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Use of Sol-Gel Analysis to Estimate Chain Scission during Vulcanization. Part II. Peroxide Vulcanization of Synthetic *cis*-Polyisoprene

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Synopsis

Sol-gel analysis indicates that in the vulcanization of synthetic *cis*-polyisoprene by dicumyl peroxide there are only 2–3 sites of scission per 100 crosslinked isoprene units, a value closely comparable with that observed for natural rubber.

In Part I[1] of this series the application of the sol-gel method to the dicumyl peroxide vulcanization of pale crepe natural rubber was described, and it was concluded that such vulcanization was accompanied by main chain scission to a very limited extent, some fifty crosslinks being formed for every scission. While the hydrocarbon backbone of natural rubber is almost certainly ca. 100% *cis*-1,4-polyisoprene, configurational abnormalities such as head-to-head (rather than head-to-tail) addition sites may exist. Further, experimental evidence exists[2] for the presence of nonhydrocarbon groupings pendent to the main chain. The possibility exists, therefore, that these abnormalities or groupings may provide the sites for relatively easy scission during peroxide vulcanization. It is therefore of interest to compare the estimates of scission for natural rubber with those for a synthetic *cis*-polyisoprene. Though these synthetic materials are $< 100\%$ *cis*-1,4 in configuration and may even contain attached catalyst residues, the chance that such abnormalities would facilitate scission to the same extent as those present in natural rubber is exceedingly remote. Any association of scission with structural abnormality of the rubber should therefore be detectable.

The polyisoprene (ca. 95% *cis*-1,4) used was obtained from the Shell Development Co. It contained some 1% of an antioxidant which was only partially removed by hot acetone extraction. Apart from some slight differences in rate and ultimate extent of cure, extraction did not affect the subsequent measurements. Mixing and curing were effected as described previously.[1] Values of number-average molecular weight needed for calculation of crosslink density were obtained from estimates of intrinsic viscosity by application of the appropriate relation.[3]

TABLE I
Sol Contents and Crosslink Densities for Dicumyl Peroxide (DCP) *cis*-Polyisoprene Vulcanizates

	Initial rubber		Cure			Wt. fraction sol	v_r *n*-decane	$q^{-1} \times 10^{-2}$
	$[\eta]$, dl./g.	$\bar{M}_n \times 10^{-5}$	DCP, %	Temp., °C.	Time, min.			
A[a]	2.87	2.32	3	130	10	0.0846	0.091	—
					20	0.0444	0.129	—
					40	0.0224	0.181	7.10
					60	0.0128	0.215	4.76
					80	0.0089	0.236	3.46
					100	0.0060	0.255	2.62
					150	0.0034	0.290	1.66
					200	0.0035	0.312	1.27
B	2.73	2.20	1	130	20	0.0503	0.093	—
					30	0.0269	0.166	—
					40	0.0156	0.200	5.58
			1	140	20	0.0114	0.220	4.27
					20	0.0165	0.202	5.44
					30	0.0068	0.240	3.20
					40	0.0041	0.261	2.37
					60	0.0042	0.282	1.82
					80	0.0027	0.300	1.45
			1	150	50	0.0031	0.316	1.21
C	2.57	2.08	3	130	10	0.1442	0.067	—
					20	0.0565	0.125	—
					40	0.0240	0.183	6.33
					60	0.0148	0.208	4.83
					80	0.0113	0.222	4.03
					100	0.0089	0.235	3.32
					150	0.0070	0.263	2.27
					200	0.0059	0.278	1.87
D	1.88	1.53	5	130	30	0.0280	0.182	5.06
					60	0.0079	0.258	2.15
			5	140	30	0.0063	0.260	2.09
					45	0.0048	0.291	1.51
					60	0.0043	0.315	1.16
			5	150	25	0.0039	0.337	0.89
					40	0.0029	0.364	0.77
E	1.36	1.12	1	130	20	0.1723	0.051	—
					40	0.0304	0.159	4.62
					40	0.0458	0.147	4.93
			1	140	20	0.0197	0.187	3.82
					30	0.0117	0.220	2.86
					40	0.0061	0.256	1.97
					60	0.0046	0.279	1.56
					80	0.0040	0.300	1.26
			1	150	25	0.0059	0.275	1.64
					50	0.0043	0.312	1.11

[a] Acetone-extracted.

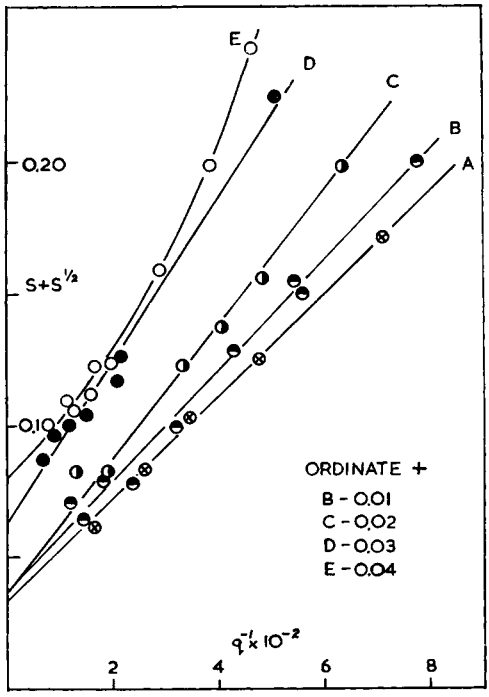

Fig. 1. Plot of $S+S^{1/2}$ (where S is the weight fraction of sol) vs. (crosslink density)$^{-1}$ for synthetic *cis*-polyisoprene vulcanized with dicumyl peroxide. (Ordinate displaced by the amounts indicated.)

The methods for determination of crosslink density and estimation of sol content have been described in Part I.[1]

The experimental data are presented in Table I and the plots of $S + S^{1/2}$ versus q^{-1} in Figure 1. (Here S is sol content; q is fraction of isoprene units crosslinked.) Samples A–D gave linear plots, and application of the method of least squares gives eqs. (1)–(4).

For sample A:

$$S + S^{1/2} = 0.0335 + 0.0195\ q^{-1} \tag{1}$$

For sample B:

$$S + S^{1/2} = 0.0266 + 0.0210\ q^{-1} \tag{2}$$

For sample C:

$$S + S^{1/2} = 0.0155 + 0.0256\ q^{-1} \tag{3}$$

For sample D:

$$S + S^{1/2} = 0.0295 + 0.0318\ q^{-1} \tag{4}$$

The data for sample E, that of lowest initial molecular weight, have been represented as a smooth curve. The deviation from linearity in this case is probably due to a marked departure from a random molecular weight distribution induced by heavy mastication. In all cases the intercept on

the ordinate which represents the ratio of scission sites to crosslinked sites is of the order of 0.02–0.03, a value closely comparable with that observed for natural rubber. There is no evidence, therefore, that scission in either of these polyisoprenes occurs at abnormal sites but randomly along the hydrocarbon chain.

References

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2. Sekhar, B. C., *J. Polymer Sci.*, **48**, 133 (1960); *Rubber Chem. Technol.*, **35**, 889 (1962).
3. Bristow, G. M., *J. Polymer Sci.*, **A1**, 2261 (1963).

Résumé

Des analyses sol-gel montrent que dans la vulcanisation du polyisoprène-*cis* synthétique, au moyen de peroxyde de dicumyle il n'y a que 2–3 sites de scission par 100 unités d'isoprène pontées; cette valeur est voisine de celle observée dans le cas du caoutchouc naturel.

Zusammenfassung

Auf Grund einer Sol-Gel-Analyse wurde festgestellt, dass bei der Vulkanisation von synthetischem *cis*-Polyisopren mit Dicumylperoxyd nur 2–3 Spaltungsstellen auf 100 vernetzte Isopreneinheiten entfallen. Dieser Wert liegt in der Nähe des für natürlichen Kautschuk bestimmten Wertes.

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