

## Quantitative Characterization of Polybutadiene Networks

GERARD KRAUS, *Phillips Petroleum Company, Bartlesville, Oklahoma*

### I. INTRODUCTION

Several years ago Moore and Watson<sup>1</sup> developed a method for determining the number of crosslinks introduced into natural rubber during peroxide vulcanization. The method was then used to develop a "calibration" of physical crosslinking, determined from equilibrium swelling or elasticity measurements, against true chemical crosslinking. This scheme has proved highly useful in a variety of studies on vulcanization and oxidative degradation of natural rubber networks. Unfortunately, the simple mechanism of peroxide vulcanization on which the technique is based does not hold for polymers with appreciable branched unsaturation. It is, therefore, not applicable to polybutadienes or copolymers of butadiene, which contain various amounts of vinyl unsaturation resulting from 1,2-addition. In the present paper a chemical vs. physical crosslinking calibration is developed for *n*-butyllithium-initiated polybutadiene, which is based on general relationships developed for natural rubber networks by Mullins.<sup>2</sup> The calibration is then used to determine crosslink yields for various vulcanization systems and the results compared with those found in natural rubber vulcanization.

### II. METHOD

According to simple network theory<sup>3</sup> the number of elastically active network chains per unit volume ( $\nu$ ) is

$$\nu = 2n - 2\rho/M \quad (1)$$

where  $n$  is the number of crosslinks,  $\rho$  the density, and  $M$  the primary molecular weight (number average). For convenience of notation let

$$2n = \nu^* \quad (2)$$

where  $\nu^*$  will be referred to as "chemical crosslinking." Equation (1) neglects entanglements but takes into account free chain ends. However, a number of crosslinks will be wasted in structures not contributing elastically active chains. Their number will decrease with increasing molecular weight so that we can take these into account approximately by writing

$$\nu = \nu^* - b/M \quad (3)$$

where  $b$  will be a constant somewhat larger than  $2\rho$ . The number of network chains contributed by entanglements which are trapped between crosslinks to become elastically active is given by<sup>2,10</sup>

$$e = a(1 - b/\nu^*M) \quad (4)$$

Note that  $e$  approaches  $a$  as either  $\nu^*$  or  $M$  becomes infinite. The quantity  $a$  is, therefore, twice the total number of entanglements in a polymer of very large molecular weight. The total number of elastically effective network chains ("physical crosslinking") becomes:

$$\begin{aligned} \nu &= \nu^* - b/M + a(1 - b/\nu^*M) \\ &= \nu^* + a - (\nu^* + a)b/\nu^*M \end{aligned} \quad (5)$$

In evaluating the parameters  $a$  and  $b$  for polybutadiene, we assume that the primary molecular weight survives processing and vulcanization unaltered, and that chemical crosslinking in a fixed vulcanization recipe is independent of the primary molecular weight of the rubber. The first assumption appears justified in view of the well-known resistance of polybutadiene to breakdown on mastication and its relative freedom from reversion reactions during cure. The second assumption should likewise hold except for very low molecular weights. If, then, a series of polymers differing in primary molecular weight only is cured to level cure in the identical recipe and  $\nu$  is determined, Equation (5) demands that a plot of  $\nu$  vs.  $M^{-1}$  be linear with intercept  $(\nu^* + a)$  and slope  $(\nu^* + a)b/\nu^*$ . By operating at two levels of crosslinking agent we obtain four equations (2 slopes and 2 intercepts) with four unknowns ( $a$ ,  $b$ ,  $\nu_1^*$ , and  $\nu_2^*$ ) so that the constants may be determined. It turns out that for both sulfur and peroxide cures the  $\nu^*$ 's are proportional to the level of curing agent, at least in the low concentrations normally used.

### III. EXPERIMENTAL

Polybutadienes were prepared by Dr. R. P. Zelinski of these laboratories using  $n$ -butyllithium as initiator, cyclohexane as solvent, and 50°C. polymerization temperature. The number-average molecular weights of these polymers were calculated from the initiator level, after correction for initiator destroyed by trace impurities. The molecular weights thus found were: 24,000, 51,000, 100,000, 169,000, 215,000, 235,000, and 250,000. Details of this work will be published elsewhere. Several of the lower molecular weights were checked by ebullioscopic measurements and satisfactory agreement was found. Intrinsic viscosities (in toluene, 25°C. produced a good fit to the equation:

$$\eta = 6.11 \times 10^{-4} M^{0.659} \quad (6)$$

Infrared determinations gave the following double bond configuration:

$$cis, 40 \pm 2\%; trans, 50 \pm 1\%; vinyl, 10 \pm 1\%$$

TABLE I  
 Polymer Recipes

|   | Sulfur-sulfenamide<br>I | Sulfur-sulfenamide<br>II | Thiuram  | Peroxide |
|---|-------------------------|--------------------------|----------|----------|
| Polymer   | 100                     | 100                      | 100      | 100      |
| Zinc oxide  | 3                       | 3                        | 3        | —        |
| Stearic acid  | 2                       | 2                        | 2        | —        |
| Disproportionated rosin acid                        | 3                       | 3                        | 3        | —        |
| Sulfur  | Variable                | Variable                 | —        | —        |
| <i>N</i> -cyclohexylbenzothiazole-2-sulfenamide     | 1.2                     | —                        | —        | —        |
| <i>N</i> -oxydimethylenebenzothiazole-2-sulfenamide | —                       | 1                        | —        | —        |
| Tetramethylthiuram disulfide                        | —                       | —                        | Variable | —        |
| Dicumyl peroxide (40% active)                       | —                       | —                        | —        | Variable |
| Antioxidant   | 1                       | 1                        | 1        | —        |

The polymers were compounded in four different recipes as shown in Table I.

Sulfur-sulfenamide Recipe I with 1.75 and 3.00 phr of sulfur was used in the series of experiments performed to establish the values of the parameters  $a$  and  $b$ . Crosslink yields were determined for all recipes using a single polymer of  $M = 235,000$ .

Vulcanizates were cured 20, 30, 45, and 60 min. at 153° C. Equilibrium swelling at 30°C. in *n*-heptane was determined on each vulcanizate and only the minimum value (corresponding to maximum crosslinking) was used in the calculations.

Swelling determinations were made gravimetrically in the manner described previously.<sup>4</sup> Physical crosslinking was calculated by the Flory-Rehner equation:<sup>5</sup>

$$\nu = -\frac{1}{V_s} \frac{\ln(1 - v_r) + v_r + \mu v_r^2}{v_r^{1/3} - v_r/2} \quad (7)$$

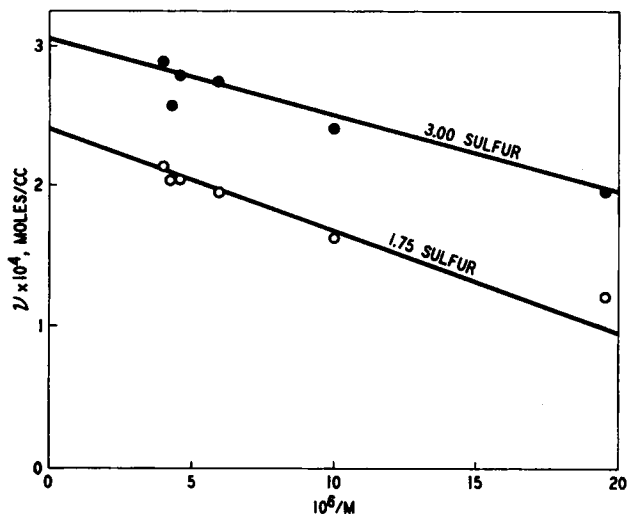
Here  $v_r$  is the volume fraction of polymer in the swollen gel and  $V_s$  the molal volume of the solvent. The value of the solubility parameter  $\mu$  was found from  $v_r$  and elastic measurements on the swollen gel,<sup>4</sup> using 12 vulcanizates covering a wide range of degree of crosslinking:

$$\mu = 0.37 + 0.52\nu_r \quad (8)$$

## IV. RESULTS

### A. Determination of Parameters $a$ and $b$

Figure 1 shows the plots used to determine the constants  $a$  and  $b$  from the sulfur-cured polymers of varying molecular weight. In drawing the straight lines the data for the lowest molecular weight polymer (23,000)

Fig. 1. Determination of  $a$  and  $b$ .

were ignored as they did not fit the required pattern. Evidently complications arise at very low primary molecular weights which cannot be accounted for simply by a  $M^{-1}$  term. The results of the present analysis are, therefore, limited to polymers of  $M = 50,000$  or above. With this restriction the values of the two parameters giving the best fit are:

$$a = 1.5 \times 10^{-4}$$

$$b = 2.73$$

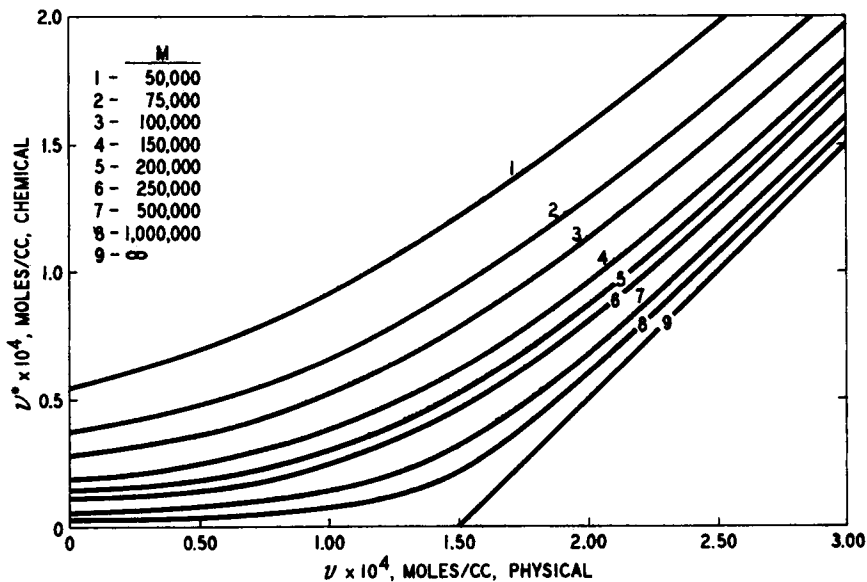


Fig. 2. Chemical vs. physical crosslinking.

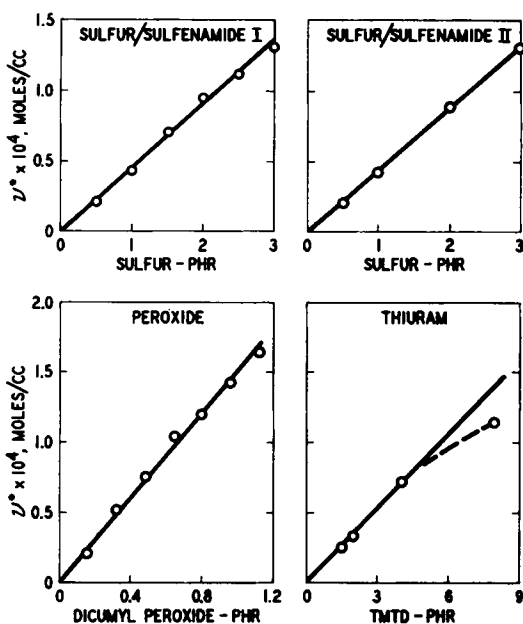


Fig. 3. Chemical crosslinking in various vulcanization systems.

A complete set of chemical vs. physical crosslinking calibrations based on these parameters is shown in Figure 2.

The value found for  $a$  corresponds to a molecular weight between entanglements of 6000 or a degree of polymerization between entanglement points of 110. This is of the order of magnitude usually found in high polymers on the basis of viscoelastic measurements.<sup>6</sup>

### B. Chemical Crosslink Yields

Figure 3 shows chemical crosslinking as a function of the level of curing agent for the four recipes shown in Table I. With the exception of a single experimental point, excellent straight lines are obtained. Crosslink yields calculated from the slopes of these plots are shown in Table II.

TABLE II  
Crosslink Yields for Polybutadiene Vulcanization

| Vulcanization system | Atoms or molecules of primary curing agent per chemical crosslink |         | Reference for Hevea data  |
|----------------------|---|---------|---|
|                      | Polybutadiene   | Hevea   |   |
| Sulfur-sulfenamamide | 12-13   | 9-10    | Lorenz and Parks <sup>7</sup>   |
| Thiuram              | 4.3   | 3.2-4.0 | Lorenz and Parks, <sup>7</sup><br>Moore, <sup>8</sup> Bevilacqua <sup>9</sup> |
| Peroxide             | 0.45  | 1       | Lorenz and Parks <sup>7</sup>   |

Comparison with natural rubber shows that the general mechanisms of vulcanization of the two polymers are apparently similar for the sulfur-sulfenamide and thiuram curing systems. On the other hand the yield of crosslinks for peroxide is much larger with polybutadiene. The fact that the yield is in excess of unity indicates a contribution from a chain reaction, presumably a polymerization of the vinyl groups. Evidence for such a reaction is also obtained from peroxide crosslinking experiments on high vinyl polybutadienes. For example, a 98.4% atactic 1,2-polybutadiene could be crosslinked to  $v_r = 0.376$  with only 0.016% dicumyl peroxide. A chemical crosslink calibration is not available for this polymer, but the fact that this rubber required essentially normal quantities of sulfur indicates a very large peroxide crosslink yield.

### References

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### Synopsis

Using a relationship found to be applicable for natural rubber networks in establishing contributions of chemical crosslinking, entanglements, and network defects to physical crosslinking, a physical versus chemical crosslinking "calibration" is developed for polybutadiene prepared by organolithium initiation. This calibration is then used to determine chemical crosslink yields for sulfur-sulfenamide, thiuram, and peroxide vulcanization. Crosslink yields for polybutadiene in the sulfur-sulfenamide and thiuram curing systems are shown to be similar to those of natural rubber. In peroxide vulcanization the crosslink yield is in excess of unity for polybutadiene. Evidence is presented which indicates that this is due to a polymerization type reaction involving vinyl groups resulting from 1,2-addition during polymerization.

### Résumé

Sur la base d'une relation applicable à des réseaux de caoutchouc naturel en vue d'établir les contributions du pontage chimique, de l'entassement et des défauts de réseau sur le pontage physique, on développe un procédé physique de calibrage des pontages chimiques dans le cas du polybutadiène préparé par initiation avec des organolithiés. Ce calibrage est alors utilisé pour déterminer le rendement du pontage chimique pour le soufre-sulfénamide, thiurame et la vulcanisation peroxydique. On montre que le rendement du pontage par le polybutadiène dans les systèmes de vulcanisation au soufre-sulfénamide et thiurame sont semblables à ceux du caoutchouc naturel. Dans la vulcanisation peroxydique, le rendement du pontage est supérieur à l'unité pour le

polybutadiène. On démontre que cela est dû au type de polymérisation comportant des groupes vinyliques résultant de l'addition-1,2 au cours de la polymérisation.

### Zusammenfassung

Unter Benützung einer für Naturkautschuk anwendbaren Beziehung für den Beitrag der chemischen Vernetzung, von Verschlingungen und Netzwerkfehnstellen zur physikalischen Vernetzung wurde eine "Kalibrierung" der physikalischen gegen die chemische Vernetzung für Polybutadien entwickelt, das mit Anregung durch Organolithiumverbindungen hergestellt worden war. Diese Kalibrierung wird dann zur Bestimmung der chemischen Vernetzungsausbeute bei der Schwefel-Sulfenamid-, Thiuram- und Peroxydvulkanisation verwendet. Die Vernetzungsausbeute für Polybutadien ist mit Schwefel-Sulfenamid und Thiuram ähnlich wie bei Naturkautschuk. Bei der Peroxydvulkanisation ist die Vernetzungsausbeute für Polybutadien höher als eins. Es wird gezeigt, dass dieser Umstand auf eine Polymerisationsreaktion der Vinylgruppen aus der 1,2-Addition während der Polymerisation zurückzuführen ist.

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