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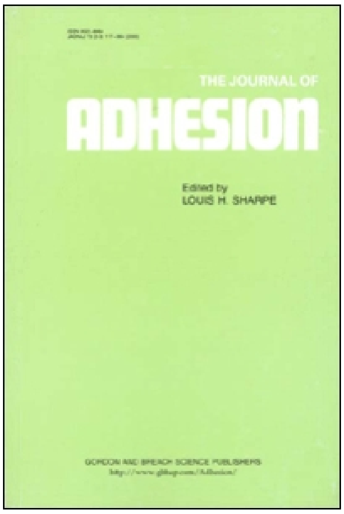

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The Influence of Structure on Autohesion (Self-Tack) and other forms of Diffusion into Polymers

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The Influence of Structure on Autohesion (Self-Tack) and other forms of Diffusion into Polymers

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Autohesion is discussed emphasising in particular the influence of polymer chain structure on apparent rates of diffusion. The full range of autohesive levels which exists amongst rubbery polymers is rationalised by proposing a distinction between inter-chain free volume and "intra-chain" free volume, the latter being a collation of free volume regions "contained" in cavities associated with permanent polymer chain structural features which especially apply for certain polymer types. The coincidence of several such cavities plus the intervening inter-chain space causes the formation of holes which may attain sufficient size during normal chain thermal fluctuations to facilitate forward motion of an incoming chain.

The concept of free volume has been used to demonstrate the proposed model semi-quantitatively. Comparison with a simple model, involving inter-chain free volume only, is made throughout the calculation. The proposed model, in showing general agreement for several elastomers between free volume considerations and autohesive characteristics, provides an explanation for the large difference in tackiness which exists between natural rubber and ethylene propylene copolymers.

The relationship of the proposed model with chain co-operative motion is discussed, and its apparent correlation with the diffusion through polymers of a range of gases and solvents is discussed in some detail.

INTRODUCTION

Autohesion, the spontaneous adherence between two unvulcanised surfaces of an elastomer, is the basis for tack, a property widely exploited in technological operations involving the construction of complex structures from elastomeric compounds. Under optimum conditions, natural rubber (NR) possesses a high degree of autohesion whereas ethylene propylene (EP) rubbers exhibit little autohesion.

Although the influence of variations in experimental conditions on autohesion has been frequently discussed,[1-4] relatively little attention has been directed to the molecular interpretation of the phenomenon. The consensus of current opinion concerning the autohesive mechanism favours the interdiffusion of chain molecular segments between surfaces,[3-9] resulting in the intermingling of chain segments and the ultimate disappearance of the interface. Other authors[10, 11] consider interfacial adsorption to afford a sufficient explanation.

Diffusion in high polymers has been considered[12] to occur by the cooperative motion of several neighbouring segments to form a hole of sufficient size to permit the ingress of a chain section: however, correlation between free volume data and autohesive strengths has not been previously shown.

The present article proposes an explanation of the large differences in the tack strengths of NR and EP rubbers by suggesting that polymer chain structure influences the location of free volume, thereby affecting autohesive diffusion. A reasonable correlation for several polymers will be shown between their allocated free space and autohesive strength data. In addition, the correlation will be extended to cover gaseous and solvent diffusion through polymers.

DISCUSSION

Autohesion and its assessment

On forming a bond between two surfaces, subsequent separation forces will be transmitted into the body of the elastomer. As the magnitude of autohesion is necessarily assessed by destructive test methods,[1, 2, 13-16] both diffusive and bulk strength characteristics are involved. During the technological construction of rubbery composites, adequate autohesive bonds must form within seconds: a contact time (t) of 1 second applies when using the Dunlop Rotary Tackmeter, tack data from which have correlated well with technical experience for compounded stocks.[16] Table I shows the considerable range of autohesive strengths (F) obtained for several elastomers at near-optimum molecular weight conditions, the relatively high contact pressures utilised evidently producing consistently intimate contact conditions.

Although both diffusive and bulk strength characteristics can be interpreted in terms of molecular weight and of chain flexibility, conformation and packing, the distinction remains valid on the grounds that the diffusive step must precede the development of bulk strength. As the low tack value for EP applies across a large molecular weight range, bulk strength is inferentially important to tack measurement only in association with adequate diffusive properties. The ability to form an adequate interpenetrating polymer layer at the interface is the primary requisite of successful autohesion.

However, for those polymers which do coalesce readily to produce unit relative tack,[1] high strength is desirable, so that a combination of low and high molecular weight fractions is necessary to optimise both diffusive and bulk characteristics. In addition, for NR, such strength characteristics are undoubtedly assisted during testing by stress crystallisation, since high local strains may be involved at an interface undergoing separation. To emphasise this point, autohesion levels for both a partially-isomerised NR and a suitable synthetic polyisoprene (neither polymer exhibiting stress crystallisation during testing) have been compared with those of other amorphous polymers (Appendix 3). Whereas the tack of these polyisoprenes was less than that of unmodified NR, reflecting the significance to polymer strength of stress crystallisation, nevertheless the autohesive levels of all other amorphous polymers were even lower. By inference, the diffusive ability of rubbery polyisoprenes should be higher than that of other polymers.

TABLE I

Measured autohesive data for several polymers
(at near-optimum molecular weight conditions)
Dunlop Rotary Tackmeter data

Polymer		Tack strength *F* kg/cm testpiece
Natural rubber	(NR)	*ca.* 12.5†
Styrene butadiene 1500-type copolymers	(SBR 1500 and 1509)	5–6†
Cis polybutadiene	(cis BR)	
Butyl rubber	(IIR)	3.7
Ethylene butene-1 copolymer	(EBR)	4.2
Ethylene propylene termonomer	(EPT)	1.75–2.5†

Applied Test Conditions:
Speed of rotation — 4 r.p.m.
Force of contact — $\geqslant$ 10 kg‡
(Area of contact is rubber dependent, but always <1 cm^2).
Normalised Test Conditions:
Speed of separation of testpieces at trailing edge — 0.35 cm/sec.
Time of contact — 1 second

† Many data.
‡ $\geqslant$ that critical force above which no increase in tack was obtained from an increase in force.

The present work is confined to a consideration of the diffusive step.

Diffusion aspects

Autohesive self-diffusion coefficients D of 10^{-11} to 10^{-14} cm^2/sec. have been observed radiometrically[3] for high molecular weight (10^4 to 10^6) polymers.

From simple Fickian diffusion, a representative mean diffusional path $\bar{s}(=(2tD)^{\frac{1}{2}})$ for the first second is 45 Å. As tracer techniques sensibly consider whole-chain diffusion, the suggestion[17] that $\bar{s}$ for small chain portions (involving higher diffusion rates) depends on a much lower power of t might be speculatively applied to the initial stages of autohesive contact. (An analogy might be the relationship between dissolution and diffusion during gas permeation through elastomers). Whatever the case, adequate interdiffusion is clearly possible in the first second of interfacial contact to allow considerable intermingling of chain portions.

Autohesive diffusion is a mutual phenomenon, recipient surfaces also supplying outgoing chain ends or portions. Chain mobility is governed by magnitude (molecular weight), and restricted by excessive cross-linking or branching and by crystallinity (packing order involving several monomer units) which also limits the useful free volume of the recipient surface.

Definition of the diffusive problem

A simple mathematical treatment[18] of elastomeric autohesive diffusion predicts that, under standard conditions, the bond strength is proportional to a complex diffusion constant, characteristic of the polymer, raised to the power $\frac{1}{2}$. In the extreme cases of NR and EP, optimum experimental data indicate $F_{NR} \sim 5 \times F_{EP}$ (high tack values developing within 1 second of contact for NR). Hence, although (in more realistic diffusive terms) a factor nearer to 3 exists between the tack levels of EP and those polyisoprenes unaffected by stress crystallisation, the self-diffusion coefficient of NR should be an order of magnitude greater than that for EP. The problem is now reduced to determining the molecular characteristics providing for enhanced diffusion in NR.

Structural characteristics influencing autohesive diffusion

The generation of holes within a polymer gives rise at the surface to apertures of commensurate size through which chain ends must pass during autohesive diffusion. The formation of holes of critical size (the size governed by the bulkiness of the effective flow unit involved in the diffusion process) is affected by several factors, including the internal pressure and the ease of internal rotation (factors adequately discussed elsewhere[19-21]). Since the internal pressures of all hydrocarbons are apparently similar,[20] their specific energies of chain displacement to overcome Van der Waals attractive forces will be of similar magnitudes: hence the relative facility with which a hole is formed is governed by the ease of internal rotations (with resultant cooperative chain properties[21]), and, according to the speculative concept expanded in the next section, by the geometric shape of the molecule. Inspection of Stuart molecular models indicates that the molecular geometry of certain polymers facilitates the formation of critical holes (or cross-sections): this aspect constitutes the major theme of the present paper.

For all polymers, hole formation is dependent on micro-Brownian thermal movements of chain elements providing local density fluctuations which continually vary throughout the polymer. However, on a time average basis, at any constant temperature, the distribution of hole sizes must vary to a certain extent around a consistent mean. Subsequent observations on the formation of critically-sized holes are made within this framework.

Proposed model—effect of molecular structure on diffusion

Whilst recognising the unique pervasive nature of free space, a distinction is proposed between inter-chain free volume (comprising both packing and classical free volume) and free volume elements localised in conjunction with

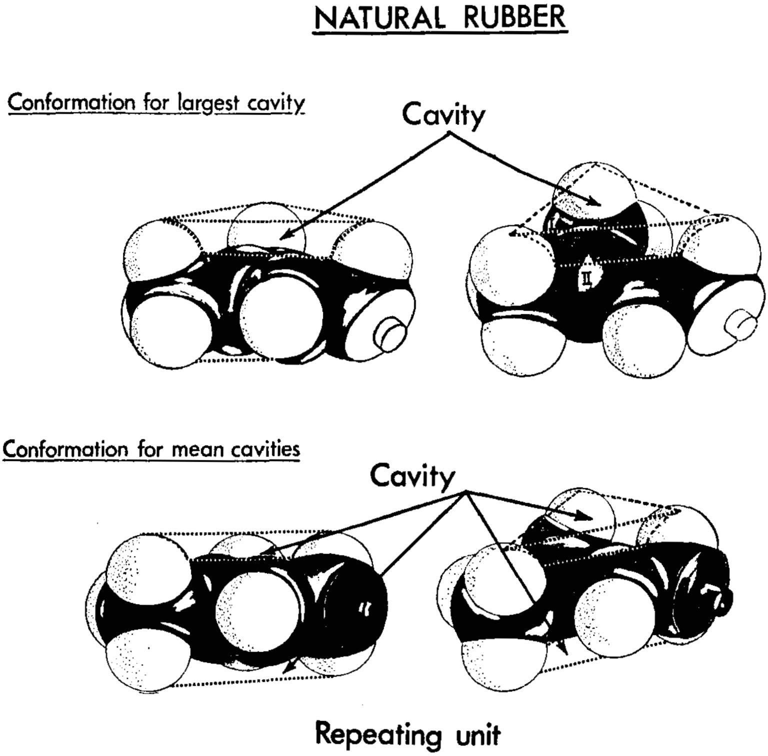


FIGURE 1(a) Stuart Models showing permanent, but flexible cavities associated with a π-bond and substituted grouping.

particular chain structural features, which are collectively defined herein as intra-chain free volume. All polymers contain inter-chain free space, whereas intra-chain free space is more evident in some rubbers than in others.

The structural features causing intra-chain free space are visualised as "containing" cavities of space between themselves, such cavities having one end open to the proximate inter-chain free space. Whereas inter-chain free space may be "displaced" by any haphazard movements of neighbouring chains, intra-chain cavities can only be occupied by a largely determinate approach from another chain portion.

The type of structural features which are considered to provide intra-chain free space cavities are illustrated by two extreme cases:

1) A monomer unit of cis polyisoprene (shown as two conformations in Figure 1(a)) possesses both unsaturation and a substituted olefinic carbon atom. Consequently the five carbon atoms illustrated in the figure exist permanently in the same relative positions (due to the rigid π-bond) independently of chain rotations. A substantial region of space (indicated by broken lines) exists permanently between the limits of influence of the chemical groupings based on the five carbon atoms, both above and below the π-bond. These cavities are easily accessible to a determinate approach by another chain segment.

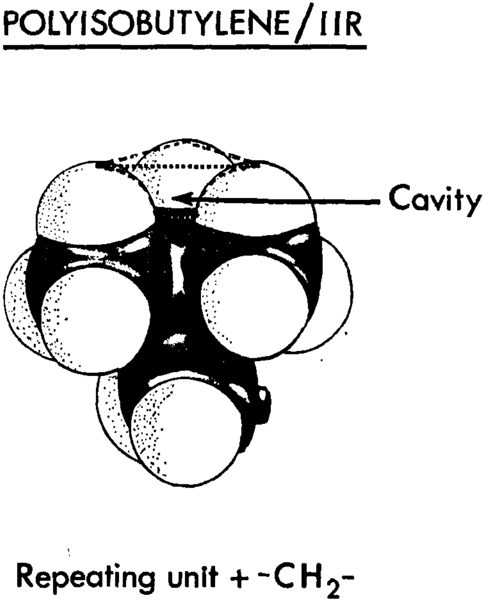


FIGURE 1(b) Stuart Model showing a temporary cavity associated with substituted groupings in the absence of π-bonds.

2) For saturated polymers with no substituted groupings the only permanent chain feature is the carbon–carbon σ-bond, next nearest-neighbour atoms adopting variable positions on the rotational cone about the preceding σ-bond. In ethylene–propylene polymers the —(CH_2)—$_n$ units therefore

TABLE II

Details of monomer units§

Polymer	Molecular weight M_M	Copolymer moiety	Molar proportion	Volume of cavity c'' ‖	Cross-sectional area of cavity a'' ‖	Length of Monomer Unit L	No. of cavities per Monomer Unit x‡
				$(Å)^3$	$(Å)^2$	(Å)	
NR	68.1			3.25	1.19	4.40	2.00
		Styrene	2	5.35	2.11		1
SBR 1500	60.8†			2.12	0.68	4.22†	1.70
		Butadiene	13	1.85	0.55		1.81
cis BR	54.1†			1.00	0.40	4.40†	1.99
IIR	56.1			1.47	0.60	2.52	2.00
		Ethylene	1	0	0		0
EBR	42.1†			1.47	0.60	2.52†	1.00
		Butene-1	1	1.47	0.60		2
		Ethylene	2	0	0		0
EPT	32.7†			1.47	0.60	2.52†	0.33
		Propylene	1	1.47	0.60		1
Emulsion BR	54.1†			1.71	0.53	4.46†	1.83

† Denotes average value (including isomers).

‡ $x = \Sigma x_i$ for copolymers (including isomers).

§ From atomic dimensions from Pauling[22] with a modified bond angle.[21]

‖ $\Sigma x_i a''_i / x$ or $\Sigma x_i c''_i / x$ for copolymers.

Butadiene microstructure.

	% cis 1, 4	% 1, 2	% trans 1, 4
Cis BR	96	1	3
Emulsion BR (typical)[39]	19	17	64
Emulsion BR in SBR	6	19	75

have no intra-chain space. The presence of substituted groupings in the propylene comonomer (and in butyl rubber (IIR) and elsewhere) causes permanent features which give rise to cavities of "medium" volume (Figure 1(b)) but of limited access in terms of cross-sectional area.

The cavities in Figure 1(b) define the smallest free space allocations considered relevant, as these cavities can only accommodate a small spherical segment of a hydrogen atom.

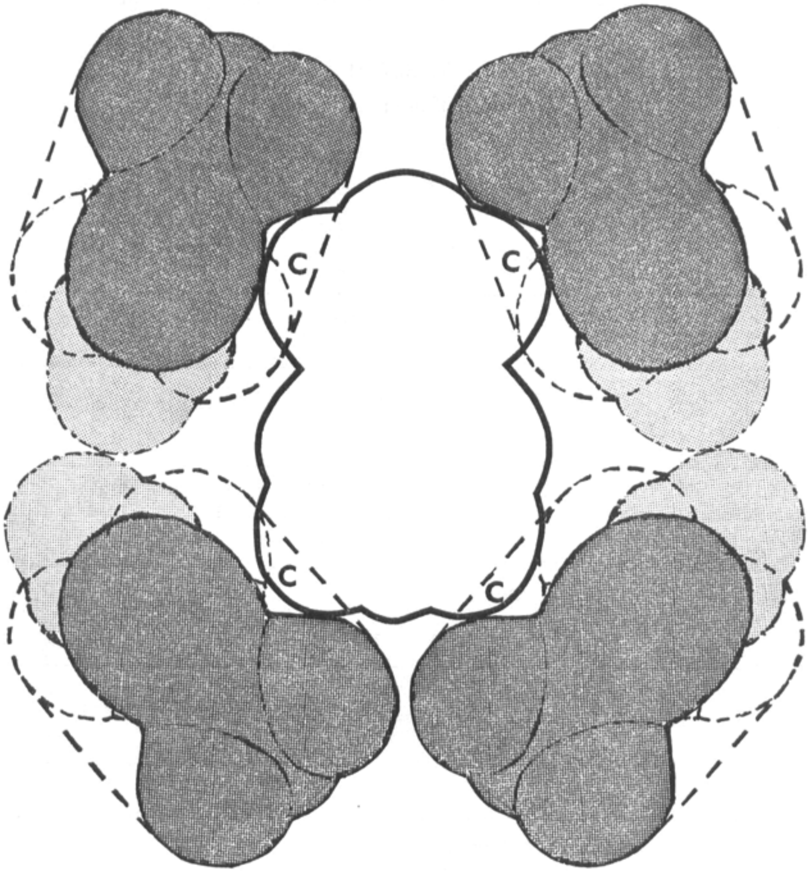


FIGURE 2(a) Hole formation involving the participation of large accessible cavities (NR-type).
Chain cross-sections in an ideal packing arrangement: $n = 4$.
Measurements indicated that the r.m.s. distance between chains has increased by only *ca.* 15% from the close-packing situation.
At C: cavities occupied by part of an incoming chain.

Whilst the existence of cavities is a permanent feature of appropriate polymer chains, rotation of groupings causes the continual size change of those individual cavities associated with π-bonds, and rotation of chains alters the whereabouts (but generally not the numbers) of cavities in substituted saturated polymers. However, use of average conformations (again considered on a time average basis) permits cavity sizes to be estimated. The shapes of the cavities for each of several common polymers have been studied using Stuart models. By approximating each cavity to a simple geometric figure and calculating the volume using atomic dimensions largely as quoted by Pauling,[22] estimates of c″, the cavity volume, and a″,† the cavity cross-sectional area, were obtained: these are given in Table II.

Within the hole-distribution framework discussed previously, hole formation is facilitated in appropriate polymers when several neighbouring segments, not necessarily from different chains, are positioned momentarily

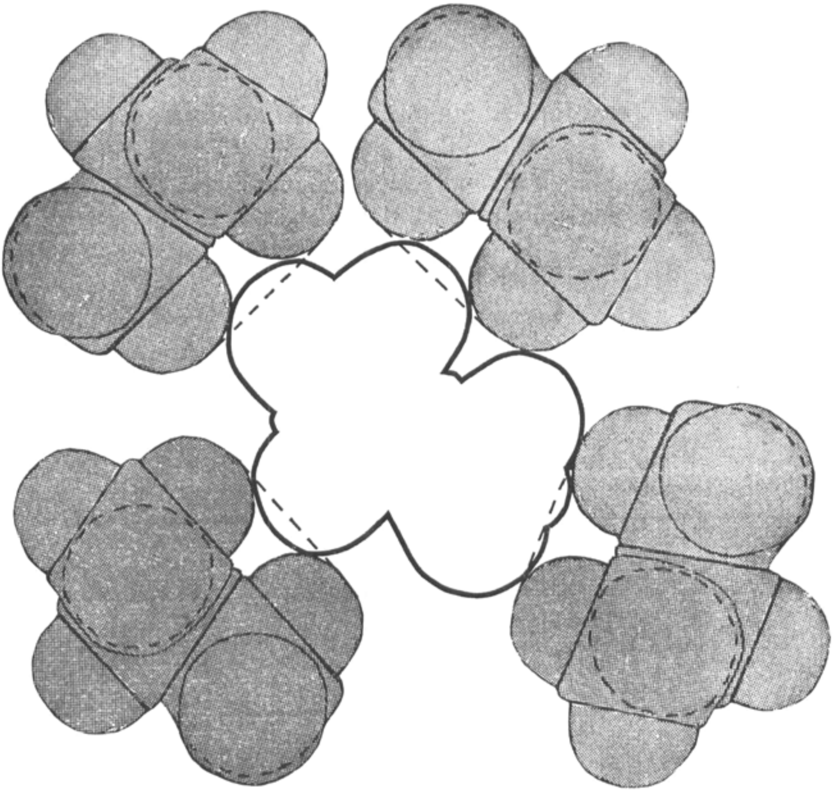


FIGURE 2(b) Hole formation involving negligible contribution from cavities (EPT/IIR-type) of limited accessibility.
Ideal packing, $n = 4$.
Measurements indicated that the r.m.s. distance between chains has required an increase of *ca.* 27% from the close-packing situation.

†*Note: a″* was generally calculated in the plane acting across the cavity at 90° to the chain direction: however, for NR, the most reasonable section for *a″*, although perpendicular to the sp^2 plane, apparently lies on the extension through the cavity of the direction given by the carbon atoms I and II in Figure 1(a).

in such a way that intra-chain cavities coincide. The space contributions of these cavities and that of the intervening inter-chain free space combine to form a hole of critical size in situations of chain proximity close enough to prohibit critical hole formation for those other polymers which possess no cavities: the concept is illustrated in Figures 2(a) and 2(b) for an ideal packing arrangement conveniently comprising four chains. Consequently, activation energy and friction coefficient[12, 23] aspects are minimised. Moreover, the number of holes attaining the critical size for diffusion during normal chain fluctuations must be considerably greater for polymers containing intra-chain cavities than that for polymers with negligible intra-chain free space.

Mathematical treatment of a simple model and the proposed alternative

Values of the free volume V at room temperature for several general purpose rubbers have been obtained on the lines of Simha and Boyer[24] by applying the expression

$$V = T\Delta\alpha$$

where T is absolute temperature and $\Delta\alpha$ is the difference in volume expansion coefficients above and below the glass transition temperature. Collated $\Delta\alpha$ data[23, 25-28] and results for V in cc/g are presented in Table III.

TABLE III

The total free volume and other data
$T = 294°\text{K}$

Polymer	ρ §	$\Delta\alpha$ (deg.$^{-1}$) $\times 10^{-4}$	Tg (°K)	V (cc/g)	General reference
NR	0.91	4.7	(201)	0.138	25
SBR 1500	0.89	4.5	(217)	0.132	26
cis BR	0.91	5.8	(170)	0.171	26
IIR	0.88	4.9	(205)	0.144	23‖
EBR†	0.90	—	217	0.153	27
EPT	0.84	5.55	(213)	0.163	26
Emulsion BR	0.89	4.85‡	(188–194)[28]	0.143	26

† Prepared within these laboratories. As no $\Delta\alpha$ data available, V calculated from Simha-Boyer iso-free volume at Tg, assuming $K_1 = 0.113$ cc/g[24].

‡ From extrapolated SBR data.

§ Density[27] at 21 °C except emulsion BR at 25 °C.[32]

‖ Data quoted for polyisobutylene.

The point has been made[29] that the use of empty volume involving the difference between observed volume and occupied chain volume (from van der Waals dimensions) would have been more apt. The main deviation of

$T\Delta\alpha$ away from the empty volume thus defined arises from non-linear extrapolations to 0°K. However, as a gradient-difference is involved, the extrapolation errors tend to counteract each other. Hence $T\Delta\alpha$ data have been considered suitable for free volume comparisons between polymers.

To distribute the free volume amongst the monomer units in the most simple model, we consider the close and semi-close packing of circles (or ellipses) representing ideal polymer chain cross-sections. The space between circles is concentrated in interstices, the number of interstitial spaces per circle (S_n) depending on the degree of packing n: when n is 3, 4, 5 or 6, S_n is 2, 1, 0.67 or 0.5 respectively.

Polymer chain packing will tend towards these ideal conditions, the degree of packing continually fluctuating about a mean value $\bar{n}$. Hence a calculated average volume of inter-chain free space for each monomer unit is shared between S_n regions of space. The mean cross-sectional area A of such a space region is given for the simple model by

$$A = \frac{VM_M}{S_n NL} \text{ for any degree of packing } n,$$

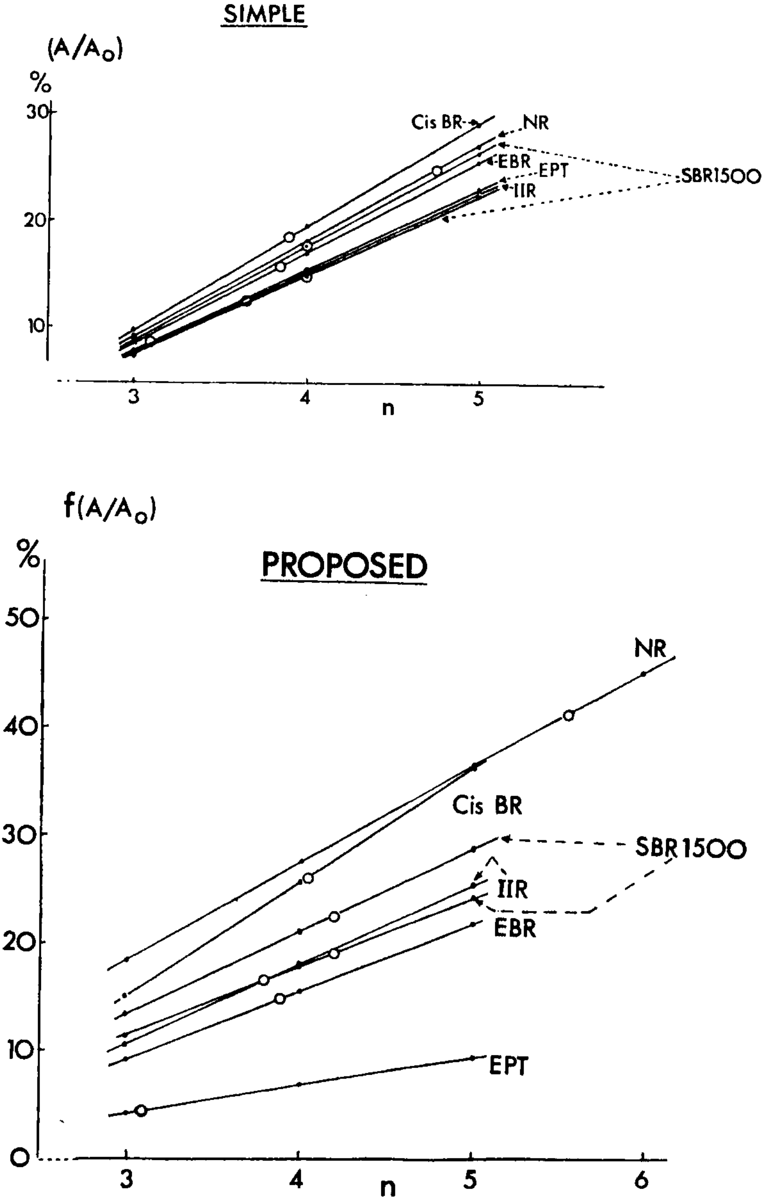
where N is Avogadro's number and M_M and L are the molecular weight and the length of a monomer unit: values of M_M and L are given in Table II.

A diffusion chain end involved in the autohesive phenomenon varies between polymers in shape and dimensions. For the simple model, the number of areas of inter-chain free space attaining the critical chain cross-sectional area A_0 (to provide access to an incoming chain end) during normal thermal movements must proportionate to the average inter-chain space area A for any chosen polymer. If A_0 were the same for all polymers, the most tacky polymer should possess the greatest A value. As A_0 varies between polymers, the ratio A/A_0 is more applicable to autohesion. Estimation details of A_0 are given in Appendix 1.

The data from Tables II and III and from Appendix 1, when applied as discussed, gave the graphs illustrated in Figure 3(a) for A/A_0 at several degrees of packing for the six rubbers studied. (The two SBR 1500 graphs resulted from two possible styrene A_0 values, see Appendix 1). At any value of n, no correlation of A/A_0 with tack data (Table I) is shown, the main discrepancy involving NR.

For the proposed model, V is shared between the total inter-chain free space V' and the total intra-chain free volume C'' where $C'' = \Sigma c''$. The calculation of C'' from the data of Table II involves the number x of cavities per monomer unit; C'' results and values for V' (obtained by subtraction) are given in Table IV.

By analogy with the simple model, the average contribution A' of inter-chain free space to the area A of a hole formed by the coinciding cavities



FIGURES 3(a) and 3(b) Mean ratio proportionating to the number of critical holes formed at different levels of packing for the two free volume models.

plus the intervening inter-chain space (Figure 2(a)), is given by $V'M_M/S_n\mathrm{NL}$: the contribution from the participating cavities, depending on the number of chains involved, is na'', so that

$$A = na'' + \frac{V'M_M}{S_nNL} \tag{1}$$

Values of A for both models when n is 4 are shown in Table IV.

TABLE IV

Calculations of the specific intra-chain (C'') and inter-chain (V') free volumes, and typical hole cross-sections‡
$C'' = xc''N/M_M$. Avogadro's Number, $N, = 6 \times 10^{23}$

			If $n = 4(S_n = 1)$		
			Simple model	Proposed model	
Polymer	C''	V'†	$A = VM_M/NL$	$A' = V'M_M/NL$	$A = na'' + A'$
	(cc/g)	(cc/g)	$(\text{Å})^2$	$(\text{Å})^2$	$(\text{Å})^2$
NR	0.057	0.081	3.56	2.09	6.85
SBR 1500	0.036	0.096	3.17	2.32	5.02
cis BR	0.022	0.149	3.49	3.05	4.65
IIR	0.031	0.113	5.35	4.18	6.58
EBR	0.021	0.132	4.26	3.68	6.08
EPT	0.009	0.154	3.53	3.33	5.73
Emulsion BR	0.035	0.108	2.88	2.18	4.33

† $V' = V - C''$

‡ For the proposed model, irrespective of the *number* of holes.

For the proposed model, the autohesive properties of any polymer sensibly relating to the number of critical holes formed will depend on both A/A_0 and the actual number of cavities per gramme (N_0) where

$$N_0 = \frac{xN}{M_M} \; (x = \Sigma\, \bar{x}_i \text{ for copolymers})$$

N_0 is not an absolute factor, as each cavity would not participate in hole formation after every chain movement. For convenience, rationalised values f representing N_0 for the various polymers, using N_0 for cis *BR* as the normallising factor, are presented in Table V.

Values for the combined factor $f(A/A_0)$, shown in Figure 3(b) at several degrees of packing n for the six rubbers, have been computed from data in Tables II–V and Appendix 1. A reasonable correlation is shown between (A/A_0) and the magnitude of autohesion (Table I).

As A is a mean area term, comparison between polymers of $f(A/A_0)$ values should arguably be made at average degrees of packing $\bar{n}$. Values of $\bar{n}$ have been estimated (Appendix 2) for ideal systems so that appropriate A/A_0 or $f(A/A_0)$ data for the two models could be obtained from the graphs ($\bar{n}$ values being indicated by circles) and collated into Table VI.

Comparison of Tables I and VI indicates that both models correlate reasonably with autohesive properties in order of magnitude. However, in terms of actual magnitude, the proposed model can explain more realistically the superiority of the autohesion of NR over that of the other five polymers.

TABLE V

Normalised factor f relating to the numbers of cavities per gramme

Polymer	N_0 $\times 10^{21}$	$f = 100\left(\frac{N_0}{N_{0(\text{cis BR})}}\right)$ %
NR	17.62	79.8
SBR 1500	16.78	76.0
cis BR	22.07	100.0
IIR	21.39	96.9
EBR	14.25	64.6
EPT	6.12	27.7
(Emulsion BR	20.30	92.0)

TABLE VI

Calculated factors to monitor autohesion for the two models at mean levels of chain packing, $\bar{n}$‡

Data from Figure 3 at appropriate values of n

Polymer	Simple free volume model		Proposed free volume model	
	$\bar{n}$	$(A/A_0)\%$	$\bar{n}$	$f(A/A_0)\%$
NR	4.8	24.8	5.6	41.6
SBR 1500	4.0	17.6(a)	4.2	22.7(a)
		14.9(b)		19.2(b)
cis BR	3.9	18.4	4.1	26.5
IIR	3.6	12.4	3.8	16.5
EBR	3.9	15.7	3.9	15.1
EPT	3.1	8.4	3.1	4.4
Emulsion BR†	3.9	—	4.1	—

NB. A_0 estimation including (a) the "end-on" cross-section of styrene units; (b) the "face-on" styrene cross-section.

‡ Applies at 21°C: $\bar{n}$ estimation details shown in Appendix 2.

† Included for consideration of gaseous diffusion only.

CONCLUSION

Relation of the proposed model, autohesive diffusion and chain flexibility

The possibility of "shaped" free volume regions[30] and regions at somewhat less than segmental magnitudes[31] has been discussed with respect to polymer structural behaviour. The effect of the localised rigidity at double bonds in increasing the possibility of hole formation has been suggested for diffusion of relatively long-chain solvents in polymers.[32] The present model, in extending similar reasoning to the autohesive phenomenon, has demonstrated semi-quantitatively (in terms of high opportunities for hole formation to give many autohesion sites) the order of tack obtained for six polymers. Comparison of the calculated data shows that the main purpose of the proposed model is to offer an explanation for the high tack of NR rather than to grade the tack of all polymers. Cis-polyisoprenes are unique amongst common rubbery polymers in containing numerous cavities of substantial size and high accessibility to incoming chains.

The spontaneity with which the most tacky polymers adhere possibly suggests a rapid initial diffusion, from each surface, of short chain ends or portions into the opposite recipient surface, utilising the relatively numerous critical holes formed by the coincidence of cavities in these polymers: such a possibility has already been mentioned in relation to $\bar{s}$ and diffusion rates. The subsequent development of bond strength, depending on the diffusion of statistical chain segments of length 20 to 40 carbon atoms,[33] requires a high degree of local co-operative segmental organisation within the polymer bulk to form critically-sized holes. The presence, generally associated with saturated systems,[21] of high internal energy barriers to rotation is not conducive to such co-operative motion: furthermore, the effective size of the saturated diffusive unit will be high. Additionally, in terms of the proposed model, at this scale of segmental organisation the presence of cavities (for NR especially) facilitates the co-operative alignment of discrete holes, thus enabling the critical segmental hole size to be attained with less chain co-operation: consequently, critical holes will again occur in greater numbers. Hence, the effects of chain structure on both flexibility and the provision of intra-chain cavities are largely complementary: the explanation in structure terms of the apparent differences of an order of magnitude between the diffusion coefficients for NR and EP is feasible under such considerations.

Correlation of the proposed model with diffusion through polymers of gases and solvents

Unlike autohesive diffusion, gaseous and solvent diffusion permits comparison of the same diffusant in a range of polymers, so that any relationship of diffusion and free volume might be studied. The absence of matrix-penetrant interaction found[34] for several solvent polymer systems permits such a comparison. Typical data[32, 35-41] are shown in Table VII. Values of D are sensibly decreased by the presence of side-groups, and with increasing diffusant size and molecular weight, the nature of the rubber matrix being the major factor in diffusion.[35] The rates of diffusion involved ($D \sim 10^{-5} - 10^{-7}$ cm^2/sec.) are high relative to those for autohesion.

A general relationship of solvent diffusion and free volume shown by

TABLE VII

Collated data for diffusion of gases and solvents in several polymers, Diffusion constant D values, cm²/sec × 10⁷

		Diffusion of gases[41]				Diffusion of solvents		Diffusion of long-chain hydrocarbon solvents				
Polymer	Diffusion temp. (°C)	H_2	N_2	O_2	CO_2	Benzene[36]	1, 1-Diphenyl ethane[40]	Dodecane[39]	Hexadecane[39]	Octadecane[32]	Oil[35]‡ (~24 -C- atoms)	Octadecyl[32] stearate
NR	25	102.0	11.0	15.8	11.0	1.4[37]	0.55	1.02	0.76	—	—	—
	40	—	—	—	—	—	1.86 (45°C)	—	—	1.69	—	1.02
	50	222.0	34.2	47.0	35.0	—	—	—	—	2.85	—	1.40
	60	—	—	—	—	—	—	—	—	3.94	—	1.94
	100	—	—	—	—	—	—	—	—	—	~3.5	—
SBR 1500	25	—	—	—	—	—	0.21	0.40	0.27	—	—	—
	40	—	—	—	—	—	—	—	—	1.38†	—	—
	50	—	—	—	—	—	0.96 (48°C)	—	—	2.29†	—	—
	60	—	—	—	—	—	—	—	—	3.22†	—	—
	100	—	—	—	—	—	—	—	—	—	~1.9	—
cis BR	25	—	—	—	—	—	4.41	5.75	4.57	—	—	—
	100	—	—	—	—	—	—	—	—	—	~6.4	—
Emulsion BR	25	96.0	11.0	15.0	10.5	—	0.83	—	0.83	—	—	—
	40	—	—	—	—	—	—	—	—	2.78	—	0.95
	50	180.0	29.0	37.0	28.0	—	—	—	—	3.62	—	1.41
	60	—	—	—	—	—	—	—	—	6.19	—	1.80
IIR	25	15.2	0.45	0.81	0.58	—	0.004§	0.007§	0.006§	—	—	—
	40	—	—	—	—	0.047§[38]	—	—	—	—	—	—
	50	43.8	2.2	3.84	2.76	—	0.03§ (48°C)	—	—	—	—	—
EP (31–33 mole %P)	23	—	—	—	—	1.05	—	—	—	—	—	—
	40	—	—	—	—	2.7	—	—	—	—	—	—
	100	—	—	—	—	—	—	—	—	—	~2.6	—

† GRS 1006. ‡ Filled compounds. § Polyisobutylene.

Typical microstructure[39, 40] of emulsion BR: cis 19%, trans 64%, vinyl 17%.

Chen and Ferry[39] cannot be applied to gaseous diffusion according to the data of van Amerongen[41] (Table VII) considered below.

Natural rubber and emulsion polybutadiene The apparently paradoxical comparative data for gaseous diffusion into NR and emulsion BR across the range of diffusants may be resolved by the proposed concept: the discussion refers to diffusion at near-room temperatures, higher temperature diffusion data facilitating certain comparisons.

For hydrogen, which diffuses more quickly through NR than through emulsion BR, a single —CH_2— unit probably possesses sufficient associated free volume to permit the occurrence of a diffusive step,[19] and the jump frequency involved is sufficiently rapid to utilise fully every hole of sufficient size,[34] as a hydrogen molecule is only of circular cross-section 4.5 $Å^2$ and elliptical cross-section 5.9 $Å^2$. During normal chain fluctuations, continually-changing regions of close-packing occur, and holes of minimum cross-section A_c for any level of packing n may still exist by the coincidence of cavities plus the closest-packing inter-chain free space. Whereas Eq. 1 described a mean hole area A, the inter-chain component of A_c may be estimated by ideal close-packing geometry. From Appendix 2 (by consideration of Eq. 3),

$$A_c = na'' + A_0\left(\frac{n}{\pi}\tan\frac{90(n-2)^\circ}{n} - \frac{(n-2)}{2}\right) \qquad (2)$$

Although both polymers possess numerous cavities, the large NR cavities cause A_c values of magnitude equal to the critical cross-sections for a hydrogen molecule to occur when n is as low as 3.0–3.3, whereas the equivalent packing for emulsion BR is 3.55–3.8. Clearly NR can offer critical holes for hydrogen diffusion even when tightly packed (with further advantage normally arising from its high mean packing level $\bar{n}$ of 5.6) whereas emulsion BR only provides large enough holes at n values much nearer to its own $\bar{n}$ level of 4.1. BR must possess many holes of insufficient size, the free volume being utilised much more fully in NR for hydrogen diffusion.

To produce larger holes from the tightest packing situation requires chain movements which combine an increase in n and an opening of the existing packing situation at constant n. In either case, the proportion of intra-chain free space decreases with increasing hole size: in these terms, the inter-chain free space increases in importance with increasing hole size, as illustrated by the data. Table VII shows that, for the other gases cited (which require for hole formation a minimum co-operation estimated at 4 or 5 —CH_2— units[19]), D values in the two polymers are similar: moreover, the diffusion coefficients of bulkier diffusants such as the hydrocarbon solvents (except the largest) follow the sequence NR < emulsion BR (<cis BR). The typical mean values of inter-chain cross-sections (A') shown for these polymers in

Table IV follow the same sequence. Nevertheless, an influence of the large NR cavities may still be reflected in the similarity for several common elastomers of the apparent activation energies for hexadecane diffusion and viscoelastic relaxation, the single exception being NR for which the former energy is distinctly smaller.[39, 23]

With the bulkiest diffusant (octadecyl stearate) the sequence of diffusion rates reverts to NR > emulsion BR. All holes discussed to date are too small, and the jump frequency has now decreased considerably. Critical hole formation only occurs by increased co-operative chain movements (the role of chain flexibility having increased), the diffusant being roughly as big as a polymer chain segment (20–40 chain carbon atoms[33]). As with autohesion, the presence of cavities should minimise the chain co-operation necessary so that many more critical holes form, for NR especially: N_0 is again a relevant factor. The appropriate diffusion coefficients are 2–3 orders of magnitude below those for hydrogen. The further decrease of *ca.* 4 orders in D values for autohesion reasonably relates to the large molecular weight differences involved.

It is of interest to note the data of Corman *et al.*[35] concerning oil ($\sim C_{24}$) diffusion into filled compounds at 100°C, where $D_{\mathrm{NR}} < D_{\mathrm{cis\,BR}}$. The increased kinetic energy at 100°C sensibly increases the inter-chain free space, thereby presumably displacing to longer chain situations the importance of cavities in complementing chain co-operation effects.

Other polymers SBR 1500 should permit only moderate diffusion rates according to its a'' and A' values (Tables II and IV). Diffusion data (Table VII) are insufficient for a full appraisal, but general agreement is indicated.

The limited data[36] of benzene diffusion into NR and EP copolymer show D_{EP} to be approaching D_{NR} in value: it could be speculated that the influence of the cavities in NR, although less pronounced than on gaseous diffusion, is offset by the larger A' value of EP important at this scale of diffusion.

However, all D values of IIR (or PIB) are very low. Although a Stuart model of PIB shows two accessible cavities per monomer unit ($x = 2$), other shielded free volume cavities exist at any micro-Brownian segmental conformation. In addition, although the cavities are of moderate size, their shape precludes more than partial ingress, even by a hydrogen atom (Figure 1(b)). Free volume data derived from the combined expansivity behaviour of all chains should include shielded free volume regions. Hence, the useful free volume for PIB may be considerably less than initially expected (the high A' value arising from an over-simplified model), to explain in part the low value of D_{PIB}. The existence in benzene-swollen IIR of many holes of insufficient size to accept further diffusing benzene molecules has already been indicated.[34]

Implications of the proposed model

For the greatest autohesion, the minimum requirement for the structure of a repeating unit combines the associated presence of both restricted rotation and one or more bulky side groups in a form of sufficient disorder to avoid substantial crystallinity at room temperatures. It is unlikely that saturated polymers, for instance, can attain high tack simply by subjection to minor changes in structure.

The speculative model has indicated the influence of that free space which is finely-distributed around chain structural features on those characteristics of a polymer which regulate a diffusing species, characteristics which can also be monitored by factors at a higher scale of organisation such as chain structural symmetry (causing crystallinity), chain magnitude (molecular weight) and free volume *per se*.

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APPENDIX 1

CALCULATION OF THE CROSS-SECTION A_0 (OR CRITICAL HOLE SIZE) FOR THE SIX POLYMERS

No comprehensive range of measured A_0 data utilising molecular sieves is available for hydrocarbons representing the polymers. For consistency, all A_0 values were therefore estimated and are given below: certain sequences of A_0 data involving molecular sieves are also provided for comparison.

Stuart models were used to determine the most representative regular chain aspect for A_0: an arbitrary length of *ca.* 5 Å was considered. The most bulky cross-section was assumed to be circular or elliptical (as appropriate to each polymer) and radii (semi-axes) were calculated trigonometrically from atomic dimensions.[22, 21]

Estimated data are shown below, the cross-section sensibly existing at 90° to the chain direction for all polymers except NR, being in the direction (perpendicular to the sp^2 plane) given by the chain carbon atoms I and II in Figure 1(a) for NR (cf. the direction of a'', page 9). Values were proportionated for copolymers, molar ratios being in Table II. The additional possibility of "end-on" diffusion of the styrene moiety (during initial diffusion) causes a second A_0 value for SBR.

Polymer	Copolymer Moiety	Estimated Polymer Cross-section A_0		Footnote for Comparison	
			$(\text{Å})^2$		
NR			19.8	a	
SBR 1500	Styrene	17.4, 41.6	18.0, 21.3		
	Butadiene†	18.1			
cis BR			18.0	a	c
IIR			35.5	b	
EBR	Ethylene	21.1	25.1	b	c
	Butene-1	29.1			
EPT	Ethylene	21.1	23.2	b	c
				b	
	Propylene	27.4			
Emulsion BR			18.2	a	c

(Butadiene isomers: cis 1, 4 = 18.0; trans 1, 4 = 16.6; 1, 2 = 24.3.)
Compare with experimental cross-sections (in $(\text{Å})^2$):

a) 2-Me-propene, >19.6; 1-butene, <19.6[42].
b) 2, 2, 4-tri Me-pentane,‡ ~ 28.5; isoparaffins, ~ 24.5; higher n-paraffins up to *ca.* C_{16}, ~ 19.0[43].
c) Propene, <12.6; propane, >12.6[44] (i.e. -ene $<$-ane).

† Appropriate emulsion. ‡ The concentration of side-groups is less than in IIR.

APPENDIX 2

ESTIMATION OF THE MEAN DEGREES OF CHAIN PACKING $\bar{n}$ FOR IDEAL MODELS OF THE SIX POLYMERS

Study of the contact-packing of circles reveals the following empirical relationship between packing n and the ratio

$$\frac{\sum \text{circle (or sector) areas}}{\sum \text{interstitial space areas}}$$

for P space areas:

$$Ratio = \frac{P\pi r^2 \dfrac{(n-2)}{2}}{Pnr^2 \tan \dfrac{90(n-2)^\circ}{n} - P\pi r^2 \dfrac{(n-2)}{2}} \tag{3}$$

(Hence a single space area can be considered similarly). The ratio from a reduced Eq. 3 also applies to ellipses packed regularly.

For 1 g of any polymer, the number of chains in an ideal model comprising parallel chains lying only between two parallel faces of a cube, side l, $= NL/M_M l$.

$$\therefore\ Ratio \frac{\sum \text{Chain Areas}}{\sum \text{Space Areas}} = \frac{(NL/M_M l)A_0}{l^2 - (NL/M_M l)A_0} = \frac{NLA_0\rho}{M_M - NLA_0\rho} \tag{4}$$

as density $\rho = 1/l^3$.

Substitution of data into Eq. 4 gives for each polymer a ratio which subsequently indicates an ideal packing value $\bar{n}$ applicable at 21°C on a graphical form of reduced Eq. 3 for the simple free volume model.

For the proposed model, chain packing in the vicinity of cavities causes the replacement of A_0 by $(A_0 - xa'')$ in Eq. 4. $\bar{n}$ is weighted on a length basis between the modified and unmodified Eq. 4 for chain regions with and without cavities respectively.

A more realistic (although still ideal) model would accommodate motion away from close packing by using $n(r+s)^2$ rather than nr^2 when obtaining (modified) Eq. 3, where s is an additional distance term. However, in practice, ratio values for all polymers from Eq. 4 realistically fit the present reduced Eq. 3, whereas in the modified form $\bar{n}$ for the closest packed polymer, *EP*, is realistic ($\geqslant 3$) only when $s \leqslant r/250$. As real polymer matrices must contain a large distribution of chain crossover points (involving bigger free volume regions) s must actually be considerably less than $r/250$. Hence the simple ideal model was used for estimations of $\bar{n}$.

APPENDIX 3

TO DEMONSTRATE THE SUPPLEMENTARY ROLE OF STRESS CRYSTALLISATION FOR AUTOHESION

The inference that the high tack levels of polyisoprene reflect enhanced self-diffusion characteristics should only be applied in the absence of stress crystallisation, when their autohesive strengths should still be greater than those of SBR and cis BR, polymers second in the scale of tack magnitude (Table I). Cunneen[45] has shown that isomerised natural rubber containing greater than 21% trans polyisoprene does not exhibit stress crystallisation.

However as $[\eta]_{\text{benz.}}$ for such polymers was four times greater than the value for the original NR[27], considerable branching or cross-linking was implied. The following modified isomerisation procedure was found necessary for studying autohesion.

100 g NR was mill-mixed with 5 g butadiene sulphone (BS) and 1.5 g tertiary butyl catechol (TBC): BS performed the isomerisation whilst TBC, a radical absorber, was intended to inhibit branching. The rubber was isomerised for 3 hours in a press at 160°C using a closed steel vessel of approximate capacity 500 ml. To obtain isomerised rubber at a suitable molecular weight for tack, the original NR used was high molecular weight ribbed smoked sheet, and mixing breakdown was kept to a minimum under the cool conditions required to handle the TBC; similarly, the compromise between branching and breakdown demanded a restricted amount only of air during isomerisation. The molecular weight in question ($M_v \sim 3\text{–}5 \times 10^5$, constant Wallace viscosity) applied to all polymers discussed below (whilst uncured).

In a series of tack measurements, the autohesion of an isomerised polyisoprene containing 23% trans polymer (by NMR[27]) was *ca.* 20% greater than that of any SBR 1500-type or cis BR polymer studied. The absence of stress crystallisation in a TMTDS/ZnO-cured compound of the isomerised polymer stretched to 500% (the elongation at break, EB_u, for the uncured polymer) was confirmed by x-ray diffraction measurements.[27] This technique also showed that stress crystallisation in a similar compound containing Cariflex IR305 polyisoprene (92% cis) of EB_u *ca.* 350% did not occur until well over 500% elongation at the molecular weight involved, whereas a NR compound exhibited stress crystallisation at relatively low elongations: the autohesion of IR305 was 35% greater than the cis BR value.