

Characterization of Networks from the Peroxide Cure of Polybutadiene

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Synopsis

Polybutadienes with molecular weights varying between 12,500 and 92,000 and containing from 23.4% to 93% 1,2-structure were cured with 1 to 8 parts per hundred of dicumyl peroxide at temperatures ranging from 130° to 175°C. The cured samples were swollen in toluene and the crosslink densities were determined by application of the Flory-Rehner equation. The unsaturation remaining after cure was measured by infrared and was found to be in good agreement with the unsaturation level calculated from the swelling data. From these measurements it was found that a molecular weight between crosslinks of less than 100 g/mole could be obtained. The number of double bonds consumed per radical formed was found to vary from 6 to 185. The highest values were obtained with polymers highest in 1,2-content cured with the lowest initiator levels and at the lowest temperatures.

INTRODUCTION

The treatment of 1,4-polybutadiene with free radicals is known to introduce a small number of crosslinks into the polymer system, making it both strong and rubbery.¹ Likewise, similar changes are brought about when polybutadienes of high 1,2- or vinyl content are treated with a small amount of a radical initiator. However, the cure of these high vinyl polymers with 1% or more of dicumyl peroxide results in a very hard thermosetting material with a high flexural strength and modulus. This material apparently has an extremely high crosslink density which probably was developed by a radical-chain polymerization mechanism.²⁻⁵ These workers have shown radical efficiencies, that is, the number of double bonds consumed per radical formed, as high as 100 for a 98% 1,2-polymer.¹ Van der Hoff⁵ observed an increase in this crosslinking efficiency as the temperature of cure was raised for high-vinyl polymers, but a decreased efficiency with increasing temperature for low 1,2-content polymers.

Since the peroxide cure of polybutadienes of varying 1,2-content has not been fully elucidated, the following study was initiated. The influence of molecular weight of the starting polymer and the 1,2-content were studied as functions of the peroxide concentration, cure time, and temperature. From infrared studies and swelling measurements of these samples, the molecular weight between crosslinks, radical-chain length, and residual unsaturation were calculated.

EXPERIMENTAL

Materials

Dicumyl peroxide (98% active) was obtained from Hercules Incorporated and was used without further purification. All solvents used were reagent grade and were not further purified. The phenyl- β -naphthylamine was obtained from R. T. Vanderbilt Company, Incorporated and was not further purified.

The polybutadienes of varying molecular weight and vinyl content listed in Table I were prepared according to the procedure of Kuntz and Gerber.⁶ The molecular weight was controlled by changes in the catalyst concentration. These polymers were free of antioxidant and were stored under nitrogen as a 40% to 60% hexane solution. The vinyl contents of these polybutadienes were measured in carbon tetrachloride by NMR at 60 MHz by the method of Senn.⁷ The molecular weights of these polymers were measured on a Waters Model 200 GPC. Intrinsic viscosities were measured in toluene at 25°C.

TABLE I
Polybutadienes Cured With Dicumyl Peroxide

Polymer no.	Intrinsic viscosity	Molecular weight $\times 10^{-3}$	% Vinyl
1	0.19	12.5	91.5
2	0.37	28.3	93
3	0.64	54.9	88
4	0.95	92.0	91.5
5	0.36	22.8	65
6	0.43	26.4	43.2
7	0.35	19.8	23.4

The peroxide was first dissolved in hexane before being mixed with the polymer solution. When a homogeneous solution was obtained the solvent was removed at 25°C under a vacuum of less than 0.10 mm of mercury. The solvent-free sample containing the peroxide was cured in a 1 $\frac{1}{4}$ in. diameter by $\frac{1}{64}$ in. mold at varying times and temperatures.

Infrared Analysis

The residual vinyl unsaturation of a cured sample was measured on a Perkin Elmer Model 337 grating infrared spectrophotometer using 4.000 parts of potassium ferricyanide per hundred parts of rubber as an internal standard. The films used were cured to approximately 2-mil thickness, and the optical density ratio of the 1830 cm^{-1} band from the first harmonic of the vinyl group of the polymer to the 2130 cm^{-1} band of the ferricyanide was measured. The potassium ferricyanide was finely ground to pass 325 mesh and was dried prior to use.

Swelling

The cured polymers were swollen to equilibrium by immersing samples of about 0.3 g in 100 cc toluene containing 0.2% phenyl- β -naphthylamine until a constant weight was obtained. A total of 16 hr on a steam bath (75° to 80°C) was sufficient to satisfy the above conditions. These samples were allowed to stand in the toluene solution for at least 2 hr at 25°C before measuring the swollen weight. The dried weight was obtained from those samples that had been completely desolventized by heating at 120°C for 2 hr under a vacuum of less than 0.10 mm of mercury.

The equilibrium swelling Q at 25°C in toluene was chosen as a measure of the crosslinking. This may be defined as the weight ratio of the swelling agent to polymer in a polymer sample that has been swollen to equilibrium. Thus, as defined, $1/Q$ increases with crosslinking.

RESULTS AND DISCUSSION

In order to measure the number of effective network chains per unit volume of sample, ν , in such a hard, highly crosslinked system, the Flory-Rehner equation^{8,9} was employed:

$$\nu = -\frac{1}{V_s} \frac{\ln(1 - v_2) + v_2 + \chi v_2^2}{v_2^{1/3} + \frac{2v_2}{f}} \quad (1)$$

where V_s is the molal volume of the swelling solvent, f is the functionality of the crosslink, χ is the solvent polymer interaction constant, and v_2 is the volume fraction of the polymer in the swollen network.

In order to apply eq. (1), the equilibrium swelling Q must be converted to the desired volume fraction. This is readily accomplished once the density of the sample is known. However, during cure the density of the sample was observed to increase steadily. The relationship of sample density to crosslink density in Figure 1 was obtained by curing sample 2 in Table I with either 4 or 6 parts per hundred of dicumyl peroxide at various times. From 18 samples varying in crosslink density, the smooth curve shown was obtained. As may be seen, the density d of the polymer increases quite rapidly from its initial value of 0.893 to 0.992 g/cc, while the reciprocal swelling $1/Q$ increases from 0 to 4. Above a $1/Q$ of 4, the density increases much more slowly, with a value of 1.00 g/cc being obtained at an inverse swelling ratio of 7. The $1/Q$ value of 7 corresponds to only a 14.3% weight increase by swelling in toluene. Because of the very slow rate of increase of sample density with degree of crosslinking, those few samples that exceeded a $1/Q$ value of 7 were estimated to have a d of 1.000 g/cc.

The crosslink density calculated from eq. (1) is influenced strongly by the value assigned to χ . Since a number of workers²⁻⁴ have shown that the radical chain length is independent of the peroxide concentration during cure, it appears that the method of Hummel¹⁰ can be used to evaluate χ . In

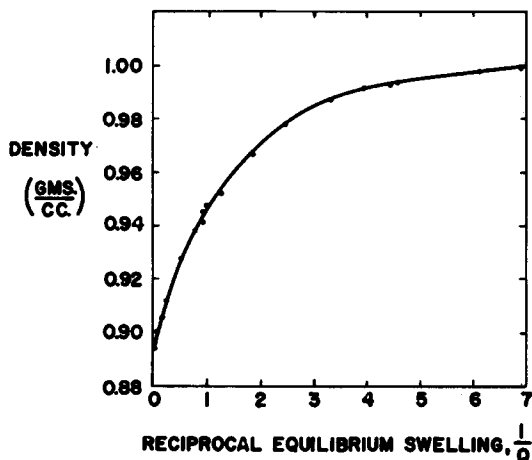


Fig. 1. Change in density of 93% 1,2-polybutadiene with degree of cure.

this method, a polymer sample is cured with at least two different initiator concentrations that vary by a factor of 2. With the SBR and natural rubber systems that Hummel used, it may be assumed that the crosslink densities obtained from the two cures will also vary by the same factor of 2. A series of curves can then be plotted of crosslink density versus v_2 for a variety of values of χ onto which the swelling data of the two cures may be fitted. With a 93% 1,2-polybutadiene cured at four different peroxide levels, no single value of χ could be found to satisfy all the samples. Thus it appears that the chain length, CL , which is the number of double bonds consumed per radical formed, was indeed varying with the concentration of the peroxide used in this study.

The method of Scott and Magat¹¹ was used for this evaluation, which employs the equation

$$\chi = 0.30 + \frac{V_s(\delta_s - \delta_r)^2}{RT} \quad (2)$$

where χ and V_s are as defined previously, δ_s and δ_r are the solubility parameters of the solvent and rubber, respectively, and R and T are the molar gas constant and temperature in $^{\circ}\text{K}$, respectively. The values of δ_s and δ_r were 8.9 and 8.45, respectively, as determined by Scott and Magat.¹¹ Thus, the value of 0.34 was calculated for polybutadiene swollen in toluene.

Having determined χ , the crosslink density may be readily calculated from eq. (1) by assuming that the functionality of the crosslinks was 4. In order to determine the molecular weight between crosslinks, M_c , the density of the sample was divided by ν of eq. (1). A plot of $1/M_c$ versus $1/Q$ is shown in Figure 2. As can be seen, over the range of most interest, this is almost a straight line with only a small deviation being noted at very high and very low values of M_c . As an indication of the extremely high crosslink densities that are being encountered, the M_c associated with a $1/Q$ of

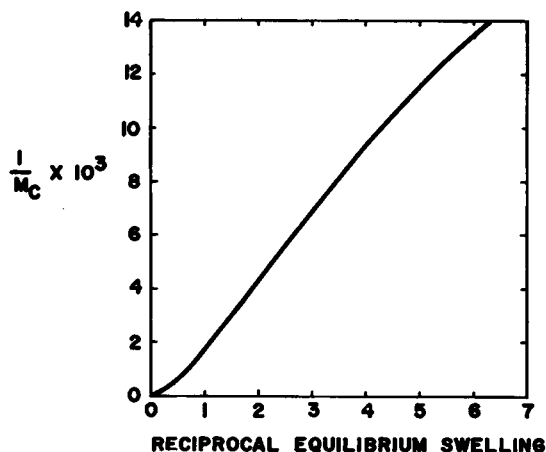


Fig. 2. Reciprocal molecular weight between crosslinks vs. reciprocal equilibrium swelling.

4 and 7 are 107.5 and 65.8 g/mole, respectively. A limiting value of only 54.1 g/mole is possible with 100% utilization of the unsaturation.

From Figure 2 it can be seen that with a reciprocal swelling value of 6, the polymer has obtained a M_c of 74. Since this corresponds to a utilization of 73% of the initial double bonds present in the polymer, the possibility that the Flory-Rehner equation may not be valid at this apparent high level of crosslink density must be considered. In order to determine if the crosslink density measured was truly representative of the number of double bonds that were consumed, an independent method of obtaining the residual unsaturation present in these samples was set up. In this method, infrared was used to measure the remaining vinyl unsaturation present in a cured sample. This was accomplished by the addition of finely ground, dried potassium ferricyanide to the polybutadiene and measuring the optical density ratio of the 1830 cm^{-1} band from the first harmonic of the vinyl group of the polymer to the 2130 cm^{-1} band of the ferricyanide. A plot of this ratio versus the per cent of 1,2-polybutadiene present in eight different samples of known composition can be seen in Figure 3. A good straight line was obtained from such a plot. Using this as a means to calculate remaining unsaturation, a sample of 93% vinyl polybutadiene was cured with 8 parts of dicumyl peroxide at 175°C , and IR and swelling measurements were made on the films obtained. The results of this measurement are listed in Table II.

As can be seen, both sets of data show a regular steady decrease in the unsaturation remaining with increased cure time. The IR procedure showed on an average about 6% less unsaturation than the swelling method over the entire range studied. The IR results all had been normalized to 100% total unsaturation from the initial 93% vinyl structure that was actually measured. This was based on the assumption that all of the double bonds were of equal reactivity, a fact that was found only to be approxi-

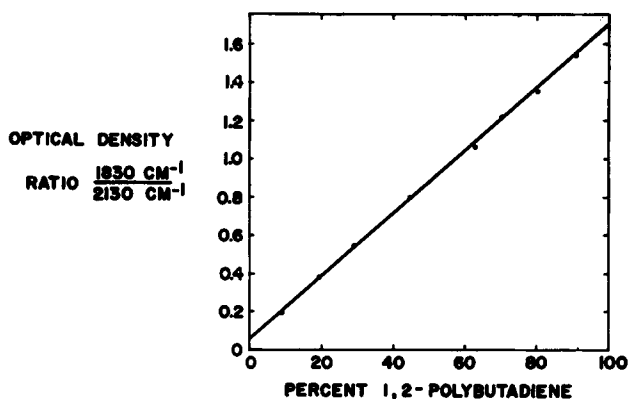


Fig. 3. Infrared calibration curve for the measurement of 1,2-polybutadiene content with 4 phr of potassium ferricyanide as internal standard.

mately true. Thus, although there was not perfect agreement of the two methods, the difference was small enough to establish that the swelling measurements which have been made were still in a range where the Flory-Rehner equation was valid.

The crosslink density of polymer 2 in Table I was followed as a function of time for four different concentrations of dicumyl peroxide at 160°C (Fig. 4). The time of cure may be related to the amount of peroxide decomposed by the following relationship:

$$C_R = C_0 e^{-kt} \quad (3)$$

where C_0 and C_R are the original and remaining concentration of the peroxide, respectively, k is the rate constant for decomposition, and t is the time. Thus, a plot of the logarithm of the time versus crosslink density would be expected to give a straight line. This relationship was indeed observed with the highest concentrations of peroxide giving the fastest and tightest

TABLE II
Unsaturations Remaining After Cure of 93%
1,2-Polybutadiene as Measured by Swelling and IR

Cure time at 175°C, min	Unsaturations remaining, %	
	by IR	by Swelling
0	100	—
0.5	61	70
1.0	50	56
1.5	39	41
2	35	41
3	31	37
4	26	32
5	24	25
7	23	31
10	21	27

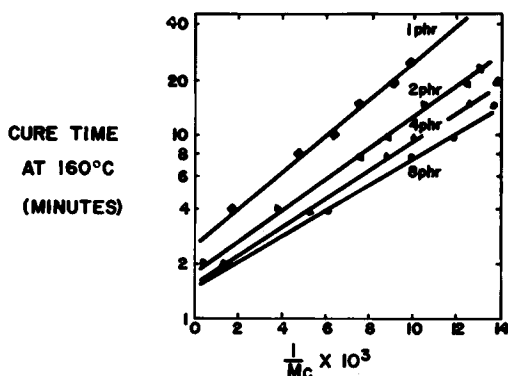


Fig. 4. Change in the reciprocal molecular weight between crosslinks with time at 160°C for a 93% 1,2-polybutadiene cured with 1, 2, 4, and 8 phr dicumyl peroxide.

curves. The influence of temperature can be seen by curing this same polymer with either 1 part (Fig. 5) or 6 parts (Fig. 6) of dicumyl peroxide at 15°C intervals from 130° to 175°C. Again straight lines are obtained in all cases with those containing the higher initiator level giving faster and more complete cures. The lines obtained at the different temperatures were essentially parallel at a given peroxide level. A plot of the extent of cure after utilization of one half of the dicumyl peroxide charged versus the temperature of cure is shown in Figure 7 for the data plotted in Figure 6. A similar plot using the data from the sample cured with 1 part of initiator is a straight line, which clearly shows that as the temperature of cure is increased, the number of crosslinks formed decreases. This can best be explained by the fact that as the temperature is increased, the steady-state concentration of free radicals is also increased. Since the primary modes of radical termination are disproportionation and coupling, there should be an increased tendency for the propagating crosslinks to encounter one another and terminate. Another way to increase the concentration of free radicals at any given time would be by increasing the concentration of

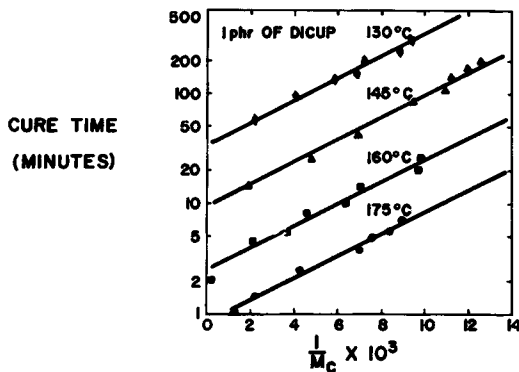


Fig. 5. Change in the reciprocal molecular weight between crosslinks with time for a 93% 1,2-polybutadiene cured with 1 phr dicumyl peroxide at 130°, 145°, 160°, and 175°C.

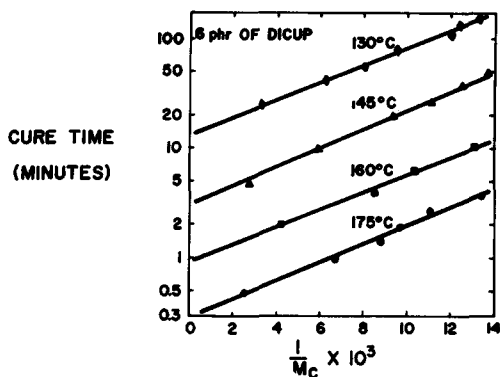


Fig. 6. Change in the reciprocal molecular weight between crosslinks with time for a 93% 1,2-polybutadiene cured with 6 phr dicumyl peroxide at 130°, 145°, 160°, and 175°C.

initiator. This did happen while trying to evaluate χ by Hummel's method, and as a result the expected retardation of the *CL* was indeed observed.

The influence of the molecular weight of the starting polymer on rate of cure was found to be very slight. Polymers number 1 to 4 in Table I were each cured with both 2 and 4 parts of peroxide at 145° and 175°C. When the four sets of data from each polymer were plotted in the usual manner of the logarithm of the cure time versus crosslink density, the plots were almost identical except for the zero crosslink density intercept. This time should represent the time needed, under those specific conditions, for the polymer to reach the gelation point and can be considered an induction time to gelation. A plot of this induction time versus the reciprocal of the intrinsic viscosity of the polymer is shown in Figure 8. The straight lines obtained show the expected trend, that is, the highest molecular weight sample requires the shortest induction time; and this time can be reduced by in-

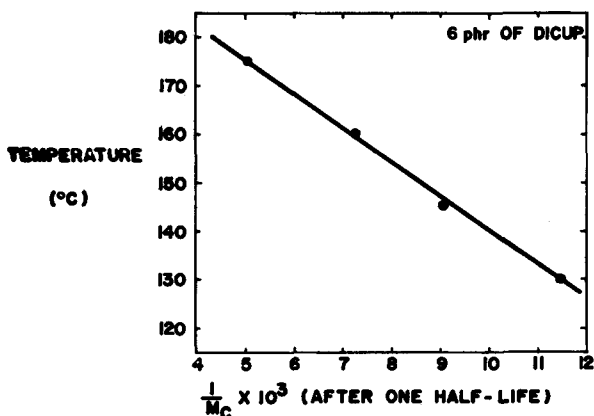


Fig. 7. Change in the reciprocal molecular weight between crosslinks with temperature after curing a 93% 1,2-polybutadiene with 6 phr dicumyl peroxide for one half-life.

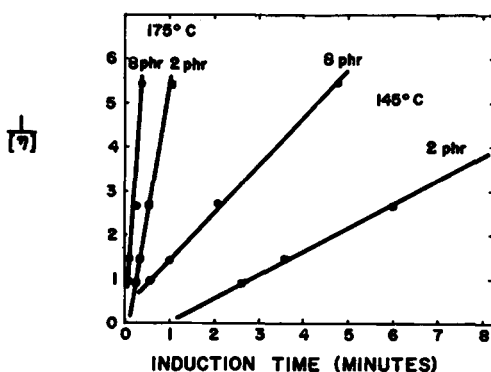


Fig. 8. Reciprocal intrinsic viscosity vs. induction time for 90% 1,2-polybutadienes cured at 145° and 175°C with 2 and 8 phr dicumyl peroxide.

creasing the catalyst concentration or the cure temperature. Except for this difference in radical utilization, all of the samples with about 90% vinyl content were observed to cure similarly, regardless of the molecular weight.

Another series studied was that of the development of crosslinks when the vinyl content of the polybutadienes was varied from 23% to 93%. These polymers, numbers 2, 5, 6, and 7 in Table I, were cured in an identical fashion as the previously mentioned molecular weight series. Straight lines were obtained in all 16 cases when the logarithm of the cure time was plotted against crosslink density. However, instead of obtaining parallel lines, as was previously observed, the results in Figure 9 were obtained. From this plot, it is apparent that the extent of crosslinking increases with time of cure in all cases, and increased crosslink densities are produced with those polybutadienes of high vinyl content. The data obtained with 8 parts of peroxide gave a similar trend; but, because of the high initiator levels, only small differences in slopes were observed with the change in the vinyl content.

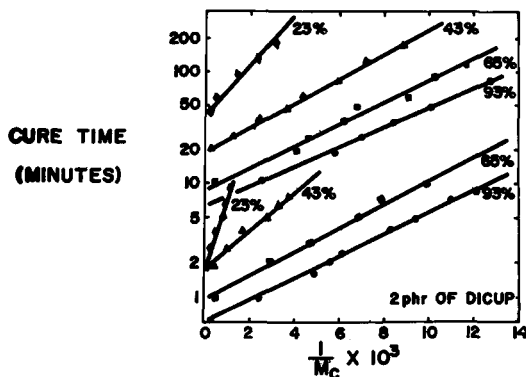


Fig. 9. Change in the reciprocal molecular weight between crosslinks with time for 23%, 43%, 65%, and 93% 1,2-polybutadienes cured with 2 phr dicumyl peroxide at 145° and 175°C.

TABLE III
 Microstructure of High-Vinyl Polybutadiene Cured
 With 8 Parts of Dicumyl Peroxide at 175°C

Cure time, min	Cis, %	Trans, %	1,2-Linkage, %
0	4.1	4.7	91.3
0.5	3.0	6.8	90.2
1	2.8	8.3	89.0
2	2.6	8.7	88.8
4	2.7	9.7	87.6
8	1.5	10.2	88.8

This observation must be attributed to a decrease in the radical chain length as the number of 1,4-double bonds is increased. The reason for this decrease can be attributed to either reduced reactivity of the mixture of cis and trans 1,4-linkages or to an increased rate of termination brought about by the presence of three more additional allylic hydrogens per 1,4-bond introduced.

If the difference in the reactivity of the 1,4-linkage was the cause of lowering *CL*, this could be easily followed by measuring the proportion of cis, trans, and 1,2-double bonds in the cured sample by means of ATR infrared spectra. The results of such a study are seen in Table III, where the final sample was shown to have only 15.7% of its initial unsaturation remaining, as measured by swelling. The loss of 2.5% of the vinyl unsaturation in completing the cure shows these double bonds to be only slightly more reactive than the remainder of the points of unsaturation. The cis bonds do appear to be considerably more reactive than the others; however, this loss could be brought about by isomerization to the trans structure,⁵ and an increase in reactivity of this structure should only cause an enhancement of the rate of crosslink formation. Thus, it appears that the primary cause of the loss of crosslinks with increasing content of the 1,4-isomers was due mainly to the increased number of allylic hydrogens available for abstraction.

The actual measure of the chain length may be easily accomplished by dividing the crosslink density obtained from the Flory-Rehner equation by two times the number of moles of peroxide that has been decomposed. The average values of the *CL* was measured from the cure of polymer 2 of Table I for a variety of peroxide levels and cure temperatures. The change in *CL* with curing condition can be seen in Table IV.

As can be seen from this table, the average chain length of the crosslinking reaction can be quite high with this polymer at low temperatures and low peroxide levels. However, as the temperature or the initiator level was increased, the average chain length decreased markedly. This again is in agreement with the previous prediction that the increased radical concentration causes an increase in the rate of radical selftermination.

Although an average chain length was calculated in the above case, a point-by-point variation of this value with changes in molecular weight

TABLE IV
Chain Lengths for Cure of 93% 1,2-Polybutadiene

Dicup parts	Temp., °C	CL
1	130	185
1	145	184
1	160	124
1	175	103
6	130	84
6	145	66
6	160	60
6	175	57
2	160	93
4	160	61
8	160	57

also is of interest. Figure 10 shows the changes in *CL* with cure time of four different molecular weight polymers. For the same conditions, the highest molecular weight sample was found to have the highest *CL*, which would then decrease asymptotically to the same value independent of initial molecular weight. After 43 min of cure time at 145°C, all of the polymers were at the same *CL* value. The *CL* of the sample of lowest molecular weight increased to a maximum at a 43-min cure time and then decreased in the same manner as the other samples. The initial chain lengths obtained with these polymers can best be attributed to the number of double bonds that must be consumed to obtain gelation. All of these curves must originate at a *CL* of zero at zero time, and then increase rapidly to a maximum value, which was before 10 min for the three highest molecular weight polymers. Thus, a reduction in the initially measured chain length will be observed by increasing the number of double bonds that must be consumed before gelation occurs. The asymptotic decay of these curves probably reflects the reduced availability of unsaturation in these highly crosslinked systems

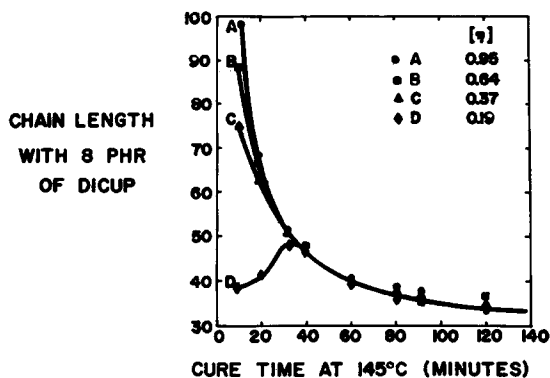


Fig. 10. Variation of chain length with time during the cure of 90% 1,2-polybutadienes with intrinsic viscosities of 0.95, 0.64, 0.37, and 0.19 at 145°C with 8 phr dicumyl peroxide.

with prolonged cure. This can be best seen by the fact that as the number of crosslinks increase, the probability increases that a growing crosslink will not be able to add another neighboring double bond and thus only leave a termination route available.

Applying the average chain length calculations to those polymers that were cured with varying 1,2-content gave the data in Table V. Here again, an increase in *CL* was accomplished by lowering the temperature. A drastic lowering of the chain length was observed with these polymers with increasing content of 1,4-butadiene linkages. This lowering can best be attributed to the increased number of allylic hydrogens in the low-vinyl polymer, giving more sites for hydrogen abstraction that would deactivate the growing chains.

TABLE V
Influence of Vinyl Content of Polybutadiene on *CL*

Temp. °C	Dicup, pts	% Vinyl	<i>CL</i>
145	2	93	132
		65	95
		43.2	41
		23.4	11
175	2	93	77
		65	53
		43.2	19
		23.4	6

Thus, in conclusion, it has been shown that the Flory-Rehner equation is indeed valid down to a 63 *M_c*. This type of a highly crosslinked network was obtained by a radical-chain process in which up to 185 double bonds were consumed per radical formed. This chain length was found to decrease with increasing cure time, temperature, and peroxide concentration. A decrease in the molecular weight of the polymer or in the vinyl content was also found to decrease this chain length.

References

1. L. D. Loan, *Rubber Chem. Technol.*, **40**, 149 (1967).
2. L. D. Loan, *J. Appl. Polym. Sci.*, **7**, 2259 (1963).
3. G. Kraus, *J. Appl. Polym. Sci.*, **7**, 1257 (1963).
4. K. Hummel and G. Kaiser, *Kaut. Gummi*, **16**, 426 (1963).
5. B. M. E. Van Der Hoff, *Ind. Eng. Chem., Prod. Res. Devel.*, **2**, 273 (1963).
6. I. Kuntz and A. Gerber, *J. Polym. Sci.*, **42**, 299 (1960).
7. W. L. Senn, Jr., *Anal. Chim. Acta*, **29**, 505 (1963).
8. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
9. P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
10. K. Hummel, *Rubber Chem. Technol.*, **37**, 894 (1964).
11. R. L. Scott and M. Magat, *J. Polym. Sci.*, **4**, 555 (1949).

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