

## Elastic Properties and Structure of Polybutadiene Vulcanized with Magnesium Methacrylate

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### Synopsis

The elastic and structural properties of polybutadiene vulcanized with magnesium methacrylate were investigated. Structural information was obtained by x-ray small-angle diffusion diagrams. Results clearly indicate that in the elastomeric network there is a random distribution of rigid particles. The elastic behavior was analyzed in terms of the Mooney-Rivlin equation. Experimental evidence for the direct correlation between elastic and structural properties is given.

### INTRODUCTION

It is well known that vulcanizates containing salt crosslinks have good physicochemical properties without reinforcing fillers.<sup>1</sup> Earlier, it was shown<sup>2</sup> that this effect may be obtained by vulcanization with salts of methacrylic acid. However, the elastic properties of such networks were not investigated in detail, and there are only some suggestions about their structure. It would be, therefore, of theoretical significance to analyze the elastic behavior of these networks and to find any possible correlation with the internal structure. For this purpose we have prepared various vulcanizates of *cis*-1,4-polybutadiene, each with a different amount of magnesium methacrylate.

Analysis of the elastic behavior was carried out by use of the Mooney-Rivlin equation,<sup>3</sup> and information regarding structure was obtained from small-angle x-ray diffusion diagrams.

### EXPERIMENTAL

#### Materials

We used *cis*-1,4-polybutadiene ANIC, supplied by the SNAM Laboratories of Milan. Magnesium salts of methacrylic acid were prepared by heating aqueous solutions of the acid and magnesium hydroxide. The salt was passed through sieves, and only particles of diameter less than 0.05 mm were used. The mixture of polymer and salt was prepared in a rubber

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mill. Vulcanization was effected in press at 155°C for 30 min, using dicumyl peroxide (DCP) as the initiator. These conditions were selected on the basis of preliminary experiments carried out with a Monsanto vulcameter. The compositions of the samples under examination are reported in Table I.

### Methods

Stress-strain curves were determined as reported in the literature,<sup>4</sup> with 20- to 25-min intervals between determinations at different elongations. In the case of swollen samples, the stress was corrected by the factor  $V_s^{1/3}$ ,  $V_s$  being the volume fraction of polymer. All measurements were carried out at 35°C.

Small-angle x-ray scattering diagrams were taken on a Rigaku-Denki SA camera (resolving power up to 800 Å) by counter technique.

We used slit collimation with restricting slits in order to minimize experimental error and worked under the following experimental conditions:  $\text{CuK}_\alpha$  radiation, 40 KV; 20 mA; time constant, 4; speed of scanning, 2'/min; distances between the slits, as follows: focal spot-1° slit, 80 mm, 1° slit-2° slit, 240 mm, 2° slit-3° slit, 50 mm, 3° slit-specimen, 20 mm, specimen-Geiger counter, 350 mm.

Background diagrams were made in all cases, and only background-corrected scattering values were used for calculations.

## RESULTS

### Mechanical Properties

The most important feature of the salt vulcanizates, PB-10, PB-20, and PB-30, is their cluster structure, the clusters consisting of a large number of ionic bonds (see below). If this type of network is contained in non-polar solvents, it can be assumed that only the rubber fraction will be swollen; on the other hand, if a polar solvent with a small amount of a strong acid is used, it is possible that the clusters will also swell and that they will be destroyed by hydrolysis. In fact, we have used the latter technique in our analysis in order to test the effect of the network structure

TABLE I  
Composition of Examined Samples

Sample	Magnesium methacrylate, wt-%	DCP <sup>a</sup> wt-%
PB-0	0	0.3
PB-10	10	0.3
PB-20	20	0.3
PB-30	30	0.3

<sup>a</sup> Dicumyl peroxide, used as vulcanizing initiator.

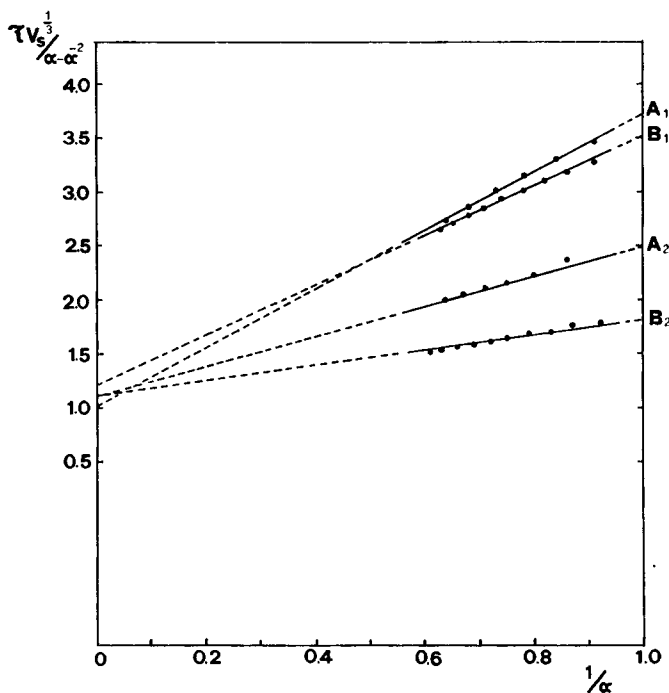


Fig. 1. Mooney-Rivlin plot for PB-O. Swelling solvent, decaline; temp., 35°C: specimen A<sub>1</sub>,  $V_s = 1$ ; A<sub>2</sub>,  $V_s = 0.726$ ; B<sub>1</sub>,  $V_s = 1$ ; B<sub>2</sub>,  $V_s = 0.658$ .

on the mechanical behavior. In Figures 1 to 4 we have reported stress-strain data obtained with the dry and swollen samples of Table I (the swelling solvent being decaline, a nonpolar solvents), in terms of the Mooney-Rivlin equation

$$\tau = 2C_1(\alpha - \alpha^{-2}) + 2C_2(1 - \alpha^{-3}) \quad (1)$$

where  $\tau$  is the force per unit of cross-sectional area,  $\alpha$  is the strain ratio, and  $C_1$  and  $C_2$  two coefficients.

The first effect we noted was that regarding the  $2C_2/2C_1$  ratio for the dry samples. Results are reported in Table II. An increase in the  $C_2$  term on increasing the salt amount was observed. Furthermore, the data in Table II indicate that a strong increase in the  $2C_2/2C_1$  ratio is related to an increase in the amount of salt. In other words, we may observe a relative increase in the  $2C_2$  term with network clustering (see below).

The second effect which is clearly shown, and which concerns only the salt vulcanizates (PB-20 and PB-30), is the non-Gaussian behavior of the swollen samples. An upturn in the Mooney-Rivlin plots is, in fact, visible. This upturn is characterized by a rapid change of the  $2C_2$  term from positive to negative values.

As reported in the literature,<sup>5</sup> this trend can be attributed either to non-

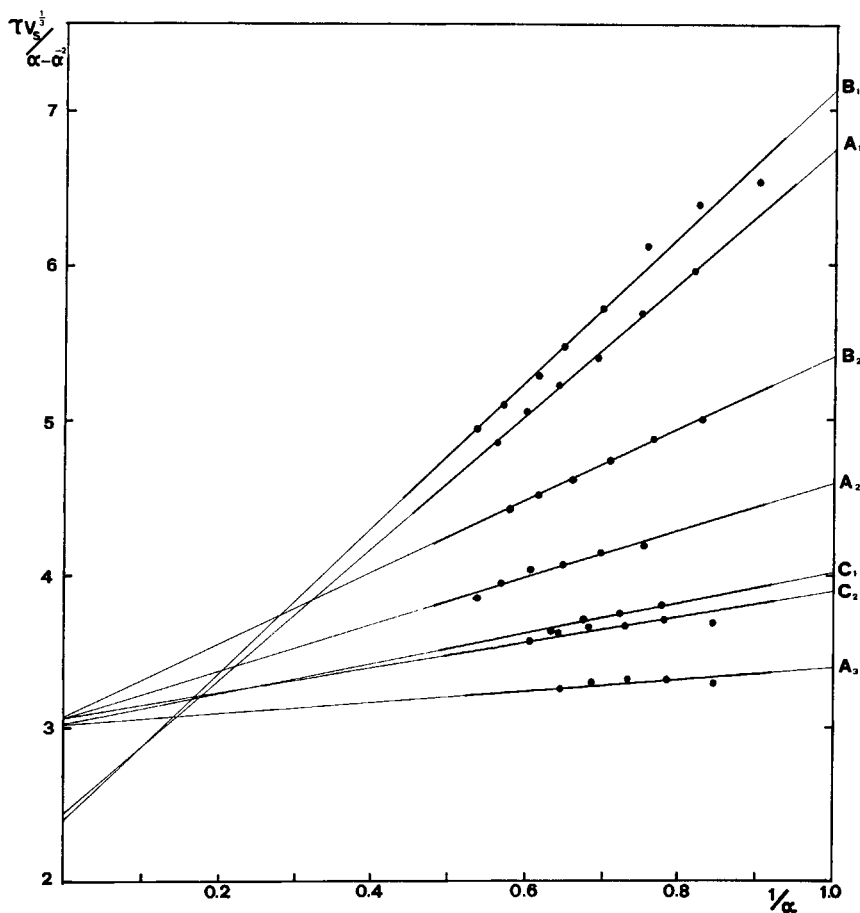


Fig. 2. Mooney-Rivlin plot for PB-10. Swelling solvent, decaline; temp., 35°C: specimen A<sub>1</sub>,  $V_s = 1$ ; A<sub>2</sub>,  $V_s = 0.677$ ; A<sub>3</sub>,  $V_s = 0.476$ ; B<sub>1</sub>,  $V_s = 1$ ; B<sub>2</sub>,  $V_s = 0.802$ ; C<sub>1</sub>,  $V_s = 0.591$ ; C<sub>2</sub>,  $V_s = 0.561$ .

TABLE II  
 $2C_1$ ,  $2C_2$ , and Mean  $C_2/C_1$  Values Calculated for Dry Samples

Sample	$2C_1$ , kg/cm <sup>2</sup>	$2C_2$ , kg/cm <sup>2</sup>	$\overline{2C_2/2C_1}$
PB-0	1.20	2.30	2.28
	1.02	2.70	
PB-10	3.42	4.76	1.32
	3.45	4.30	
PB-20	2.08	3.42	2.03
	2.06	4.98	
PB-30	2.16	5.70	2.43
	2.15	4.80	
	2.00	4.85	

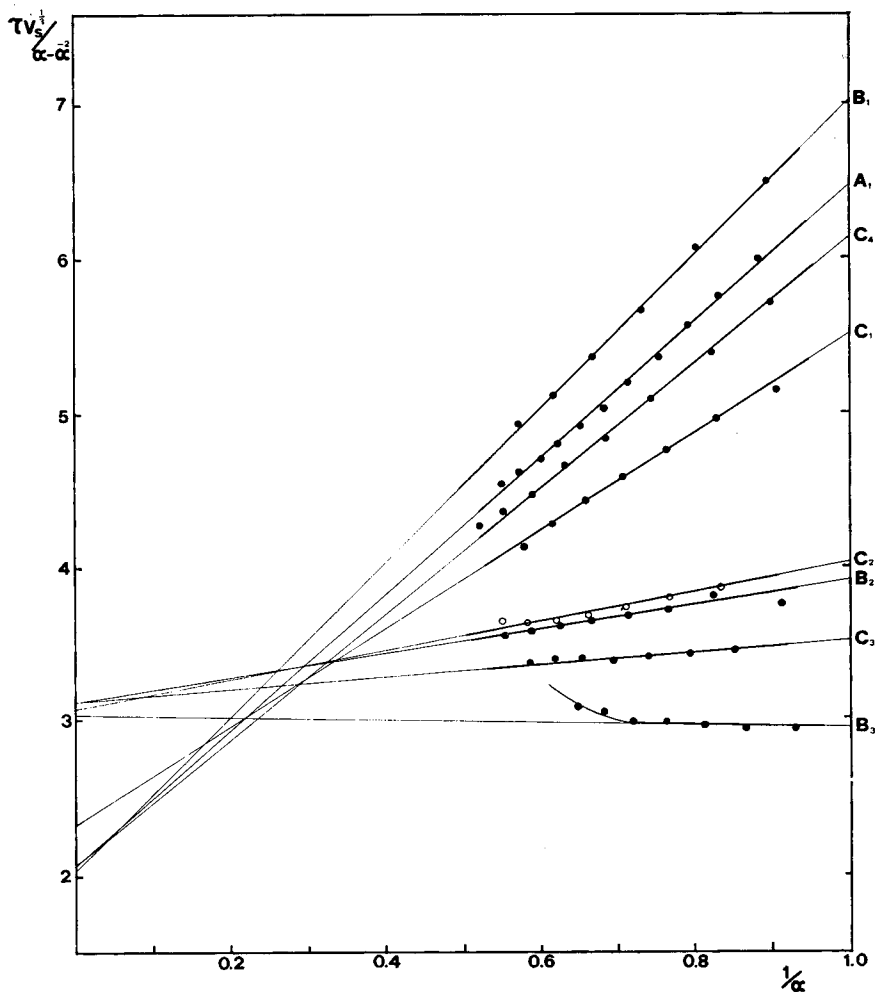


Fig. 3. Mooney-Rivlin plot for PB-20. Swelling solvent, decaline; temp., 35°C: specimen A<sub>1</sub>,  $V_s = 1$ ; B<sub>1</sub>,  $V_s = 1$ ; B<sub>2</sub>,  $V_s = 0.679$ ; B<sub>3</sub>,  $V_s = 0.402$ ; C<sub>1</sub>,  $V_s = 0.809$ ; C<sub>2</sub>,  $V_s = 0.754$ ; C<sub>3</sub>,  $V_s = 591$ ; C<sub>4</sub>,  $V_s = 1$  (after deswelling).

Gaussian behavior or to crystallization under stress. In the present case, crystallization phenomena in highly swollen samples may be excluded.

The final effect has to do with the swelling behavior of the  $2C_1$  coefficient. Keeping in mind that a cluster structure simulates a filled network, the  $2C_1$  values of Figures 2 to 4 have been corrected by use of the Guth-Smallwood equation:<sup>6</sup>

$$2C_1(F) = 2C_1(1 + 2.5\Phi_s + 14.1\Phi_s^2) \quad (2)$$

where  $\Phi_s$  is the volume fraction occupied by the domains, and  $2C_1(F)$  and  $2C_1$  are the Mooney-Rivlin coefficients for the filled and unfilled rubber, respectively.

In Figure 5, the data so obtained versus the  $V_s$  values are reported (it is important here to keep in mind that only the rubber fraction is swollen).

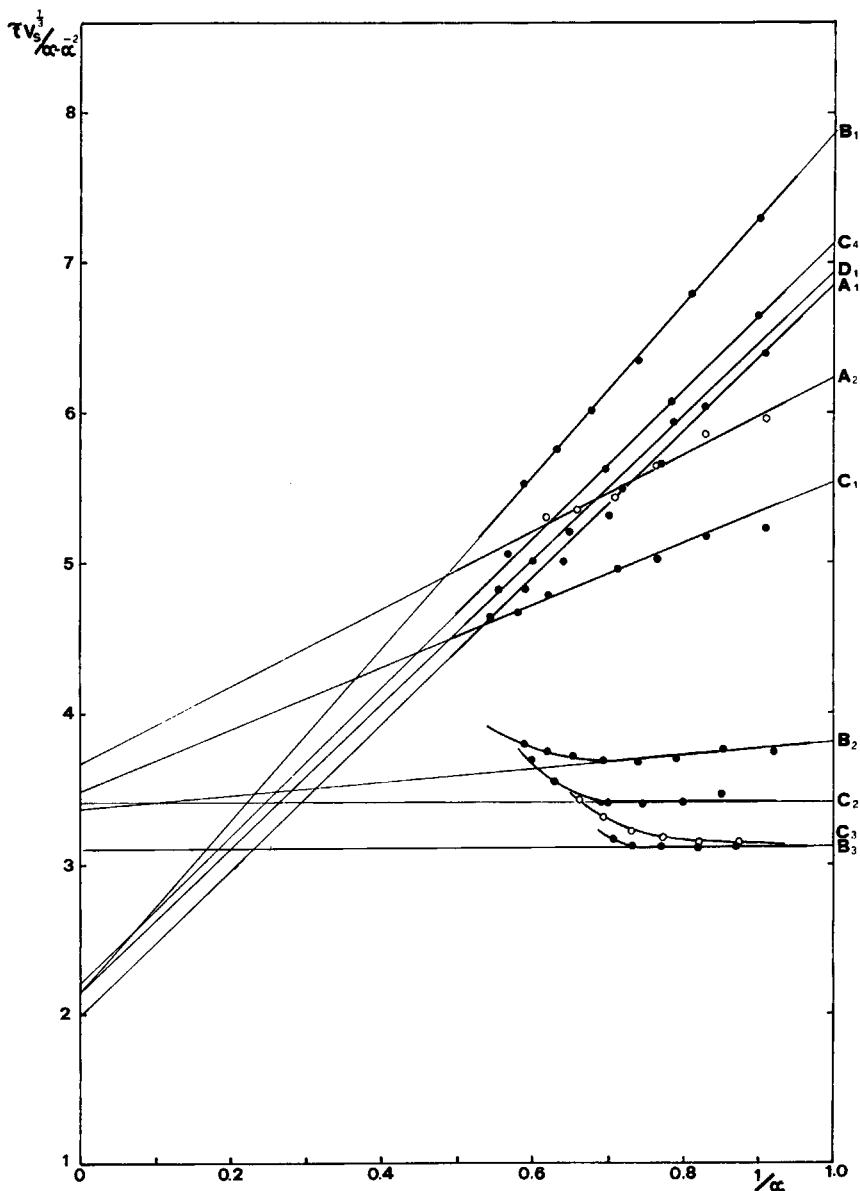


Fig. 4. Mooney-Rivlin plot for PB-30. Swelling solvent, decaline; temp., 35°C: specimen A<sub>1</sub>,  $V_s = 1$ ; A<sub>2</sub>,  $V_s = 0.873$ ; B<sub>1</sub>,  $V_s = 1$ ; B<sub>2</sub>,  $V_s = 0.568$ ; B<sub>3</sub>,  $V_s = 0.414$ ; C<sub>1</sub>,  $V_s = 0.789$ ; C<sub>2</sub>,  $V_s = 0.578$ ; C<sub>3</sub>,  $V_s = 0.456$ ; C<sub>4</sub>,  $V_s = 1$  (after deswelling).

Equation (2) must be considered valid only for noninteracting fillers. In our case, therefore, the results of Figure 5 are only indicative of the experimental trend.

Turning now to the other aspect of our analysis, we report the results obtained from the salt vulcanizates after the destruction of the clusters. The sample were swollen with *N,N*-dimethylformamide with 5% dichloroacetic acid (DCA) and allowed to remain in this solvent for two days. (No difference was observed by increasing the hydrolysis time.) After

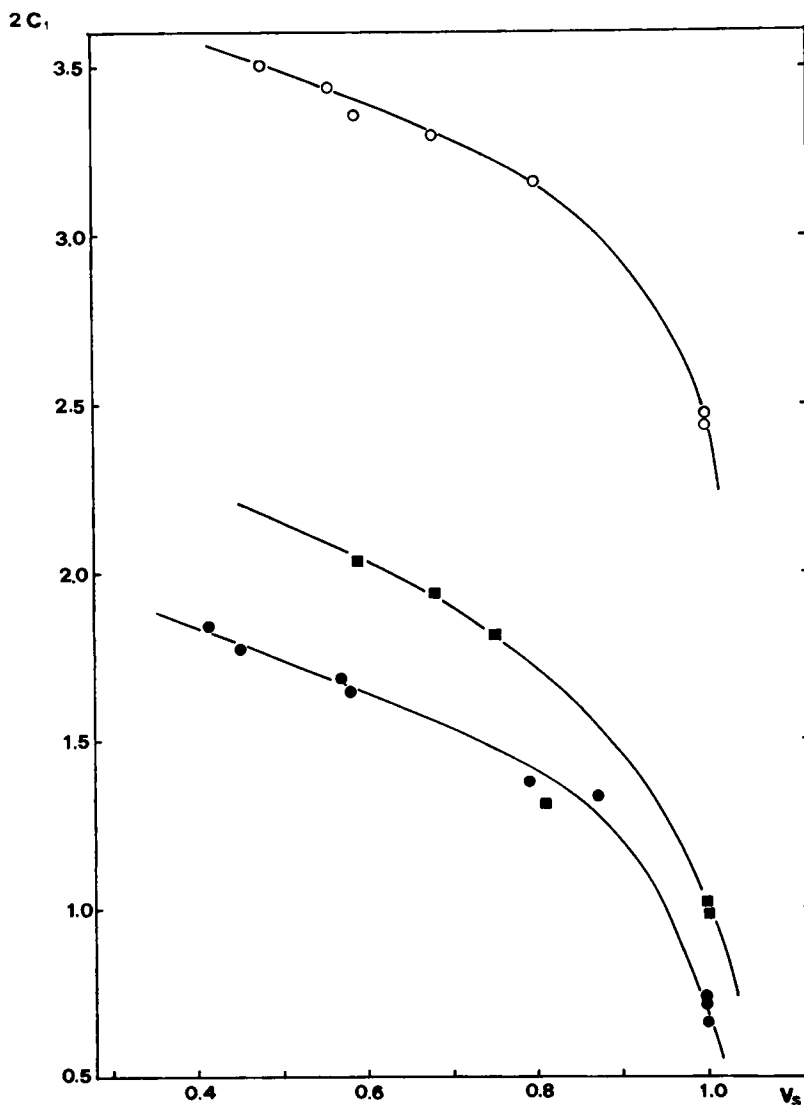


Fig. 5. The first coefficient  $2C_1$  of the Mooney-Rivlin plots of Figs. 2, 3, and 4 versus swelling degree  $V_s$ . The  $2C_1$  experimental values are corrected by means of the Guth-Smallwood equation, eq. (2);  $2C_1$  in kg/cm<sup>2</sup>: (○) PB-10; (■) PB-20; (●) PB-30.

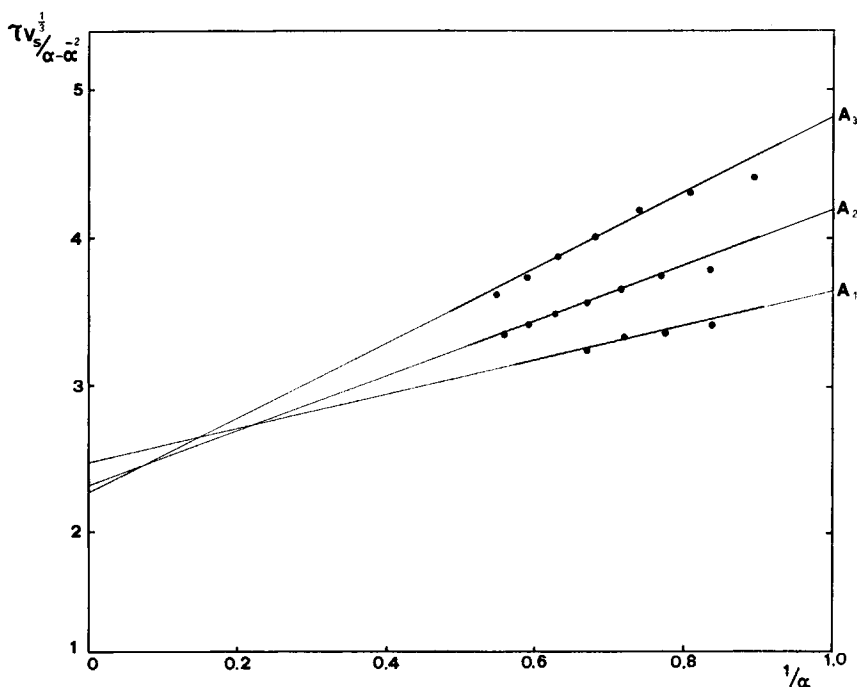


Fig. 6. Mooney-Rivlin plot for salt vulcanizate PB-10. Swelling solvent, mixture of N,N-dimethylformamide and dichloroacetic acid (5% acid); temp., 35°C:  $A_1$ ,  $V_s = 0.594$ ;  $A_2$ ,  $V_s = 0.709$ ;  $A_3$ ,  $V_s = 0.848$ .

an initial deswelling, and beginning with  $V_s \simeq 0.4$ , stress-strain curves were drawn while the swelling degree was gradually decreased to drying.

In Figures 6, 7, and 8, results are reported in terms of the Mooney-Rivlin equation. No significant difference is observable between the behavior in Figures 6, 7, and 8 and that in Figure 1 (PB-0).

### X-Ray Analysis

The method of small-angle x-ray diffraction was applied to the investigation of the internal structure of the vulcanizates.

Small-angle scattering diagrams were drawn within the range of  $2\theta = 5'$  to  $60'$  (Figs. 9 and 10). In the data of Figures 9 and 10 one may observe a markedly diffused scattering within the range  $2\theta = 5'-6'$  to  $40'-45'$ . This indicates that in the polybutadiene network small discrete particles are distributed. As would be expected, the relative intensity of the x-ray scattering rises with increases in the salt concentration; however, this growth is nonuniform in the range of the scattering. The higher increase is observed at the smaller angles. When the scattering angles grow, the curves are drawn together and finally become a single curve. It is essential that the shapes and disposition of the curves which represent bulk and



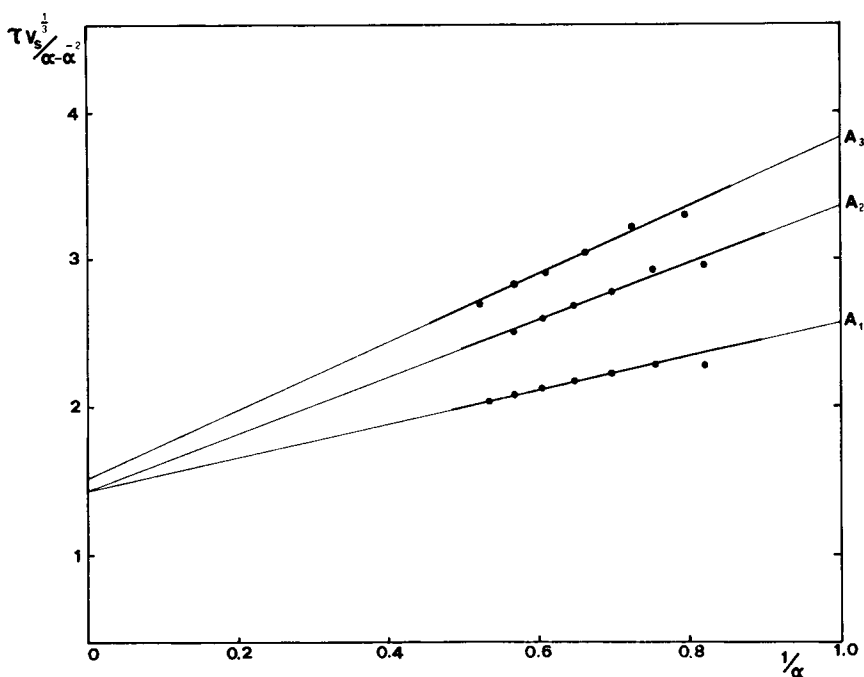


Fig. 7. Mooney-Rivlin plot for salt vulcanizate PB-20. Swelling solvent, mixture of *N,N*-dimethylformamide and dichloroacetic acid (5% acid); temp., 35°C:  $A_1, V_s = 0.663$ ,  $A_2, V_s = 0.778$ ;  $A_3, V_s = 0.864$

decaline-swollen samples in Figures 9 and 10 are similar. Indeed, in both figures the curves for PB-20 and PB-30 are joined at  $2\theta = 18'-20'$ , and then this joined curve unites with the PB-10 curve at  $2\theta = 28'-30'$ . The relatively lower intensity of the x-ray scattering for swollen specimens with respect to dry specimens may be explained by an increase in the thickness of the sample due to swelling.

It was shown above that the elastic behavior of the PB salt vulcanizates is changed markedly after treatment with strong acid, which destroys salt links. This effect is related to the drastic change in the x-ray small angle scattering. In fact, after treatment with DCA, the vulcanizates do not diffuse x-rays in the small-angle range. For the resolution of the diffusion scattering spectrum, we applied the method of successive tangents of minimum slope.<sup>7</sup> A practical example of this method is given in Figure 11 for the untreated PB-20. The experimental curve, after the background had been subtracted, was reported in terms of  $\log I$  versus  $b^2$ , where  $I$  is the corrected relative intensity and  $b = 2 \sin \theta / \lambda$ , with  $\lambda = 1.54 \text{ \AA}$ . At first, the diameter of gyration was calculated from the slope of the linear portion of this curve (curve 1). After subtracting the intensity of the first linear component, it was possible to plot the remaining visible in-

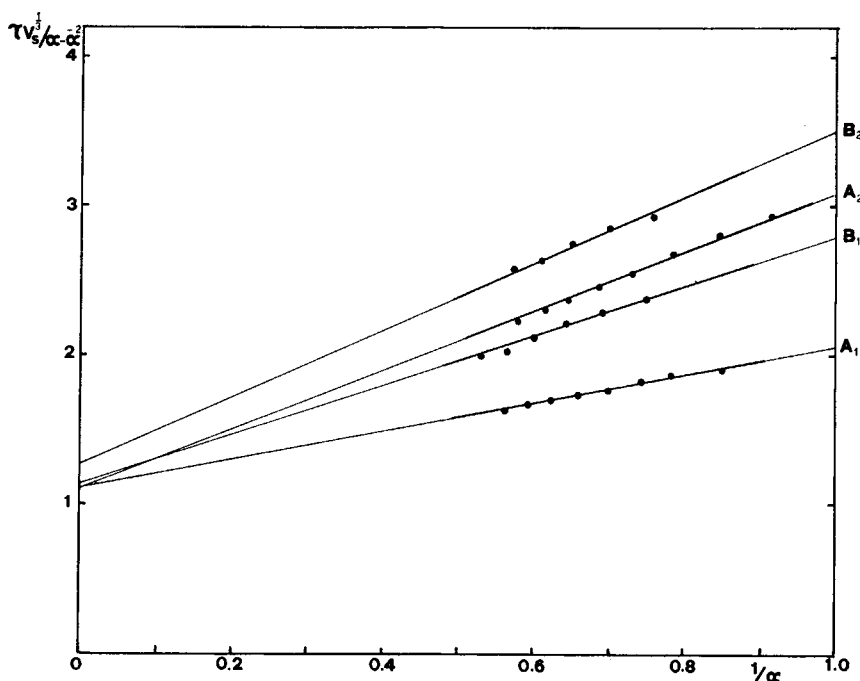


Fig. 8. Mooney-Rivlin plot for salt vulcanizate PB-30. Swelling solvent, mixture of *N,N*-dimethylformamide and dichloroacetic acid (5% acid); temp., 35°C: A<sub>1</sub>,  $V_s = 0.414$ ; A<sub>2</sub>,  $V_s = 0.710$ ; B<sub>1</sub>,  $V_s = 0.897$ ; B<sub>2</sub>,  $V_s = 0.954$ .

tensity in the form of another straight line (curve 2), which gives a second diameter. Calculations were effected with the use of the following equation, which was obtained by transformation of the Guinier law:<sup>7</sup>

$$D = 2R = \sqrt{1.166 \cdot \frac{\Delta \log I}{\Delta b^2}} \quad (3)$$

The results of our calculations are reported in Table III.

TABLE III  
Resolution of X-Ray Small-Angle Scattering Diagrams

	Sample	$\Delta \log I$	$\Delta b \times 10^3$	$\frac{\Delta \log I}{I/\Delta b ^2} \times 10^6$	Diameter, Å
Dry vulcanizates	PB-10	1.223	8.860	0.0156	135
	PB-20	1.146	7.546	0.0201	153
		1.286	4.778	0.0563	256
		1.124	7.600	0.0195	151
	PB-30	1.635	4.880	0.0687	283
		1.377	3.890	0.0910	326
1.455		10.347	0.0136	126	
Decaline-swollen vulcanizates	PB-10	1.265	5.350	0.0442	227
		1.207	7.027	0.0224	169
	PB-20	1.467	3.943	0.0943	332
		1.238	7.000	0.0253	172
	PB-30	1.771	4.098	0.1054	351

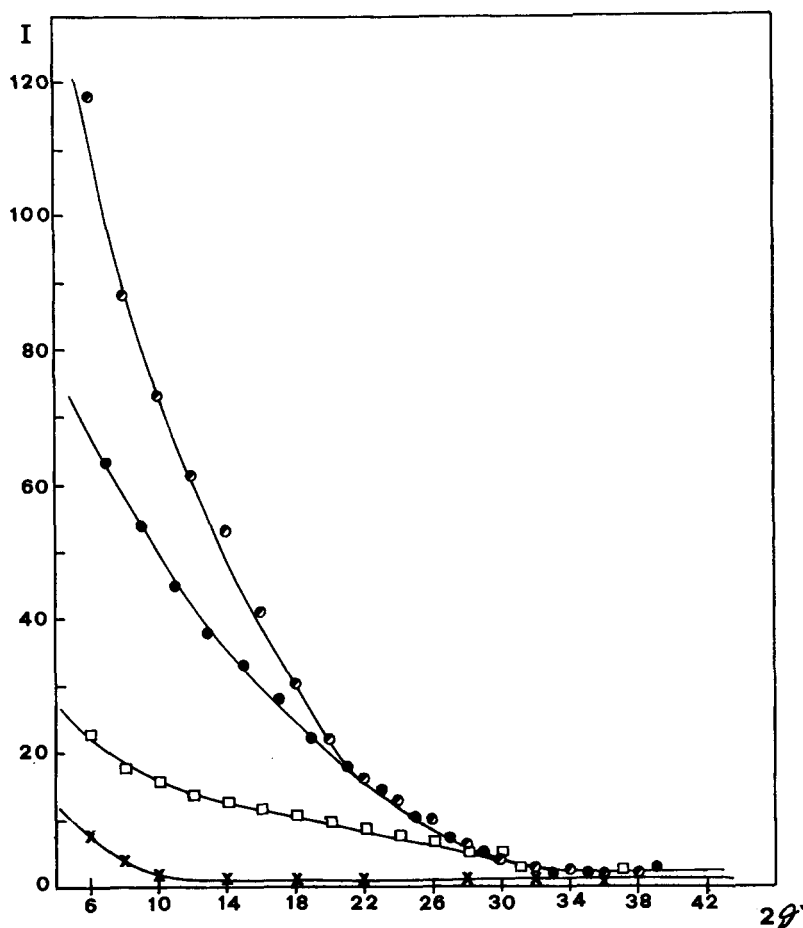


Fig. 9. Small-angle x-ray scattering diagrams taken on PB-10, PB-20, and PB-30 samples. The scattered intensity in counts/sec is reported versus the scattering angle  $2\theta'$ : (X) background; (□) PB-10; (●) PB-20; (⊙) PB-30.

### DISCUSSION

The results of the x-ray analysis seem to indicate clearly that in the salt vulcanizates PB-10, PB-20, and PB-30, there is a random distribution of rigid particles. As reported in Table III, the diameter of such particles increases with increase in salt concentration. It is thus easy to understand their chemical nature; we can indeed assume that during crosslinking, polymerization of magnesium methacrylate occurs\* with partial grafting on polybutadiene chains. The polysalt thus generated is distributed in the form of rigid particles, linked to the elastic network by chemical bonds, bonds that coming into existence as a result of the grafting process. The data obtained with swollen samples further support this picture; the results described in the previous sections, demonstrate, in fact, that when polar solvent is employed, there is one definite response to the

\* This suggestion is supported by experimental results.<sup>2</sup>

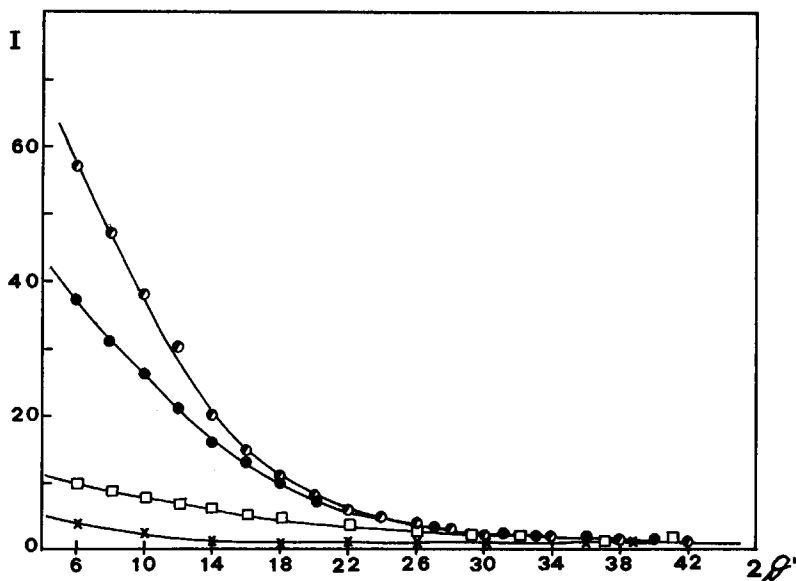


Fig. 10. Small-angle x-ray scattering diagrams taken on decaline-swollen samples. The scattered intensity in counts/sec is reported versus the scattering angle  $2\theta'$ : (X) background; ( $\square$ ) PB-10; ( $\bullet$ ) PB-20; ( $\bullet$ ) PB-30.

treatment, whereas when nonpolar solvent is employed, the response to the treatment is quite different. Decaline does not change the structure, and only a small increase in particle size is observed. On the other hand, a polar solvent with a hydrolyzing agent (DCA), penetrating into the particles, destroy the ionic bonds. Therefore, x-ray diffusion disappears and the present behavior becomes similar to that of the usual peroxide vulcanizate.

Taking into account these observation, we have analyzed the elastic behavior of our samples in terms of the Mooney-Rivlin equation. The Gaussian theory for the elasticity of rubber-like materials<sup>3,8</sup> supplies the following expression for the stress:

$$\tau = nKT \frac{\langle r_i \rangle^2}{\langle r_0 \rangle^2} (\alpha - \alpha^{-2}) \quad (4)$$

where  $n$  is the number of network chains in the unit volume,  $K$  is the Boltzmann constant, and  $\langle r_i \rangle$  and  $\langle r_0 \rangle$  are the end-to-end lengths for the network chain and the free chain, respectively. However, it is well known that the experimental behavior is much better represented by the Mooney-Rivlin phenomenological equation, eq. (1), where  $2C_1$  and  $2C_2$  are two coefficients that apparently do not have any molecular significance. Molecular informations, however, can be given by the  $2C_1$  term, which, as indicated by Mullins<sup>9</sup> and as recently reported<sup>10,11</sup> for highly swollen systems, can be identified with the  $nKT\langle r_i \rangle^2/\langle r_0 \rangle^2$  term of eq. (4). But,

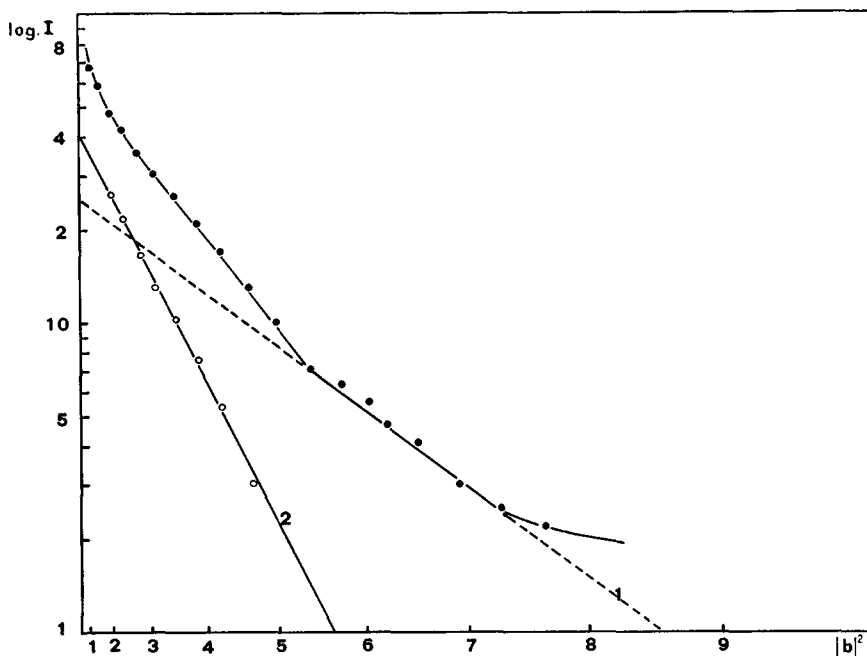


Fig. 11. Resolution of diffusion scattering spectrum for PB-20 dry sample.

on the other hand, for the  $2C_2$  term, none of the suggested explanations seems to have gained general acceptance at the present time. Recently, Prins<sup>12,13</sup> has indicated the presence of a supermolecular structure as the possible explanation at the molecular level of the  $2C_2$  term. Taking the cluster structure as a certain kind of supermolecular order (a strong interaction existing between network chains and surface particles), the data of Table II, which concerns the  $2C_2$  behavior with regard to the network clustering, could agree with the Prins suggestion.

Another effect directly correlated with the cluster structure is the non-Gaussian behavior exhibited by samples with the larger amount of salt when they were swollen with decaline. In fact, it is easy to calculate from the data of Table III that the mean distance between the particles is much the same as their diameter. From this we may conclude that, statistically, a large fraction of each elastic molecule is enclosed by or linked to the surrounding clusters, without possibility of deformation. This diminishing of the elastic fraction undoubtedly supplies an explanation for the non-Gaussian trend.<sup>5,14</sup> Decaline, in fact, by swelling the rubber's network, increases the mean distances between clusters and stretches the elastic chains up to non-Gaussian regions. Further proof for the above conclusion is found in the elastic behavior of the samples treated with DCA (Figs. 6, 7, and 8). Indeed, the hydrolysis of the salt bonds and the consequent destruction of the clusters restore complete freedom to the network chains;

the non-Gaussian behavior disappears and we may observe the same elastic properties as those of a conventional PB vulcanizate (Fig. 1).

Finally, in the same way, we may explain the effect of swelling on the  $2C_1$  coefficient (Fig. 5). To this end, it is interesting to note the increase in particle thickness by decaline swelling, as reported in Table I. This effect appears to indicate a solidification of some rubber chains on the surface of the particles; the joint points so generated act as chemical cross-links, and from reference to them we may explain the increase in the  $2C_1$  term,  $2C_1$  being proportional to  $n$ .<sup>9-11</sup> This analysis assumes the exclusion of decaline, a nonpolar solvent, in the ionic structure of the clusters.

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### References

1. H. P. Brown, *Rubber Chem. Technol.*, **36**, 931 (1963).
2. A. A. Dontsov, V. F. Soldatov, et al., *Colloid J. USSR*, **31**, 293 (1969).
3. L. R. G. Treolar, *The Physics of Rubber Elasticity*, Oxford, 1958.
4. A. Ciferri and P. J. Flory, *J. Appl. Phys.*, **30**, 1498 (1959).
5. K. J. Smith, A. Greene, and A. Ciferri, *Kolloid-Z. Z. Polym.*, **194**, 49 (1964).
6. E. Guth, *J. Appl. Phys.*, **16**, 20 (1945).
7. L. E. Alexander, *X-Ray Diffraction Methods in Polymer Science*, Wiley, New York, 1969.
8. P. J. Flory, *J. Amer. Chem. Soc.*, **78**, 5222 (1956).
9. L. Mullins, *J. Appl. Phys.*, **2**, 1 (1959).
10. F. de Candia and A. Ciferri, *Makromol. Chem.*, **134**, 335 (1970).
11. F. de Candia and L. Amelino, in press.
12. R. Blokland and W. Prins, *J. Polym. Sci.*, **7**, A2-1595 (1969).
13. K. Důšek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).
14. K. J. Smith, A. Ciferri, and J. J. Hermans, *J. Polym. Sci.*, **2A**, 1025 (1964).

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