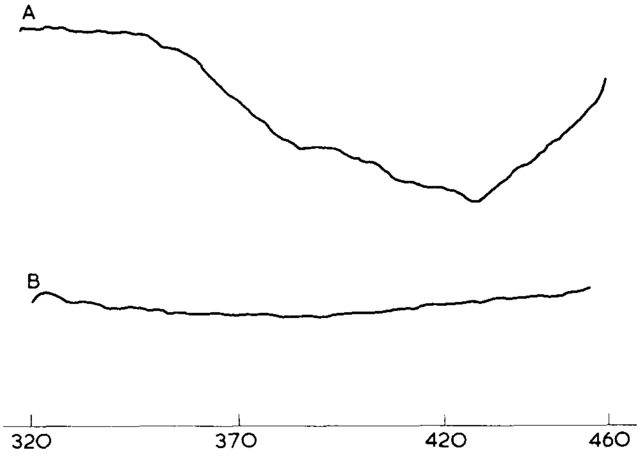


Figure 9 D.s.c. scan of highly chlorinated *cis*-1,4-polybutadiene at temperature range above T_g: A, first scan; B, rescan after quenching from 460K to 300K

Figures 7 and 8, in which we compare samples precipitated from dichloromethane solutions into methanol and samples that were cast from solvents. Some quenching experiments were carried out by cooling the sample at a rate of more than 100° per minute from 400K to 140K. As can be seen in *Figure 7*, the T_g of PB can be identified in the samples of lower degree of chlorination, regardless of the thermal history, but the T_g of the -CHCl-CHCl- rich domain can be seen only in the first scan, taken after the sample was precipitated. The crystallization peak of PB disappeared after slow cooling in the d.s.c. scans of both the precipitated and cast films. We also see a difference in the areas of the melting peaks of the PB domain in the solution-cast films and precipitated samples. The peak is much bigger in the cast films than in the precipitated polymer samples, which indicates that a higher degree of order exists in the cast film caused by the possibility of organization of polymer segments as the solvent is evaporated. A clear interaction in the PVC segment in the cast film could also be seen at the higher temperature part of the d.s.c. scans. Above 330K at the onset or shortly after the T_g of the sample had been observed, a broad exothermic deviation was noticeable which could be attributed to the crystallization of H-H PVC domains as shown in the experiment in *Figure 9*. The first d.s.c. scan had a large and broad exothermic peak whose centre was located at 428K, but on the second scan, after cooling from 463K, no 320K peak could be seen. It is believed that the exothermic peak was not present in the second d.s.c. scan. Even at 22% chlorinated PB the DSC scan showed an exothermic deviation of the baseline above 330K which might suggest that a $-CH_2-CHCl-CHCl-CH_2-$ rich domain exists even in polymers of low degrees of chlorination.

Clear phase separation of partially chlorinated PB has been revealed by studying d.s.c. scans of samples of PB chlorinated to various degrees. It was expected that additional and direct evidence, obtained by measuring the dynamic mechanical properties, and by studying the samples by transmission electron microscopy, would provide a more complete picture of the phenomenon.

Dynamic-mechanical behaviour of samples of partially chlorinated PB were studied in the Rheovibron Dynamic Viscoelastometer in the temperature range of 140K to 360K. *Figures 10* and *11* show the temperature dependence of dynamic-mechanical properties [storage modulus (E'), loss modulus (E''), and loss tangent (tan δ)] for 40% and 58% chlorinated PB. E' vs. temperature curves of both samples do not give clear cut information on the phase separation of the polymers. From E'' and tan δ vs. temperature curves, however, three definite transitions were observed at 173 to 178K, 275 to 294K and 321 to 348K, listed in *Table 5*. The transition at 275 to 294K is related to an α transition of *cis*-1,4-PB which is near the melting point[17]. The transition at 173 to 178K was clearer in a sample of lower degree of chlorination than that of higher degree of chlorination. From the comparison with the data obtained from our d.s.c. studies, the lower transition at 173 to 178K is believed to be a β transition (β_{low}) of *cis*-1,4-PB and the higher transition at 321 to

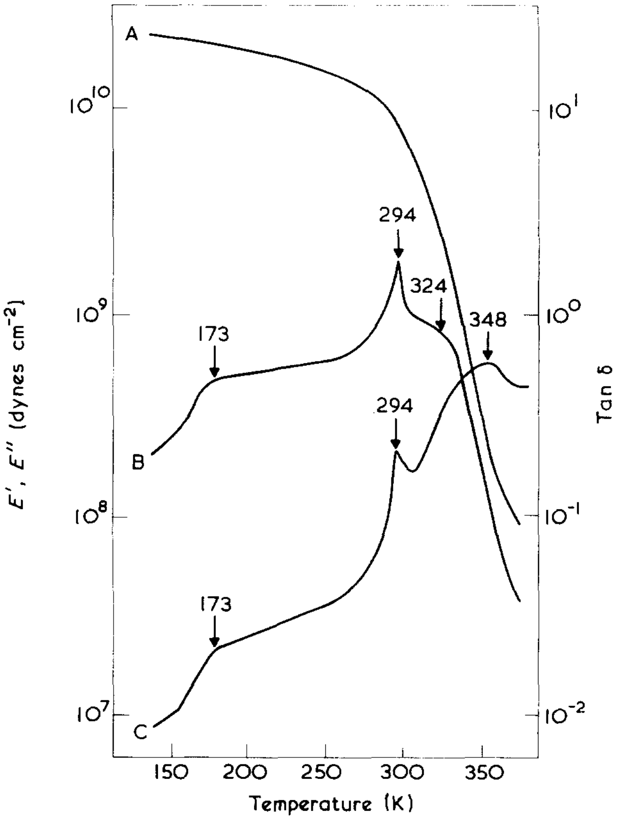


Figure 10 Dynamic mechanical data (Rheovibron) of partially chlorinated *cis*-1,4-polybutadiene: degree of chlorination = 40%: A, E' curve; B, E'' curve; C, tan δ curve

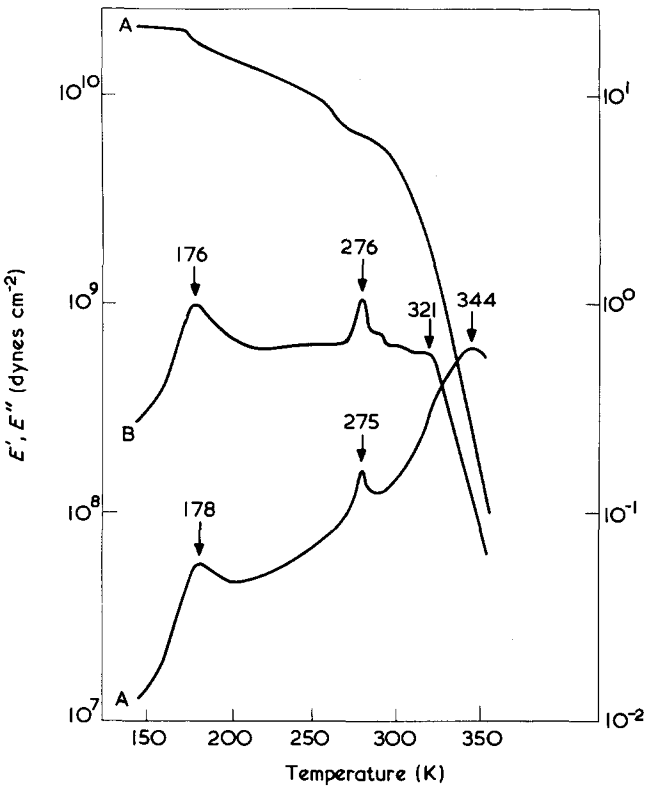


Figure 11 Dynamic mechanical data (Rheovibron) of partially chlorinated *cis*-1,4-polybutadiene: degree of chlorination = 58%: A, *E'* curve; B, *E''* curve; C, tan δ curve

348K is that of the β transition (β_{high}) of –CHCl–CHCl– rich domain, respectively. Thus we confirmed the presence of definite phase-separation with rheovibron dynamic–mechanical studies. It is important to point out that the positions of two β transitions do not change for samples of different degrees of chlorination. The position of the β transition peak observed in the *E''* vs. temperature curve is in places generally accepted as the precise T_g of the polymers[20], the T_g data from the *E''* vs. temperature curves are also plotted in *Figure 6.*

In order to verify the presence of microphase-separated structures of our partially chlorinated PB, and to get information on the boundary layer between the polymer phases, some photomicrographs of the polymers were taken with a transmission electron microscope which show definite phase separation.

Figure 12 shows a transmission electron micrograph of an unstained thin film of 53% chlorinated PB. The lightest areas (region 1) are holes in the film, whereas slightly darker areas may be phase separated regions of unchlorinated PB or holes only partially penetrating the film (region 2). This is illustrated in *Figure 13* where the film has been shadowed at a glancing angle of 20° with gold-paladium. The partial holes (region 2) show a shadow, whereas the holes (region 1) do not. The size and number of partial holes vary with casting conditions so that any phase separation in the polymer is obscured. This problem may be overcome by staining the remaining double bonds in the PB with osmium tetroxide. After staining *Figure 14* shows partial holes again appearing (region 2), but now dark areas of osmium tetroxide stained PB (regions 3 and 4) are present. Some of the unchlorinated PB domains occur on partial holes and, therefore, have dark edges and light centres (region 4). The matrix of chlorinated PB is unstained by the osmium tetroxide so it appears lighter than the stained phase because PVC has a lower electron scattering cross section than osmium. It was not possible to confirm the presence of phase separated domains by X-ray microanalysis because of the loss of C-1 from the polymer caused by beam damage. The results were supported, however, by

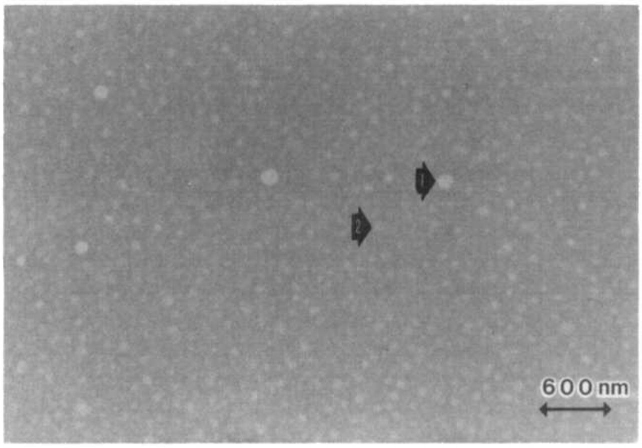


Figure 12 Transmission electron micrograph of a solution cast film of 53% chlorinated PB. Region 1 = holes. Region 2 = partial holes or unchlorinated PB domains

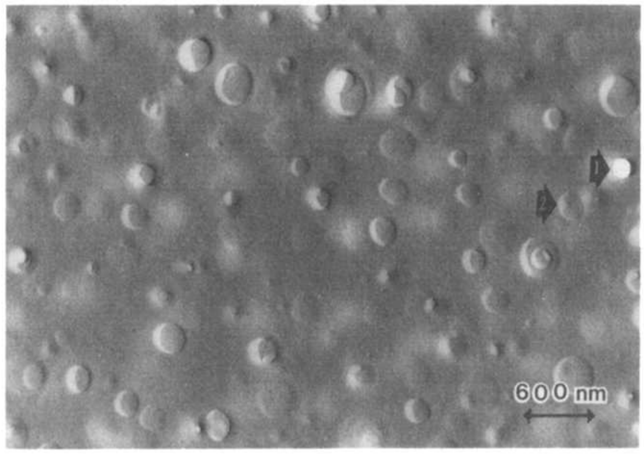


Figure 13 Transmission electron micrograph of a chlorinated PB film shadowed at 20° with gold-palladium. Region 1 = holes. Region 2 = partial holes

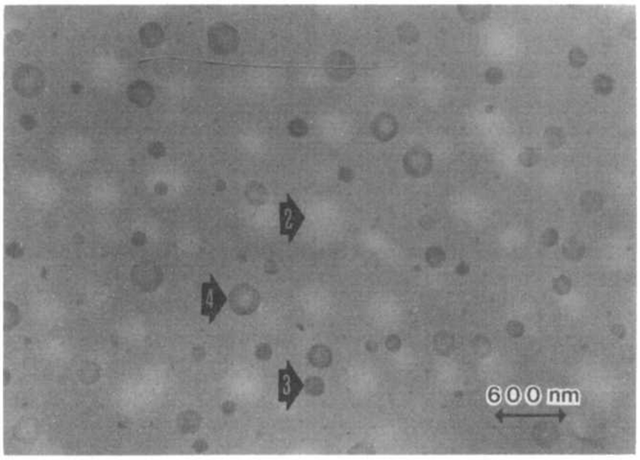


Figure 14 Osmium stained film of chlorinated PB. Region 2 = partial holes. Region 3 = stained PB domains. Region 4 = stained PB domains on partial holes

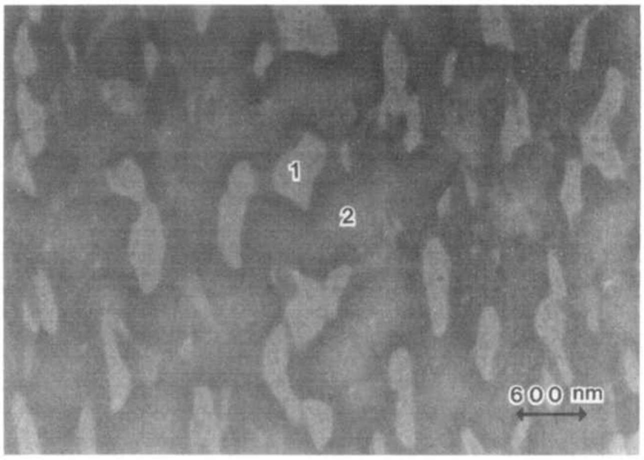


Figure 15 Solution cast film of a mixture of PVC and PB stained with osmium tetroxide. Region 1 = chlorinated phase. Region 2 = stained PB phase

comparison with the solution cast films of the PVC and PB mixture. These films (*Figure 15*) show a morphology similar to that of the chlorinated PB with light areas of PVC (region 1) and dark osmium tetroxide stained areas of PB (region 2).

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