

Anomalous Freezing Point Depression of Swollen Gels*

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Synopsis

The anomalous freezing point depression, ΔT , of benzene-swollen vulcanizates has previously been attributed to the limitation of (benzene) crystallite size by the polymer network. This study was initiated to determine the benzene crystallite size in a number of rubber and benzene systems. A special low-temperature specimen holder was designed and constructed in the Cambridge Laboratories for running diffraction patterns at temperatures near -30°C . X-ray line broadening techniques were used to study a series of filled and unfilled vulcanizates of varying crosslink density. The results indicate that crystallite size is not depressed to the degree predicted by freezing-point measurements. Benzene crystallite sizes were similar in all rubber benzene systems, regardless of degree of crosslinking or benzene fraction, although carbon black loading appears to increase crystallite size. This effect may be attributed to lesser depth of penetration of the x-rays due to greater density as carbon black loading increases. Additional studies measuring the ΔT for solutions and similar vulcanizates of NR and SBR over a wide range of rubber concentrations showed that at the same rubber in benzene fraction, crosslinking increases ΔT but the addition of carbon black reduces ΔT . An explanation for the observed phenomena is advanced.

INTRODUCTION

It has long been known that the freezing points of aqueous gels of poly(acrylic acid) and poly(vinyl alcohol) are depressed to a greater extent than can be accounted for on the basis of colligative property measurements. Kuhn¹ suggested that in such gels, the entanglement of macromolecular chains constituted a "mesh" and that crystals of frozen solvent could grow only in the interstices of this mesh and were limited in size by the mesh width.

To demonstrate this, Kuhn² prepared a series of vulcanized rubber sheets, swelled them to equilibrium in benzene and examined their compression moduli. On the basis of "statistical considerations" he related this modulus to the mesh dimensions of the swollen gel, and hence calculated

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the size of the corresponding microcrystals. Using an estimated value for the interfacial tension between solid and liquid benzene, he was able to predict the freezing point depression. The predicted value turned out to be approximately one-third of the experimental value, and Kuhn² has presented a discussion of some of the factors which may be responsible in accounting for the discrepancy. He also reported³ that the expected broadening of the x-ray diffraction peaks did not occur with ice crystals in a poly(vinyl alcohol) gel which showed a freeze point depression which should correspond with crystals of 150–200 Å. diameter which would result in considerable line broadening.

Westlinning and Butenuth,⁴ assuming the validity of Kuhn's treatment, examined the freezing point depression of a series of vulcanizates of increasing crosslink density and found that the freezing point depression increased as the network became more tightly crosslinked. The authors tested the linearity of a plot of E (modulus of the swollen material) versus $q^{2/3}$ (swelling ratio) divided by a_H^2 (mesh dimension), a relationship derived by Kuhn. Satisfactory linearity was obtained, but since the value of a_H was derived from the freezing point using the same theoretical model as was used to predict the relationship between E , q , and a_H , the agreement is less striking than it might have been if an independent physical measurement had been used to evaluate a_H .

Westlinning^{4,5} also examined the freezing-point depression of swollen carbon black loaded vulcanizates, and here found that an increase in the carbon loading was accompanied by decreased swelling (thus apparently indicating a tighter network) but was also accompanied by a slightly decreased freezing point depression (thus apparently indicating a looser network). The discrepancy was attributed to inhomogeneous crosslink density.

Kanig and Karge⁶ attempted to determine the basic dimensions of crystallites of benzoin, triphenylcarbinol, and tetrachlorobenzene in cross-linked polystyrene by swelling above the glass transition point of polystyrene, then cooling below this temperature and evaporating the crystallized swelling agent in high vacuum; the dimensions of the cavities left by the sublimed crystals were determined. A wide distribution was found, with a maximum occurring near 200 Å. These authors, using a dilatometric technique, found good agreement between freezing and melting curves, whereas with Kuhn's thermal analyses, the melting point or range was always higher than the freezing point. Since the large freezing point depressions encountered with the use of benzene swollen in rubber (5–15°C.) would correspond to very small crystals (25–70 Å.), this should become very evident in broadening of the x-ray diffraction peaks of the crystallized benzene in the swollen gel.

A program of work was therefore set up to determine: (1) the effect of crosslink density and carbon loading on the freezing-point depression of rubber solutions in benzene and benzene-swollen vulcanizates; (2) the size of the benzene crystallites by an independent physical measurement (*viz.*, line broadening in x-ray diffraction).

EXPERIMENTAL

Three series of vulcanizates were mixed, and pills 0.5 in. high and 0.75 in. in diameter of each batch were cured. Details of the variations in cure system, cure time, and carbon loading are given in Table I. Only one black (Vulcan 3) was used in the study, since evidence is available to show the HAF blacks do not noticeably interfere with the curing systems used.⁷

The pills were swollen in measured amounts or excess of benzene for approximately one week prior to their being tested. Solutions of NR and SBR extracted with acetone were also measured.

Determination of Freezing Point

The apparatus used for the freezing point determination is shown diagrammatically in Figure 1.

A sample of the swollen gel (approximately $\frac{1}{4}$ in. by $\frac{1}{4}$ in. by $\frac{3}{4}$ in.) was speared on a welded iron-constantan thermocouple junction (S) and corked into a small glass vial (V). This assembly was placed inside an empty Dewar vessel (D) as shown. The Dewar vessel was surrounded by an insulated bath (B) containing a mixture of Dry Ice and alcohol.

A second reference thermocouple junction was immersed in a mixture of pure ice and boiled-out distilled water contained in a second Dewar vessel (R), the contents of which were mechanically stirred (stirrer not shown). The two iron wires carrying the output of the two thermocouples were connected to a Sargent X-T recorder with the use of an amplification such

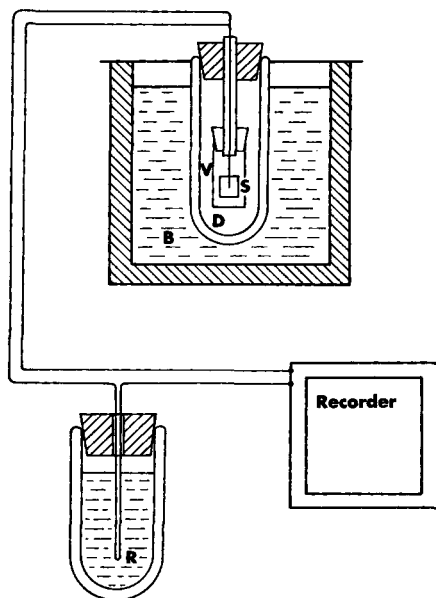


Fig. 1. Sketch of the apparatus for measuring freezing point depressions: (B) cold bath; (D) Dewar vessel; (S) sample with embedded thermocouple; (R) cold junction.

TABLE I
Freezing Point Depressions of NR Vulcanizates
at Equilibrium Swelling in Benzene

Designation	MBTS ^a	DiCup R, phr	Car- bon phr	Cure time, min. ^b	Freezing point depression ΔT , °C.			V_r in benzene	ΔT , °C. (average of 3 cures)
A-1-40	0.6	—	—	40	5.20	4.90	—	0.190	
A-1-65	0.6	—	—	65	4.90	4.80	4.90	0.198	
A-1-95	0.6	—	—	95	4.85	4.90	—	0.202	
								0.197	4.92
A-2-40	2.4	—	—	40	6.50	6.60	—	0.221	
A-2-65	2.4	—	—	65	6.00	6.05	—	0.218	
A-2-95	2.4	—	—	95	6.00	6.00	6.40	0.215	
								0.218	6.22
A-3-40	4.8	—	—	40	9.20	9.00	—	0.242	
A-3-65	4.8	—	—	65	7.85	8.20	8.35	0.235	
A-3-95	4.8	—	—	95	8.00	8.10	—	0.235	
								0.238	8.39
A-4-40	0.6	—	30	40	4.20	4.05	—	0.236	
A-4-65	0.6	—	30	65	4.05	4.25	4.45	0.235	
A-4-95	0.6	—	30	95	4.25	4.35	4.50	0.234	
								0.235	4.30
A-5-40	2.4	—	30	40	6.40	6.45	—	0.263	
A-5-65	2.4	—	30	65	5.78	5.90	6.10	0.260	
A-5-95	2.4	—	30	95	6.05	6.05	—	0.253	
								0.259	6.10
A-6-40	4.8	—	30	40	8.40	8.00	8.40	0.284	
A-6-65	4.8	—	30	65	8.15	8.25	8.50	0.274	
A-6-95	4.8	—	30	95	8.20	8.15	—	0.275	
								0.278	8.25

that full-scale deflection was obtained for a potential difference of 1.25 mv. The recorder was calibrated by using the freezing points of pure water (0°C.) and pure dry benzene (5.49°C.) as standards. During determination of freezing point the chart was run at 1 in./min.; the rate of cooling is about 5°C./min. (average value). A typical cooling curve is illustrated in Figure 2. The small blip (*a*) is thought to represent the freezing of a small sheath of benzene surrounding the thermocouple wires, since the momentary temperature rise occurs in less than 1 sec. (thus indicating that the cause of the change must be situated extremely close to the thermocouple junction) and the blip itself can be induced by gently tapping the thermocouple wire at any temperature below 5.5°C.

The slightly convex portion (*b*) of the curve in which the temperature remained almost constant for several minutes, was identified with the freezing transition, and the highest temperature reached was taken as the

TABLE I (continued)

Designation	MBTS ^a	DiCup R, phr	Car- bon phr	Cure time, min. ^b	Freezing point, depression ΔT °C.			V_r in benzene	ΔT , °C. (average of 3 cures)
A-7-40	0.6	—	50	40	3.75	3.85	4.10	0.251	
A-7-65	0.6	—	50	65	4.10	4.20	4.65	0.263	
A-7-95	0.6	—	50	95	4.05	4.05	—	0.259	
								0.258	4.10
A-8-40	2.4	—	50	40	6.45	6.50	6.35	0.290	
A-8-65	2.4	—	50	65	6.45	6.50	6.35	0.289	
A-8-95	2.4	—	50	95	6.00	6.40	6.15	0.286	
								0.288	6.35
A-9-40	4.8	—	50	40	9.20	9.40	9.50	0.307	
A-9-65	4.8	—	50	65	8.70	8.70	—	0.302	
A-9-95	4.8	—	50	95	8.40	8.30	8.35	0.300	
								0.303	8.88
D-1	—	1.5	—	60			4.10 ^c	0.237	
D-2	—	3.0	—	60			7.10 ^c	0.258	
D-3	—	4.5	—	60			9.13 ^c	0.285	
D-4	—	1.5	30	60			3.84 ^c	0.231	
D-5	—	3.0	30	60			6.94 ^c	0.285	
D-6	—	4.5	30	60			9.29 ^c	0.320	
D-7	—	1.5	50	60			3.80 ^c	0.264	
D-8	—	3.0	50	60			7.00 ^c	0.309	
D-9	—	4.5	50	60			9.40 ^c	0.348	

^a In addition to the MBTS, the following additives were mixed in with all the MBTS batches: 2.5 parts sulfur, 3.0 parts zinc oxide; 2.0 parts stearic acid.

^b All MBTS vulcanizates cured at 280°F., all DiCup batches cured at 300°F.

^c Mean of four.

freezing point. Results were expressed in terms of freezing point depression, ΔT , i.e., freezing point of pure benzene minus freezing point of benzene in the swollen vulcanizate.

Determination of Swelling Volume

Samples were swollen for 24 hr. in benzene at room temperature by using a standard method⁸ in which appropriate corrections are made for the loading and density of the filler, and for the loss of soluble nonrubber components.

Determination of Crystallite Size

A special sample holder and a novel cooling system were designed for carrying out x-ray diffraction studies at a temperature well below the freezing point of benzene. The equipment is illustrated in Figure 3.

The brass block (4) has a series of $1/8$ in. channels drilled through the base through which coolant may be circulated. Copper inlet and outlet

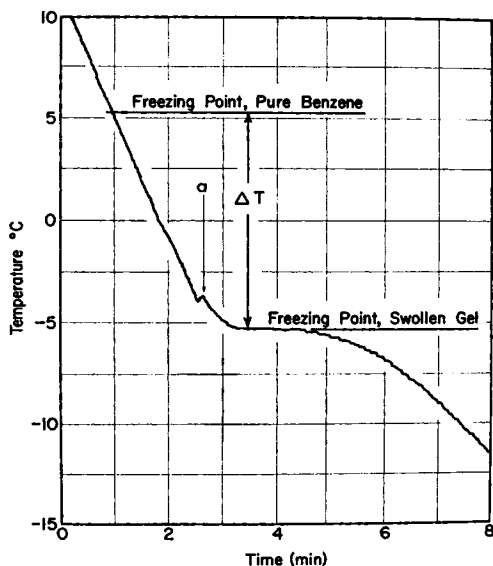


Fig. 2. Typical temperature-time curve of a rubber vulcanizate swollen in benzene. The peak *a* is a small irregularity, probably due to a small pocket of benzene around the thermocouple.

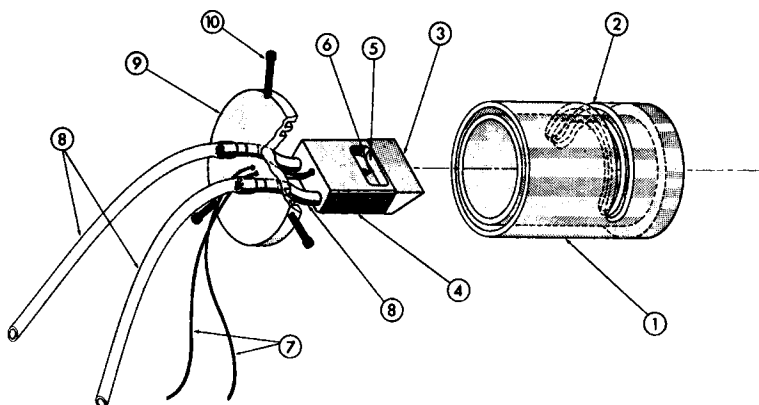


Fig. 3. Specimen cooling system: (1) concentric Lucite tubes with about $\frac{1}{4}$ in. air space; (2) slot in Lucite cylinders covered with Mylar film; (3) fiber bracket for insulation and mounting; (4) brass block with drilled circulation channels; (5) trough, containing sample; (6) thermocouple junction; (7) thermocouple wires; (8) tubing for cooling liquid circulation; (9) plastic cap; (10) set screw.

tubes (8) are used to connect the system of channels to Tygon tubing through which the coolant is circulated. The sample itself is contained in the $\frac{1}{4}$ in. deep trough (5). An empty channel makes it possible to introduce the thermocouple junction (6) into position within the sample while it is being frozen in the trough (5). A machined fiber (3) bracket serves as both a thermal insulator and a rigid mounting device by which

the apparatus is screwed in place in the path of the x-ray beam in the Phillips Norelco diffractometer (copper target x-ray tube). The detector is a scintillation counter which is used in conjunction with a bent crystal monochromator.

The equipment was protected from moisture by means of hollow Lucite cylinders (1), designed to fit snugly onto the goniometer shaft of the diffractometer. The cylinder was equipped with a plastic cap (9) through which the coolant tubes (8) could pass and the thermocouple connections (7) could be made. A semicircular cut (2) was made in the cylinder walls to permit the transmission of the x-ray beam, and the cut was covered by a thin Mylar film to exclude atmospheric moisture. In operation, the space under the sample holder was filled with Drierite to ensure the absence of moisture.

Cooling was provided by pumping alcohol from the reservoir through a copper helix which is immersed in a Dewar vessel containing a Dry Ice-alcohol freezing mixture. The cooled alcohol was circulated through the sample holder (4) and returned to the reservoir.

During cooling, the temperature of the sample was continuously recorded by connecting the thermocouple (6) in series with a 0°C. reference thermocouple to the input of a Sargent X-T recorder, as used for the determination of freezing points.

The diffraction patterns were run at a goniometer speed of 0.5°C./min. The intensity of the diffracted beam was recorded on a chart moving at a speed of 1/2 in./minute, and the widths of the peaks at half-height were measured. During the initial phase of the work the peak at $2\theta = 19.4^\circ$ was chosen for study because it appeared prominently and reproducibly in the diffraction patterns of pure benzene and of all the solutions and swollen vulcanizates which were tested.

RESULTS AND DISCUSSION

Freezing Point Studies

Vulcanizates Swollen to Equilibrium

Experimentally observed values of freezing point depression and swelling ratios for natural rubber are listed in Table I.

The swelling measurement V_r is reported as the volume fraction of rubber/volume fraction of rubber plus the volume fraction of solvent in the swollen gel.

In the case of the DiCup cures, the freezing point depression listed is the mean of four values. In the sulfur-cured samples, the actual experimental values themselves are listed, both because they serve to indicate the degree of experimental determinations and to apply statistical methods meaningfully. Thus the mean deviation of any individual experimental result from the average for the result is 0.095°C. and the corresponding standard deviation is 0.123°C. Since most of the experimentally observed

freezing point depressions are in the range 5–10°C., one must conclude that the precision of measurement is quite sufficient.

To isolate the effect of any one variable, one may average all results in which that particular variable has the same value. Thus to find the effect of cure time, one may average the results of all 40 min. cures, all 65 min. cures and all 95 min. cures (see Table II).

TABLE II
Effect of Cure Time on Freezing Point Depression
of NR Vulcanizates at Equilibrium Swelling

	Freezing point depression, °C.	V_r in benzene
Σ 40-min. cures	6.57	0.254
9		
Σ 65-min. cures	6.33	0.253
9		
Σ 95-min. cures	6.25	0.251
9		

The differences between the averages are small in this case, and since their magnitude is about equal to one standard deviation, their significance is very dubious. Thus, the cure time in this system has not influenced freezing point depression or swelling.

To isolate the effect of accelerator, one may take averages of all vulcanizates with the same accelerator content (see Table III).

TABLE III
Effect of Accelerator on Freezing Point Depression
of NR Vulcanizates at Equilibrium Swelling

	Freezing point depression, °C.		V_r in benzene	
	Dicumyl peroxide cures	Sulfur cures	Dicumyl peroxide cures	Sulfur cures
Σ 1, 4, 7 (low accel.)	3.87	4.42	0.244	0.230
9				
Σ 2, 5, 8 (med. accel.)	7.02	6.24	0.284	0.278
9				
Σ 3, 6, 9 (high accel.)	9.27	8.49	0.318	0.273
9				

It is clear that an increase in accelerator content brings about an increased freezing point depression and decreased swelling, both presumably as a result of a more tightly crosslinked network. These experimental results are very similar to those of Westlinning and Butenuth.⁴

Finally, on evaluating the appropriate averages, to isolate the effect of carbon loading, one finds the results reported in Table IV. One must conclude that carbon loading exerts a profound effect on restricting the swelling of vulcanizates, but has no significant influence on the freezing point depression. Again, Westlinning and Butenuth⁵ found similar results for some carbon-polymer systems; in other systems they reported a decrease in freezing point depression with increasing carbon.

TABLE IV
Effect of Carbon Loading on Freezing Point Depression
of NR Vulcanizates at Equilibrium Swelling

	Freezing point depression, °C.		V_r in benzene	
	Dicumyl peroxide cures	Sulfur Cures	Dicumyl peroxide cures	Sulfur cures
Σ 1, 2, 3 (no carbon) 9	6.75	6.53	0.260	0.217
Σ 4, 5, 6 (30 phr loading) 9	6.69	6.21	0.279	0.235
Σ 7, 8, 9 (50 phr loading) 9	6.73	6.41	0.307	0.283

Concentrated Rubber Solutions

Freezing point depressions were also measured on a series of concentrated solutions of unfractionated natural rubber in benzene. The results are reported in Table V.

TABLE V
Freezing Point Depressions of Concentrated Natural Rubber Solutions

V_r in benzene	Freezing point depression (mean), °C.
0.127	0.60
0.172	1.30
0.241	2.00
0.290	2.75
0.338	4.10

If the concentration of the solution is changed over a rather wide range, it appears that the more concentrated solutions have freezing point depressions of such a magnitude that it is difficult to attribute those large effects to the decreasing crystallite size (see Fig. 5).

Craig and Trivisonno⁹ have carried out similar measurements up to a concentration of 50% of polybutadiene in benzene and, assuming the theory of ideal solutions to be valid, calculated the molecular weight of the

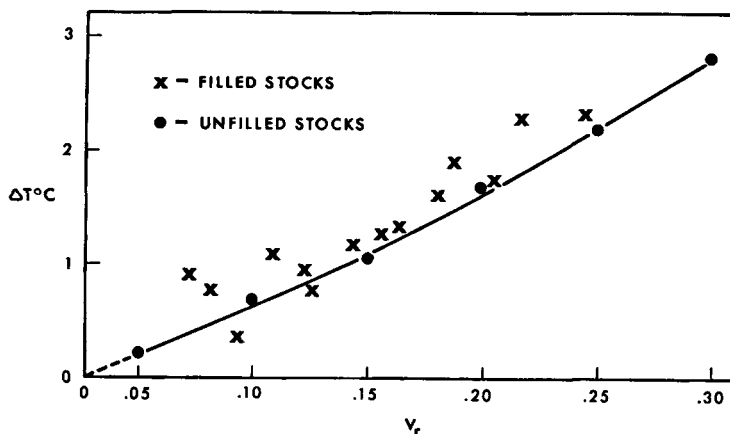


Fig. 4. Freezing point depression ΔT vs. volume concentration of natural rubber in benzene.

dissolved species from the Clausius-Clapeyron equation. Using a molar heat of melting of 2.370 kcal. for benzene, they calculated molecular segment weights (M_f) for a number of fractions as a function of concentration.

If we apply these idealized treatments to our case of natural rubber up to the very high concentration of 67 vol.-% of rubber ($V_2 = 0.67$) the wholly unrealistic value of $M_f = 66$ (one isoprene unit) is obtained for the cryoscopic segment weight.

This is not amazing, since it is well known that even dilute polymer solutions do not behave like ideal solutions. Since the chemical potential of the concentrated solutions may be calculated by using the Flory-Huggins theory (see Appendix I), the large freezing point depressions are clearly anomalous.

Effect of Carbon Black in Solutions

The effect of carbon black on the freezing point of natural rubber solutions is shown in Figure 4. Although the spreading of the test data do not allow a quantitative comparison, there is an obvious tendency for the solutions of the black-containing compounds to show higher ΔT values. The black-containing stocks may not be proper solutions since part of the rubber is "bound" to the carbon black. Since crosslinking increases the freezing point depression, the tendency of higher ΔT for the black stock may be explained by the formation of crosslinks through the carbon black particles. Against this assumption stands the experimental fact that the benzene in swollen bound rubber gel by itself, as obtained in the course of the bound rubber determination, shows no freezing point depression.

Effect of Carbon Black in Vulcanizates Swollen to Various Levels

The strong dependence of ΔT on concentration made us suspect that also in vulcanizates, concentration might be one of the determining factors.

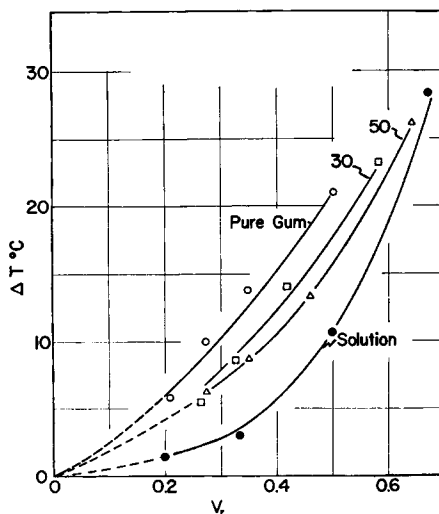


Fig. 5. Freezing point depression ΔT of benzene in SBR vulcanizates plotted vs. volume concentration of rubber in the swollen matrix gel. Effect of loading of HAF black.

Accordingly, gum and black vulcanizates were swollen to predetermined rubber fractions by adding the calculated amounts of benzene and allowing this to diffuse completely into the rubber (2–5 days at 30°C.).

These experiments were carried out with natural rubber and SBR vulcanizates cured with three different levels of curing ingredients, causing three levels of crosslink densities, and with carbon black contents of 0, 30, and 50 parts by weight per 100 rubber.

The results of these measurements for natural rubber are summarized in Figure 5, and this shows clearly that the curves for the carbon black vulcanizates fall below that for the pure gum vulcanizate.

If compared at the same apparent V_r (rubber concentration in the solvent) of the rubber matrix, the carbon black compound has the smaller freezing point depression than the gum vulcanizate, and the decrease in ΔT from 0 to 30 phr of black is larger than that from 30 to 50 phr. However, the apparent V_r of the carbon black vulcanizates, when equal to that of a gum vulcanizate, does not represent the same crosslink density but probably a much lower one, since the carbon black by itself reduces the swelling for different reasons.

The data from Table I show that, for the same curing system in gum and black compound, the effect of carbon black on ΔT is only a small one if it exists at all. However, we are then comparing ΔT values at different V_r values, the one for the black vulcanizate being the larger.

If ΔT is considered as the true measure of the crosslink density, then the increase in V shown in the graphs represents the restricting effect of the presence of carbon black on swelling as such, and the present curves provide the means to correct for this effect.

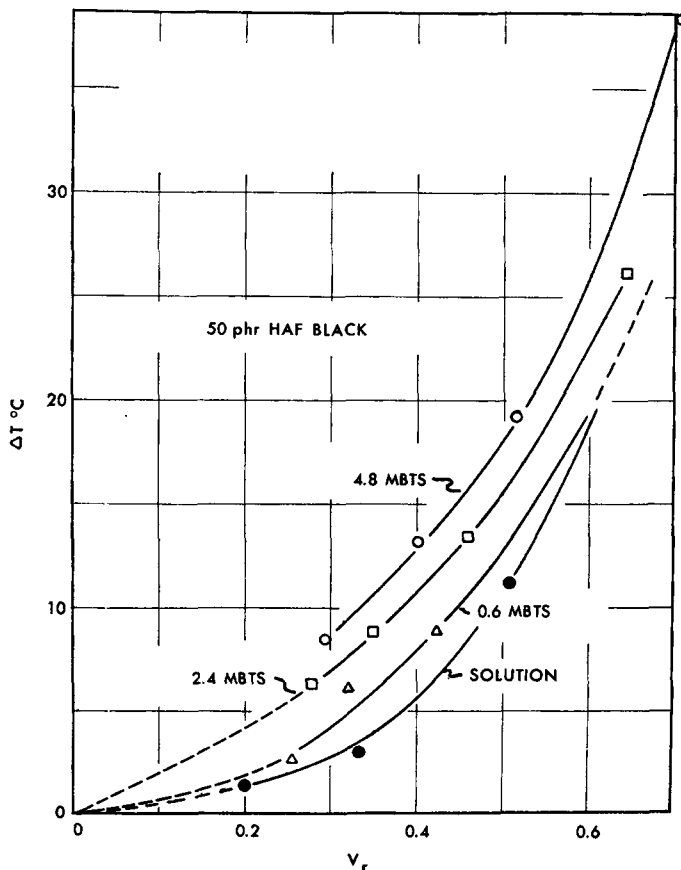


Fig. 6. Freezing point depression of benzene in SBR vulcanizates plotted vs. volume concentration of rubber in the swollen matrix gel.

However, from the presented evidence it is clear that the concentration of the rubber in benzene itself has a dominant role in the freezing point depression.

The freezing point depression is increased by increasing the proportion of accelerator, in both DiCup and sulfur cures, and it appears that apart from the concentration, the increased crosslink density of such vulcanizates is the most obvious common factor. Figure 6 shows the effect of increased curative level at various concentrations. Points of attachments between polymer chains and carbon particles are apparently not capable of affecting the freezing point measurably (Fig. 4).

In Figure 7, a set of curves is shown illustrating the effect of carbon black loading in SBR where special precautions had been taken to extract all soluble material from the vulcanizates. This was deemed necessary since the high V_r values were obtained by adding relatively small amounts of benzene to the vulcanizate. If appreciable amounts of soluble materials

of low molecular weight remained in the vulcanizate, their concentration might be high enough to cause a sizable freezing point depression in itself.

It is obvious from Figure 7 that the extraction of the vulcanizate does not reduce ΔT at high V_r ; the curves are essentially the same as those for the samples that were not so completely extracted.

Similar extractions were carried out for the natural rubber compounds of the series of Figure 5. After 2×24 hr. + 1×24 hr. Soxhlet extraction with acetone, the extracts were taken up in the same amount of benzene as

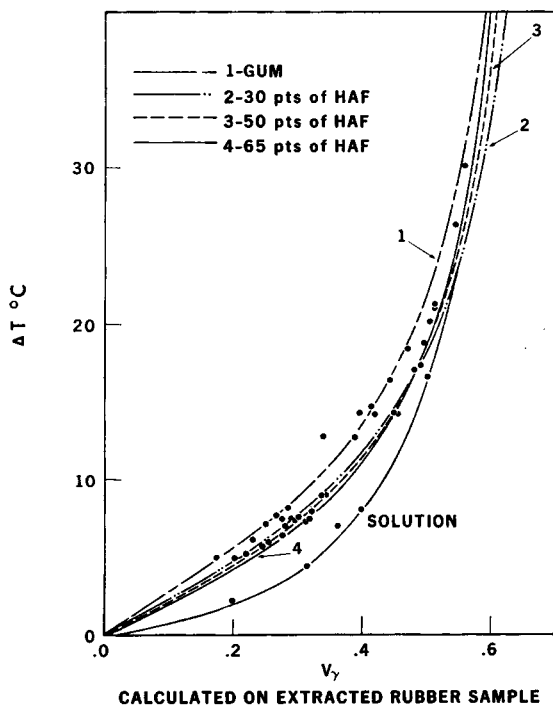


Fig. 7. Freezing point depression of benzene in acetone-extracted SBR vulcanizates.

was used for the swelling of the rubber sample and the freezing point depression of this solution was determined. The highest amount of extract was found with the pure gum sample vulcanized with 4.8 phr of MBTS. For this extract, dissolved (only partly soluble) in the amount of benzene to correspond with $V_r = 0.4$ of the vulcanizate (0.05 wt.-% in benzene), the freezing point depression was determined and found to be 0.35°C . Compared to the measured freezing point depression of the vulcanizate of more than 15°C . at $V_r = 0.4$, this correction can be considered negligible.

The formula used to relate crystallite size and freezing point depression in its simplest form reads:

$$\Delta T = -4\sigma T_0/aL\rho$$

where σ is the surface tension of the solid-liquid benzene interface. (This value is taken rather arbitrarily as 4 erg/cm.² on considerations given by Kuhn.²) T_0 is the freezing point of pure benzene (278.5°K.); a is the size of the crystallite, taken as the side of a cube; L is the heat of melting of benzene, taken as 30.4 cal./g.; and ρ is the density of benzene (0.87 g./cm.³).

For a in Angstroms, the formula reduces to approximately:

$$\Delta T = 400/a$$

Therefore, a freezing point depression of 10°C. would require crystallites as small as 40 Å.

Neither the crystal size nor the theory of polymer solution gives a satisfactory explanation for the large freezing point depressions of benzene in concentrated solution or gels; the problem could be considered, however, from a different angle. If one looks upon the benzene-rubber compositions as binary mixtures and tries to determine the melting (or freezing) points of these mixtures, this can be done conveniently from both the benzene side and the 100% NR side. So far the all-benzene side has had most of the attention, but taking NR for the rubber component, it is of interest to consider that its melting temperature is about 0-30°C., its crystallization range -40 to +20°C., and that very small amounts of solvent reduce this temperature very drastically. The reason is that the crystallization is only possible at this relatively high temperature because the mobility of the isoprene units is so strongly reduced by the long chain ends which they are tied to and actually the crystallization temperature is dependent on the molecular weight (although rate effects play a role here).¹⁰ Isoprene itself crystallizes only at about -146°C. By introducing small amounts of benzene molecules, which have great affinity for the polymer, the interaction forces between the polymer chains are greatly reduced and the mobility of the chain segments is increased. As a consequence, the crystallization temperature is reduced sharply. In the swollen frozen gel, there are actually two phases: (1) the pure benzene crystallized inside the meshes of the network, (2) the network chains solvated by benzene molecules which system is in more energetic motion than the pure benzene and thus has less tendency to crystallize.

If crystallization is nucleated in the pure benzene in the meshes of the network, the crystal size may be limited not for mechanical reasons but because the boundaries consist of a binary mixture of benzene and polymer of a much lower freezing point. When mixtures of increasingly lower benzene content are frozen, the room for benzene crystals to grow becomes smaller and smaller and this may account for the lowering in freezing point according to Kuhn's original concept. When, however, the mixture is so low in benzene that there is hardly any or no benzene unassociated with polymer left in the intramesh areas, then the point is reached where the freezing point is determined by the composition of the binary mixture of polymer and associated solvent. The temperature-composition (T - X) diagram will, therefore, have the general appearance shown in Figure 8. This

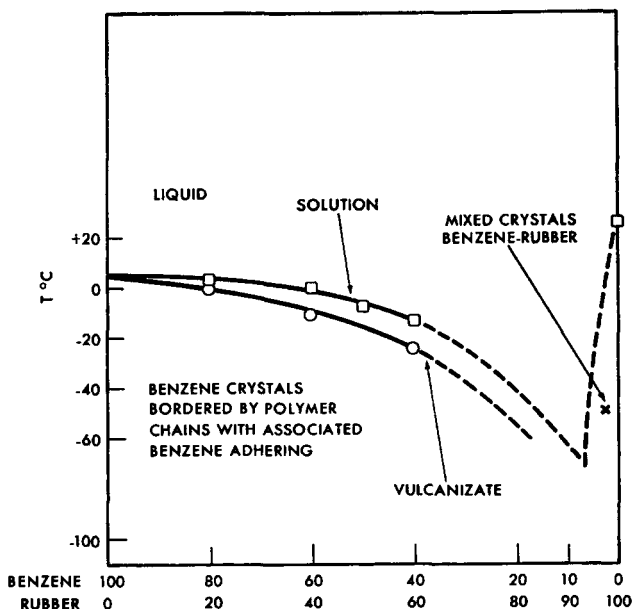


Fig. 8. Schematic phase diagram of the binary mixture of benzene and natural rubber.

model can explain the large freezing point depressions of the concentrated gels and solutions, the insignificant depression of the melting point of the frozen gels, the effect of crosslink density on the freeze point depression and the relatively small effect of carbon black. The carbon black surface immobilizes part of the polymer chains and thereby makes them ineffective as a component of the low-freezing binary, polymer-benzene mixture. With a noncrystallizing rubber such as SBR, the left part of Figure 8 would be essentially the same; the right-hand side would not show any true freezing

TABLE VI
Freezing Damage in Natural Rubber Vulcanizates

Cooling history	Number of cycles	M_c after freezing by swelling in benzene ^a
Dropped into liquid nitrogen	1	10,620
	2	10,600
	3	10,780
Cooled at 5°C./min.	1	10,600
	2	10,780
	3	10,660
Cooled at 0.2°C./min.	1	10,605
	2	10,620
	3	10,620
Cooled at 5°C./min., then annealed at 0°C. for 48 hr.	1	10,710

^a From swelling measurements.

point since SBR does not crystallize but could be characterized by the second-order transition point or glass temperature.

This picture may also offer an explanation of another observation: If the Kuhn-Westlinning concept were correct, it might be expected that the forces which the growing benzene crystals would exert on the network would cause some, if not considerable, damage to the rubber network molecules. However, it should be borne in mind that crystallization is a process of addition of units to a growing crystal phase and that this is not likely to exert pressure on the surrounding network chains. To confirm this point, experiments were carried out to freeze a rubber gel repeatedly after which the equilibrium swelling was determined.

It is obvious from Table VI that no significant reduction in crosslink density has occurred.

Initial X-Ray Diffraction Patterns

The x-ray diffraction patterns were run on pure benzene, on dilute and concentrated solutions of rubber in benzene, and on some of the swollen vulcanizates, the equipment and procedure already described being used at a temperature of -30°C . The pattern of pure benzene contained a strong peak at an angle $2\theta = 18.24^{\circ}$ which did not appear in the patterns of the solutions. Conversely, two peaks at 24.9° and 23.2° , which were quite small in pure benzene, appeared to be enhanced in the solutions. The principal peak ($2\theta = 19.45^{\circ}$) appeared prominently and reproducibly in all patterns, and was therefore chosen for study. Table VI lists the width of this peak at half-height for all the samples tested.

The exact relationship between peak broadening and crystal size may be solved rigorously by Fourier analysis, but simplified relationships are available.

The most widely used of these relationships is based on an equation suggested by Scherrer:

$$L = K\lambda/B_{(\text{rad})} \cos \theta$$

where L is the dimension of the crystal (in Angstroms), K is a form constant value of 0.94, λ is the δ wavelength of incident radiation = 1.54 Å., $B_{(\text{rad})}$ is the width of the peaks at half-height, measured in radians, and θ is the glancing angle.

$B_{(\text{rad})}$ was corrected for instrumental broadening and penetration broadening by assuming (1) the pure benzene crystals are very large (1000 Å. or more), and (2) that the x-ray beam penetrates the sample, thus causing additional broadening. Therefore, the entire width of the pure benzene peaks was considered due to instrumental and penetration broadening (due to low absorption coefficient of the component atoms). By subtracting this width from the width of the broadened peaks in the swollen vulcanizates, one obtains a corrected value for $B_{(\text{rad})}$ and hence obtains the crystal dimensions listed in Table VII. The implicit assumption is that the distri-

TABLE VII
Dimensions of Benzene Crystallites^a

Polymer	Curing system	Volume fraction of benzene	Volume fraction of carbon	Minimum crystallite size, A. ^b	Maximum freezing point depression expected from crystallite size, °C.	Freezing point depression observed, °C.
Benzene	—	1.00	—	∞°	—	—
Natural rubber	—	0.99	—	460	0.76	Negligible
Natural rubber	—	0.66	—	635	0.55	4.1
Natural rubber	Dicumyl peroxide	0.76	—	565	0.62	4.00
Natural rubber	Dicumyl peroxide	0.77	0.23	364	0.96	3.8
Natural rubber	Sulfur	0.77	—	420	0.83	8.1
<i>cis</i> -4-Polybutadiene	Sulfur	0.75	0.23	280	1.25	5.9

^a The three strongest lines in the frozen benzene pattern are located at d spacings of 4.56 A. (19.45° 2 θ), 3.834 A. (23.18° 2 θ), 3.573 A. (24.90° 2 θ).

^b Crystallite size for these samples, as expected from Kuhn-Westphal Theory, would be 40–90 A.

^c Larger than 1000 A.

bution of crystallite sizes may be represented by the Cauchy distribution function. Although this has not been established, it should be noted that an alternative correction, assuming a Gaussian distribution function, leads to results not differing on the average by more than about 30% from the given values.

It is important to note that, while no absolute significance is claimed for these results, it is certainly justifiable to regard them as the minimum possible dimensions for crystals, since experimental variables other than crystal size could conceivably cause line broadening, but none could make the diffraction peaks sharper.

It should also be noted that the line broadening caused by benzene crystals in a 1% solution of natural rubber in benzene (in which both crosslinks and entanglements are absent) is of the same order as the line broadening caused by benzene crystals in the tightly crosslinked gels.

The freezing point depressions attributable to crystals having the dimensions found in the diffraction study are listed in Table VII. It is clear that they cannot account for more than a small fraction of the total observed freezing point depression.

The minimum dimensions of the crystals, as listed in Table VII, are almost an order of magnitude higher than would be predicted by the Kuhn-Westlinning treatment. If the latter were correct, the widths of the peak at half-height would have been close to 2° , rather than the observed value of about 0.5° (see Appendix II). These values are in agreement with those found by Kanig and Karge⁶ using the dimensions of the cavities left by the crystallites and with those of Kuhn on ice crystals in poly(vinyl alcohol).

The reality of the observed freezing point depression was illustrated by sealing samples such as A-2-95 (apparent freezing point $-2.5^\circ\text{C}.$) in small polyethylene bags and immersing for several hours in ice water. Although this is $5.5^\circ\text{C}.$ below the freezing temperature of pure benzene, the sample remained soft and flexible. The same sample, when cooled to $0 \pm 2^\circ\text{C}.$ in the x-ray diffraction apparatus for 1 hr., gave no peaks whatever. When the temperature was dropped by an additional $5^\circ\text{C}.$, however, a peak appeared at once at an angle $2\theta = 19.5^\circ$. These phenomena would indicate that the rate of cooling plays no dominant part in the freezing point depression. In another similar experiment, the sample was kept overnight at $0^\circ\text{C}.$ without crystallizing, after which a $5^\circ\text{C}.$ drop in temperature caused rapid appearance of the 19.5° line.

No annealing of crystals could be detected over a period of 1 hr. at a temperature of $-30^\circ\text{C}.$, but on warming above $-10^\circ\text{C}.$, annealing occurred quite rapidly, as evidenced by the diminishing width of the 19.5° peak. However, annealing caused no freezing damage as was shown by Table VI.

Over a long period at $-30^\circ\text{C}.$, the character of the principal peak appeared to change. Originally it appeared as a doublet with a sharp maximum at 19.60° and 19.45° , and during a 90 min. period, the latter peak grew at the expense of the former. The width, measured at half

the height of the lower peak, did not change, however. (See Appendix II for more detailed discussion.)

It was also established that no interference was being encountered from ice crystals, from incipient crystallinity of the polymer itself, or from the materials of construction of the sample holder.

It is possible in principle that much smaller crystallites were formed originally, which may have caused wider lines and which grew rapidly before being analyzed by x-rays. Heating curves of frozen samples show some hysteresis as compared to the cooling curves, but still maintain most of the depression of the freezing point of the sample on cooling and show no tendency to approach the melting point of pure benzene.

CONCLUSIONS

(1) The dimensions of the benzene crystals appear to be essentially similar in dilute rubber solutions, concentrated rubber solutions, and cross-linked vulcanizates, filled and unfilled.

(2) The measured crystal size is much larger than that expected from the Kuhn-Westlinning treatment, and cannot account for more than a fraction of the observed freezing point depression.

(3) The freezing point depression has a real physical significance and appears to be positively correlated with crosslink density at constant rubber concentration. The freezing point depression increases rapidly with increasing rubber concentration. At the same rubber in solvent concentration, the effect of carbon black is to reduce the freezing point depression in both solutions and vulcanizates.

(4) The anomalous freezing point depressions observed may be accounted for by assuming greatly increased mobility of the benzene molecules solvated around the polymer chains, which are still thermally mobile at temperatures down to the glass transition temperature. Carbon black reduces this mobility, and therefore, causes smaller freezing point depressions.

APPENDIX I

Calculation of Freezing Point Depression of Benzene by Dissolved Rubber*

The partial molal free energy of pure benzene at its freezing point and that of benzene in a rubber solution at its freezing point is determined according to classical thermodynamics and the classical approximation by the equation:

$$\begin{aligned}\mu_0 - \mu_s &= -\Delta F = -(\Delta H - T_m \Delta S) \\ &= \Delta H [1 - T_m (\Delta S / \Delta H)] \\ &= \Delta H [1 - (T_m / T_0)]\end{aligned}$$

* The derivation in this form was made by Dr. A. M. Rijke, Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida.

or

$$\begin{aligned} &= \Delta H(T_0 - T_m)/T_0 \\ &= \Delta HT_m[(1/T_m) - (1/T_0)] \end{aligned}$$

The Flory-Huggins theory for lowering the thermodynamic potential of a molecule of solvent in a polymer solution gives:

$$-(\mu_0 - \mu_s) = RT\{\ln 1 - v + [1 - (1/x)]v + \chi v^2\}$$

or

$$\Delta H[(1/T_m) - (1/T_0)] = R\{\ln 1 - v + [1 - (1/x)]v + \chi v^2\}$$

where χ is the interaction parameter, v is the volume fraction of rubber in solution, x is the average number of benzene molecules associated with one segment of polymer.

On substituting the values, ΔH for benzene = 2370 cal./mole, T_0 for benzene = 278.5°K., χ for benzene in NR = 0.43, the equation becomes

$$1/T_m = 1/278.5 - 2/2370\{\ln 1 - v + [1 - (1/x)]v + \chi v^2\}$$

and a series of values was calculated for T_m with $v = 0.05, 0.10, 0.15,$ and so forth up to 0.70. Although the validity of the theory up to the high concentration is not to be expected, the data are plotted in Figure 9 for two values of χ , namely, 0.43 and 0.40, and for two values of x (which can be expressed as the molal volume of a polymer segment divided by the molecular volume of benzene and which indicates the number of benzene molecules which are solvating the average polymer segment). Usually x is so large that $1 - (1/x)$ equals 1. Even the wholly unrealistic value of $x = 20$ which makes $1 - (1/x) = 0.95$, does not change the theoretical curve sufficiently to come close to the experimental values. The change in χ from 0.43 to 0.40 moves the curve only to an insignificant degree. Kawai¹⁴ has actually used freezing point depression to determine χ over a range of

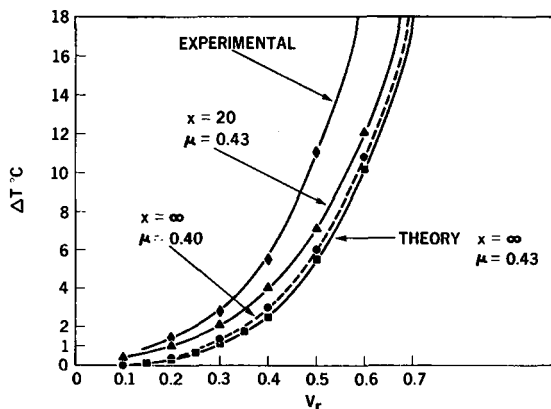


Fig. 9. Theoretical and experimental freezing point depression of benzene in natural rubber solutions.

concentrations of polymer solutions and gels. Consequently, there is no reasonable explanation for the large freezing point depressions unless one wants to assume that the active segment of the polymer chain consists of a length that would only involve some ten benzene molecules.

Entanglements of molecular chains cannot explain the anomalous freezing points; according to Bueche¹⁵ the molecular weight between entanglements in rubber solutions is of the order of 17,000 which value does not at all fit into this picture.

APPENDIX II

Benzene Crystallite Measurement

Experimental

In the initial x-ray diffraction study, it was observed that the intensities of the diffraction peaks in the benzene pattern changed radically with time. In fact, some peaks disappeared entirely and other peaks appeared and became very strong. This phenomenon could be attributed to two causes: (1) annealing accompanied by reorientation of crystallites due to vapor transport recrystallization or (2) appearance of a new crystal phase. The possibility of appearance of a new crystalline phase was eliminated by a differential thermal analysis which gave no evidence of a phase change in the range -15 to -65°C ., within which all diffraction analyses took place.

Therefore, it seems reasonable to attribute all changes in the benzene pattern (with time) to the reorientation of benzene crystallites; for example, the changes in the doublet (19.60° and $19.45^{\circ} 2\theta$) found in the initial study. This latter difficulty was minimized by the following experimental procedure:

Samples of swollen vulcanizates were quick-frozen by immersion in a Dry Ice-alcohol bath at -70°C . They were wiped clean of alcohol and quickly placed in labeled, precooled vials containing about 5 ml. of frozen benzene, capped, and stored at temperatures between -15 and -25°C . at least overnight. (If the storage time exceeded three days, most of the frozen benzene diffused out of the samples, even though the air in the tightly capped vial was saturated with benzene vapor.) The above procedure produced equilibrated samples whose x-ray patterns (run at around -45°C .) were stable over the 2-4 hr. analysis period. However, this procedure is subject to at least one criticism; it is possible that the average crystallite size at the time of x-ray analysis was significantly larger than at the time freezing point depression measurements were made. Since no suitable means was devised to perform both analyses under similar conditions, this consideration must be borne in mind. Other aspects of the experimental procedure have been described adequately in the experimental section of the paper. An illustration of the x-ray diffractometer tracings of the 111 peaks (at $\sim 19.45^{\circ} 2\theta$) in pure benzene and benzene in SBR is given in Figure 10.

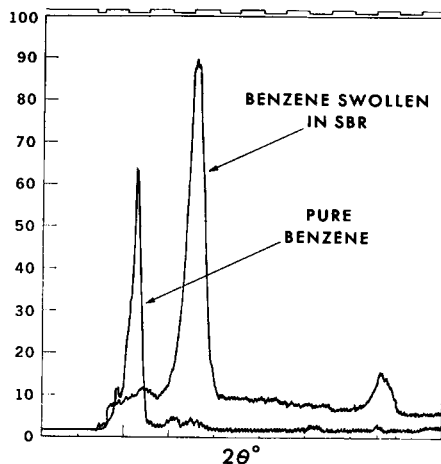


Fig. 10. 111 reflections of pure benzene and benzene in SBR. Broadening of the $2\theta = 19.5^\circ$ peak is mainly due to reduced crystallite size; peak for benzene swollen in SBR has been deliberately shifted to the right to facilitate comparison of widths. Actually the peaks occur at the same 2θ .

Results and Discussion

Published unit cell dimensions^{11,12,16} of frozen benzene (over a wide temperature range) are in serious disagreement, as shown in Table VIII.

TABLE VIII

Temperature, °C.	a, Å.	b, Å.	c, Å.	Reference
-3	7.460	9.666	7.034	Cox ¹¹
-22	7.455	9.168	6.824	Kozhin ¹²
-25	7.464	9.626	6.986	This work
-80	7.08	9.55	6.13	Falqui et al. ¹⁵
-195	7.292	9.471	6.742	Kozhin ¹²
-195	7.292	9.471	6.742	Cox ¹¹

TABLE IX
hkl Values in Benzene at -25°C .

hkl	d, Å.
020	4.813
111	4.507
021	3.964
200	3.732
{121	3.500
{002	3.493
{210	3.480
012	3.283
102	3.164

TABLE X
Benzene Crystallite Parameters in Swollen SBR Vulcanizates with Increasing Black Loadings^a

<i>hkl</i>	Benzene calculated			No Black		30 parts HAF		50 parts HAF		65 parts HAF	
	2θ	<i>d</i> , A.	<i>d</i> , A.	<i>d</i> , A.	<i>B</i> , rad $\times 10^{-6}$	<i>d</i> , A.	<i>B</i> , rad $\times 10^{-6}$	<i>d</i> , A.	<i>B</i> , rad $\times 10^{-6}$	<i>d</i> , A.	<i>B</i> , rad $\times 10^{-6}$
020	18.43°	4.813	4.800	4.800	323	4.844	206	715	4.824	220	670
111	19.70°	4.507	4.507	4.507	406	4.533	110	∞	4.512	83	∞
200	23.84°	3.732	3.745	3.745	454	3.744	0	∞	3.737	103	∞
{121	25.44°	3.500									
{002	25.50°	3.493	3.487	3.487	399	3.504	186	805	3.500	151	990
{210	25.60°	3.480									

^a *B* (the peak breadth at half maximum) is approximately corrected for instrumental broadening and penetration broadening by subtracting *B* for the 020 in pure benzene. All figures are given as infinity when the corrected *L* exceeds 1000 A. which, under the conditions of the analysis, is considered infinite. Broadening due to penetration should be accompanied by a shift in *d* spacing toward lower angle, i.e., a given *d* should appear slightly larger than normal. However, the *d* spacings tabulated above do not show such a trend because of unavoidable differences in specimen height during analysis.

Therefore we calculated unit cell dimensions shown above in Table VIII from our patterns run at about -25°C . According to Cox and Smith¹³ the crystal symmetry of frozen benzene is orthorhombic, space group *Pbca*.

The *d* spacings of frozen benzene were calculated (for the unit cell dimensions obtained experimentally) by means of the equation:

$$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$$

The calculated and indexed values of *hkl* (in the angular range where peaks occurred in our experimental patterns) are given in Table IX. This listing does not include higher order *hkl*'s because they are of no value in indexing the observed peaks.

The data on benzene crystallite size in four different swollen samples are given and their *d* spacings are compared to calculated and indexed *d* spacings in pure benzene in Table X.

Of the peaks listed in Table IX only the following were usable for crystallite size measurement, 020, 111, and 200. Of these three peaks only two, the 020 and the 200, give crystallite dimensions uniquely. The 020 planes are perpendicular to the *b* axis and parallel to the *a* and *c* axes; therefore the 020 reflection gives the average crystallite dimension in the *b* direction, L_b , uniquely and unambiguously. The 200 planes are perpendicular to the *a* axis and parallel to the *b* and *c* axes; therefore, the 200 peak width gives L_a uniquely. Fortunately, no other *hkl*'s fall close enough to interfere with these peaks. The 111 unfortunately gives a crystallite dimension in a direction which is inclined (at some angle other than 90°) to all three crystallographic axes. Finally three peaks, 121, 002, and 210, fall very close together. If all of these peaks have appreciable intensity, a triplet which is not resolvable in a powder pattern will occur. Therefore, it is indeterminate whether the observed peak contains intensity from one, two, or all three peaks in that angular vicinity. Thus, the crystallite dimension calculated from this peak (or peaks) may be appreciably smaller than it should be. The crystallite dimensions given in Table X were calculated from duplicate patterns by the Scherrer equation ($L = K\lambda/B \cos \theta$) and are approximately corrected for instrumental and penetration broadening.

At first glance it appears that crystallite size in general increases with carbon black loading. However, it must be borne in mind that the average density of the sample increases with carbon black loading and thus its capacity to absorb x-rays increases. Therefore, as sample density increases, peak broadening due to penetration decreases, thus giving slimmer peaks the higher the sample density. Unfortunately, no means was devised for estimating differences in the broadening due to penetration in these samples where a significant range of densities exists. Therefore, it is indeterminate whether crystallite size has changed appreciably from one stock to the next.

In conclusion, it can be stated that 330 Å. (L_a in the swollen, frozen SBR gum vulcanizate) is the minimum average crystallite dimension found in

this study. In Table X, one can see that all other crystallite dimensions are somewhat larger. Since the unique crystallite dimensions L_a and L_b are comparable to the dimension in an oblique direction, given by the 111, for example, it appears that the average benzene crystallite is a box whose dimensions are roughly equal in all directions.

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