

$$\alpha^5 - \alpha^3 = 2C_M\psi_1[1 - (\theta/T)]M^{1/2}$$

the thermodynamic parameters of poly(ethylene oxide) in this solution can be estimated. This is done in Figures 2 and 3 where the data for the temperature dependence of the intrinsic viscosity of polyisobutylene in benzene² are compared with that of poly(ethylene oxide) in potassium sulfate solution. An appropriate correction for the temperature dependence of the parameter, C_M , is applied by multiplying by the ratio of the constants K_T and K_θ , the constants of the intrinsic viscosity-molecular weight equation at the respective temperatures.

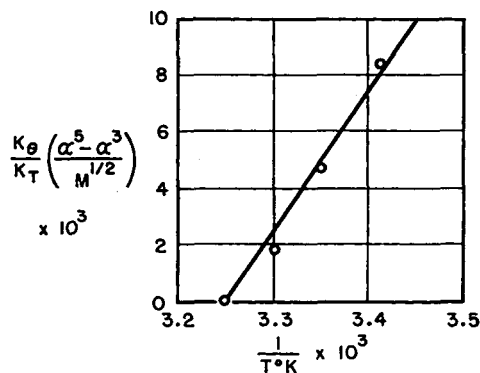


Fig. 2. Poly(ethylene oxide) in 0.45 M K_2SO_4 .

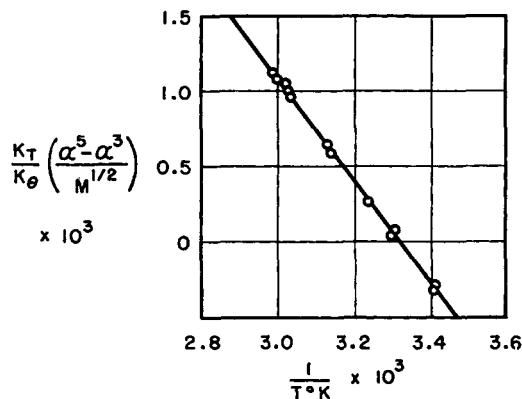


Fig. 3. Polyisobutylene in benzene.²

It is noted that the curves of Figures 2 and 3 have opposite slopes. The negative slope of the curve for polyisobutylene in benzene is the expected result for a polymer in a poor solvent in which both the heat of dilution and entropy of dilution are positive. The opposite slope of the curve for poly(ethylene oxide) in potassium sulfate solution is interpreted as the result of the heat of dilution and entropy of dilution in this case being negative. (The entropy and heat of dilution parameters can be calculated from the slope of the curve, Figure 2, since $2C_M\psi_1\theta = -49$ and $\theta = 208^\circ K$.)

The negative entropy of dilution and heat of dilution of poly(ethylene oxide) in aqueous solution implies a high degree of polymer-solvent interaction and doubtless the orientation of solvent with respect to the polymer chain. The existence of a lower consolute temperature in water solutions of higher poly(ethylene glycols) and the extensive measure-

ments of Malcolm and Rowlinson³ tend to confirm the view that negative entropies of dilution control the solution properties of poly(ethylene oxide) resins in water. The unusual pseudo-plastic character of fairly concentrated solutions of the higher molecular weight polymers in water⁴ may also be a result of the "entropy control" of the flow of these solutions.

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Effect of Carbon Black on TMTD Vulcanization*

It has been shown previously that it is possible to obtain an estimate of the amount of tetramethylthiuram disulfide (TMTD) required to produce one crosslink, and of the amount of firmly bound sulfur formed per crosslink, during the vulcanization of natural rubber by comparing stress-strain properties of gum rubber samples vulcanized with TMTD and with cumyl peroxide.¹ The earlier work led to values of 3.8 molecules of TMTD and 1.9 atoms of sulfur per crosslink in the presence of sufficient zinc oxide to obtain maximal crosslinking. By direct application of the absolute calibration of crosslink density by Moore and Watson,² Moore has subsequently arrived at values of 3.6 and 3.0, respectively, for these quantities.³ Partly on theoretical grounds, Bevilacqua⁴ has since concluded that in the reactions leading to crosslinking the expected values should be three of TMTD and two of sulfur. These values would also be expected on the basis of the mechanism discussed by Bielstein and Scheele.⁵

It is widely believed that there is chemical interaction of carbon black with rubber during vulcanization as well as during processing.⁶ The nature of this interaction has not been elucidated. If hydrocarbon radicals interact with black and the same radical intermediates are formed in TMTD vulcanization and in peroxide vulcanization, the effect of carbon black should be the same with each vulcanizing system. Alternatively, if there is no or negligible interaction between the black and the rubber during vulcanization, the superficial effect of carbon black should be identical in the two systems. In either event it should be possible to make the same sort of comparison which was previously re-

* This is contribution number 182 from these laboratories.

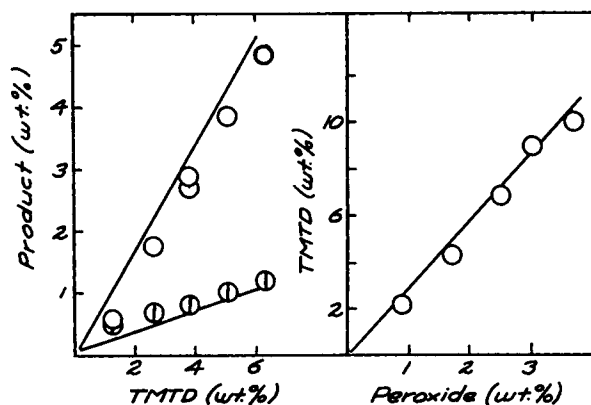


Fig. 1 (left). Zinc dithiocarbamate (upper curve) and combined sulfur formed, as a function of TMTD taken, in the presence of 40 parts of MPC black. Sulfur values multiplied by two for purposes of plotting. Solid lines in this and following figure have theoretical⁴ slope.

Fig. 2 (right). TMTD and cumyl peroxide (parts per hundred of rubber) imparting the same modulus at 100% strain) to MPC-loaded vulcanizates.

ported for gum vulcanizates; any gross discrepancy between the two vulcanizing systems may be expected to give information about hydrocarbon-black reactions. This report describes the results of such a comparison. Since no absolute calibration of methods for estimating crosslink density in vulcanized rubber containing carbon black has been achieved, the experiment described here is the most direct available approach.

For comparison of properties two series of samples were used. In the first, the samples contained pale crepe 100, MPC black 40, zinc oxide 8, zinc laurate 1, and variable amounts of TMTD. These samples were cured 24 hours at a nominal temperature of 108° in a platen press. This temperature was chosen because experience, since the experiment¹ previously reported, supports the suspicion then expressed that substantial amounts of TMTD may be wasted

in side reactions at temperatures as high as the 150°, which was the temperature used in that experiment. The second series of samples contained pale crepe 100, MPC 40, zinc oxide adjusted to keep the total inorganic material at 8 parts, and cumyl peroxide (as a dispersion on calcium carbonate) variable. These samples were cured 2 hours at 155° in a press. All ingredients used were stock samples of commercial materials.

Results of the experiment are given in Table I and Figures 1 through 3. In Figure 1 the firmly bound sulfur and zinc dithiocarbamate formed are plotted as a function of TMTD taken. Sulfur was determined after digestion with acid and extraction with butanone; dithiocarbamate by the method of Hilton and Newell.⁷ The lines drawn in the Figure 1 have theoretical slopes⁴ which correspond to yields of two moles of zinc dithiocarbamate⁸ and two gram-atoms of sulfur per three moles of TMTD taken. It is apparent that the yield of dithiocarbamate is uniformly slightly low and that of combined sulfur slightly high. This is attributed to direct reaction of a portion of the vulcanizing agent with carbon black. In Figure 2 the amounts of cumyl peroxide and of TMTD which give the same stress at 100% strain, interpolated from a plot of the raw data of Table I, are plotted against each other. The line is drawn with theoretical slope of three moles of TMTD equivalent to one of peroxide. In Figure 3 crosslink densities estimated from measurements of swelling in chloroform (ignoring corrections for finite molecular weight of the polymer used) are plotted against chemical crosslink densities estimated from the assumption that either one mole of peroxide² or three moles of TMTD⁴ will give one mole of crosslinks. The values for the TMTD samples are adjusted for the amount lost by direct reaction with black. For the comparison it is assumed in interpreting the swelling measurements that all volume changes occur in the rubber and that the carbon can be considered an inert diluent. In Figure 3 the solid line was obtained from gum vulcanizates cured with cumyl peroxide under conditions similar to those used for the samples containing carbon black. This curve has a slope about 85% of that of the calibration by Moore and Watson, in good agreement with their results since no correction was made to the data of Figure 3 for impurities in the peroxide or inhibitors in the crepe used.

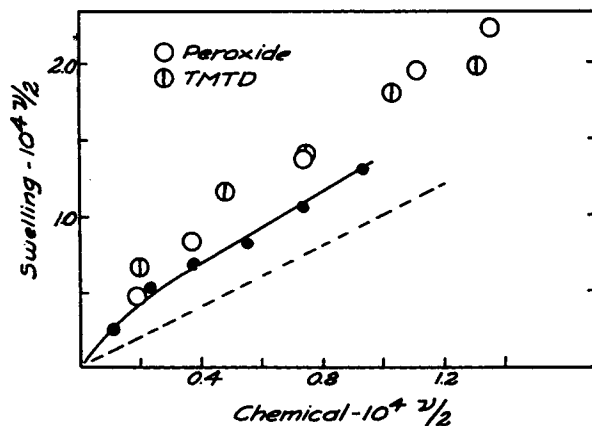


Fig. 3. Comparison of crosslink densities (in moles/gram) estimated from swelling and from crosslinking agent taken. Large circles: Samples containing carbon black. Solid line: Gum (peroxide) vulcanizates. The dotted line has a slope of one.

TABLE I
Modulus^a of Fully Cured Vulcanizates

TMTD ^b	100% stress	Peroxide,	100% stress
2	115	0.5	75
4	200	1.0	135
6	265	2.0	230
8	345	3.0	385
10	440	4.0	560

^a "Autographic" stress/strain, stress in lb./in.²

^b Parts per hundred of pale crepe.

From these results it may be concluded that the MPC black used in these experiments does not obscure the comparison of vulcanizing efficiency between two distinct chemical systems and that its contribution to stress-strain and to swelling properties is not affected by the nature of the vulcanizing system. As a result, no information about poly-

mer-filler interaction can be obtained directly from the experiments. On the assumption that a small amount of TMTD is rendered ineffective by direct reaction with the carbon black, the yields of dithiocarbamate, of combined sulfur, and of crosslinks are substantially those expected on theoretical grounds.⁴

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The Preparation and Polymerization of Triallyl Phosphite

Permanent flame retardant compounds for application to cellulose are of considerable interest to the Government and to industry. From the application of inorganic compounds to cloth it was found that a combination of phosphorus and bromine conferred flame and glow resistance. To attain permanency it was necessary to use polymeric phosphates.¹ For example, triallyl phosphate was prepared, polymerized, partially brominated, and applied to cloth with good results.² Because of the high cost of triallyl phosphate, related compounds which might be easier and cheaper to prepare were investigated.³ In the course of this investigation, triallyl phosphite was prepared and was polymerized with di-*tert*-butyl peroxide. However, with benzoyl peroxide, triallyl phosphite readily underwent an oxidation-reduction reaction rather than polymerization.

Experimental

Triallyl Phosphite. Three hundred and seventy grams (6.4 moles) of allyl alcohol, 475 g. (6.1 moles) of pyridine, and 300 g. of toluene were placed in a 2-liter three-necked flask fitted with a thermometer, dropping funnel, and a Hershberg stirrer. The reaction mixture was cooled in an ice bath to 15°C. and then 275 g. (2.0 moles) of phosphorus trichloride in 100 g. of toluene was added through the dropping funnel over a period of 2 hours. The reaction mixture was stirred during the addition and for an additional half hour. The pyridine hydrochloride was filtered and

washed with two 150 ml. portions of toluene which were added to the filtrate. The total filtrate was washed with 1 liter of water, 500 ml. of 8% aqueous sodium carbonate, and finally 1 liter of water. The toluene solution was dried over sodium sulfate, filtered, and placed in a vacuum distillation apparatus. The toluene was removed by vacuum distillation up to 70°C. at 10 mm. reduced pressure. The residue was distilled at a reduced pressure of 0.5 mm. and a temperature of 58–60°C. Three hundred sixty-one grams of water white liquid corresponding to a 90% yield of triallyl phosphite was obtained. $N_D^{25} = 1.4572$. Anal.: Calc. for $C_9H_{15}O_3P$: P, 15.4. Found: P, 15.1.

Polymerization of Triallyl Phosphite. Two hundred grams of triallyl phosphite and 200 g. of β,β' -dichloroethyl ether were placed in a 2-liter, three-necked flask fitted with a Hershberg stirrer, thermometer, 5 ml. pipet, and an air condenser. The reaction mixture was heated to 150°C. by means of a Glasco mantle. The efflux time from the pipet was recorded and 5 ml. of di-*tert*-butyl peroxide was added. The temperature increased. The heat liberated by the reaction required intermittent replacement of the heating mantle with a wet cloth in order to maintain a temperature between 150–155°C. Viscosity measurements were made at frequent intervals until the efflux time from the pipet was four times the original value. The reaction mixture was then cooled in an ice bath to stop the polymerization and then poured, with stirring, into an equal volume of Solvasol No. 3. The polymer was washed four times with Solvasol. It had a taffy-like appearance. After drying *in vacuo* a yield of 130 g. (65% per cycle) was obtained.

Brominated Triallyl Phosphite Polymer. Triallyl phosphite polymer was brominated using a method analogous to that used for triallyl phosphate.^{2,4} One hundred thirty grams of triallyl phosphite polymer was dissolved in 800 ml. of 30–70 methyl alcohol–dichloroethylene solution in a 2-liter beaker fitted with a stirrer, a thermometer, and a dropping funnel. The solution was cooled in an ice bath to 10–15°C. and 68 g. of bromine was added over a period of 1 hour. When the addition of the bromine was completed, the solution was stirred for an additional half hour. The solution had an orange color. It was neutralized with 34 ml. of triethylamine. The color of the solution changed to light green-gray. The brominated polymer imparted good flame retardant properties to cloth but is of dubious value as a practical flame retardant due to its removal under laundering condition.

Reaction of Triallyl phosphite with Benzoyl Peroxide. Two hundred grams of triallyl phosphite and 200 g. of β,β' -dichloroethyl ether were placed in a 2-liter, three-necked flask, fitted with a Hershberg stirrer, thermometer, 5 ml. pipet, and an air condenser. The reaction mixture was heated to 100°C. by means of a Glasco mantle. The efflux time from the pipet was recorded and 3 g. of benzoyl peroxide added. The temperature rose to 110°C. but no increase in efflux time occurred in 1 hour. An additional 3 g. of benzoyl peroxide was added with similar results, i.e., a temperature rise but no polymerization. The infrared spectrum showed the presence of phosphate and benzoic anhydride as described below. (Spectra were taken in carbon tetrachloride solutions using a Perkin-Elmer Model 112 Spectrometer with sodium chloride optics.)

In another experiment 102 g. of doubly-distilled triallyl phosphite was placed in a two-necked flask equipped with an