

CROSS-LINKING OF COPOLYMERS FROM METHYL VINYL KETONE AND *n*-BUTYL ACRYLATE¹

BY W. COOPER AND E. CATTERALL

ABSTRACT

Copolymers of *n*-butyl acrylate and methyl vinyl ketone can be cross-linked by a combination of sulphur and zinc oxide; the reaction is associated with the methyl vinyl ketone units in the polymer chain. From studies on the copolymers and model compounds, it is suggested that adjacent pairs or groups of methyl vinyl ketone units in the polymer cyclize to give $\alpha\beta$ unsaturated ketone groups. These contain reactive hydrogen which is attacked by sulphur; disulphide or zinc mercaptide cross-links are then formed. Water is produced in the cyclization reaction and hydrolyzes some of the ester groups; additional cross-links are thus formed by reaction of the acid groups with zinc oxide. The ease of cyclization and, therefore, the extent of cross-linking is dependent on the method of preparing the copolymers, emulsion copolymers being much more reactive than those prepared in solution. A comparison has been made between the sulphur + zinc oxide system and other cross-linking agents which may be used for polyacrylates.

INTRODUCTION

The elastomeric polymers and copolymers of acrylic esters are of growing importance and have attracted much attention in recent years. Some of the lower polyalkyl acrylates are attractive rubbers of reasonable strength with good resistance to heat and oils. Polymers containing high proportions of *n*-butyl acrylate possess in addition good resistance to freezing and high resilience. They are, however, usually difficult to process and give products of low strength. Efforts to improve these features have been made by copolymerization with a more polar type of monomer, such as acrylonitrile, methyl isopropenyl ketone, and methyl vinyl ketone, though with some sacrifice of other desirable properties.

The copolymers of *n*-butyl acrylate with methyl vinyl ketone are of some interest in that they can be cross-linked by means of sulphur + zinc oxide in addition to the more usual cross-linking agents (11) (such as lead oxide, calcium hydroxide, or polyamines), and give products of good strength when reinforced by means of carbon black or finely divided silica (4).

A preliminary study of the reactions involved indicated that they were rather complex and this paper describes the attempts made to elucidate those of greater importance and, as a practical measure, to compare the sulphur + zinc oxide vulcanizates with those prepared with other cross-linking agents.

DISCUSSION

Polymer

Methyl vinyl ketone and *n*-butyl acrylate copolymerize readily, the polymers containing a higher proportion of methyl vinyl ketone than in the initial monomer. Determination of the composition of low conversion copolymers for

¹Manuscript received October 24, 1955.

Contribution from the Chemical Research Division, Dunlop Research Centre, Birmingham, England. This paper was read at the Sixth Canadian High Polymer Forum at St. Catharines, Ontario, April 14th, 1955.

monomer reactivity ratios proved to be difficult (see Appendix for details), and a completely satisfactory method has not been found. Reasonable agreement was found, however, between several methods of analysis, and values of $r_1 = 1.6 \pm 0.1$ and $r_2 = 0.65 \pm 0.07$ were obtained (MVK is monomer 1). The data are shown in the polymer composition curve (Fig. 1).

Integral and differential copolymer distribution diagrams (13) (Figs. 2a (i) and (ii) and 2b (i) and (ii)) show that, up to about 50% conversion, copolymers made with 20–35% by weight of methyl vinyl ketone (i.e. 30–50 mole %) have only a narrow distribution of polymer compositions. The copolymers were made by solution polymerization and in emulsion. Solution polymers were prepared in benzene solution at 70° using 0.5% benzoyl peroxide as catalyst and isolated by pouring into petroleum ether, or aqueous alcohol mixtures. They were normally of relatively low molecular weight ($[\eta] = 0.2\text{--}0.3$) and completely soluble in organic solvents. The emulsion copolymers were made at 50° using potassium persulphate (1% on monomers) as initiator. For copolymers of low methyl vinyl ketone content, the sodium salt of sulphated methyl oleate (4.2%) was used as the emulsifier, while for high ketone contents sodium lauryl sulphate (4%) was more suitable. The emulsion copolymers were

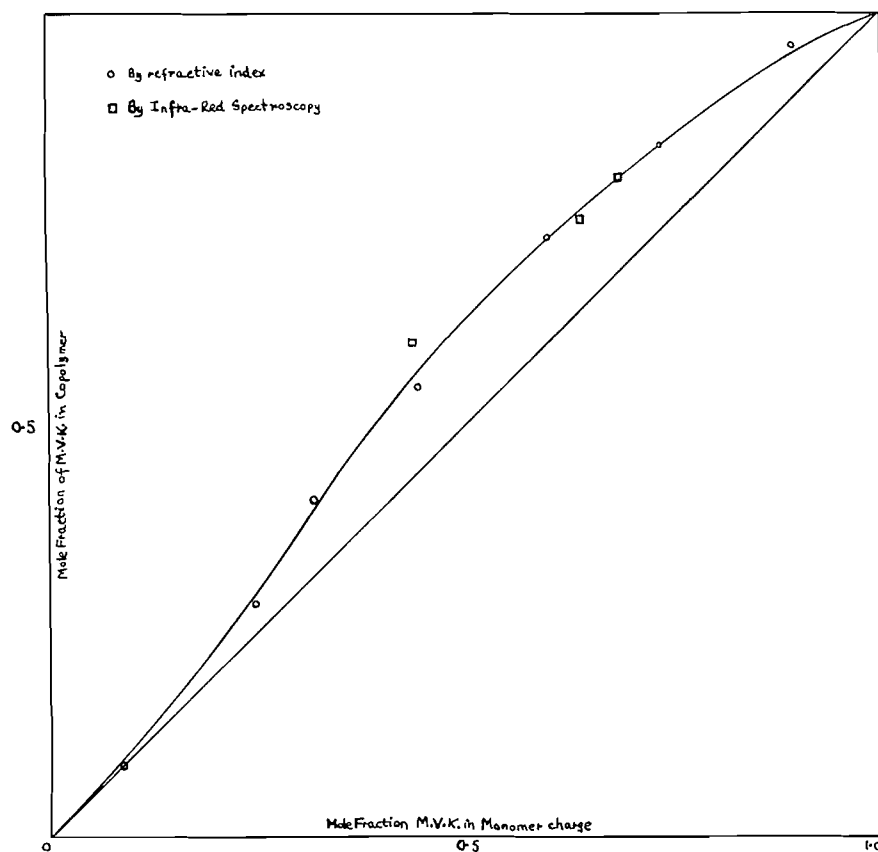


FIG. 1.

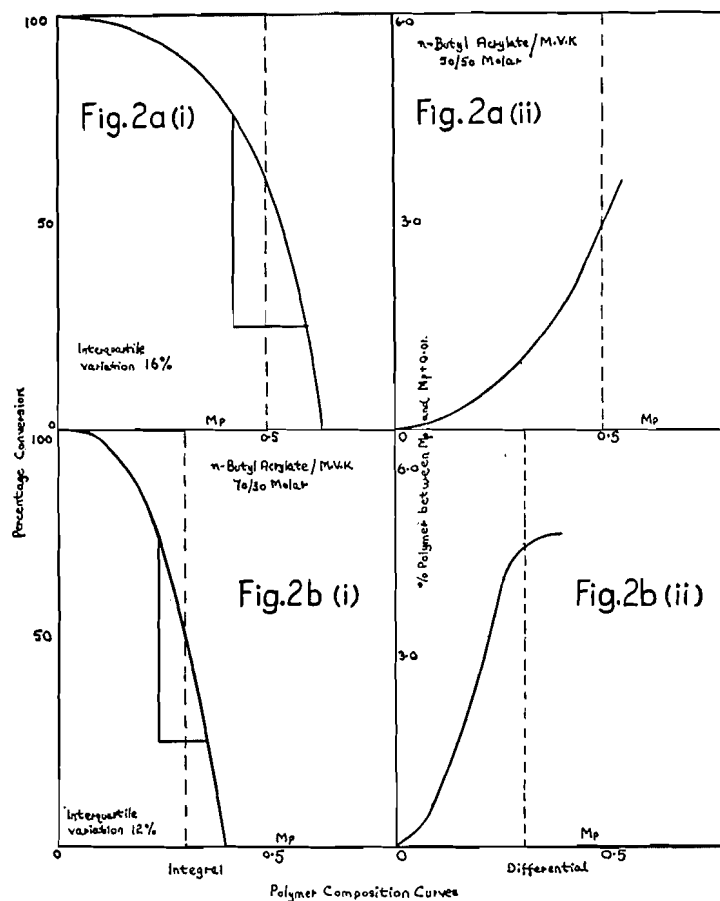


FIG. 2.

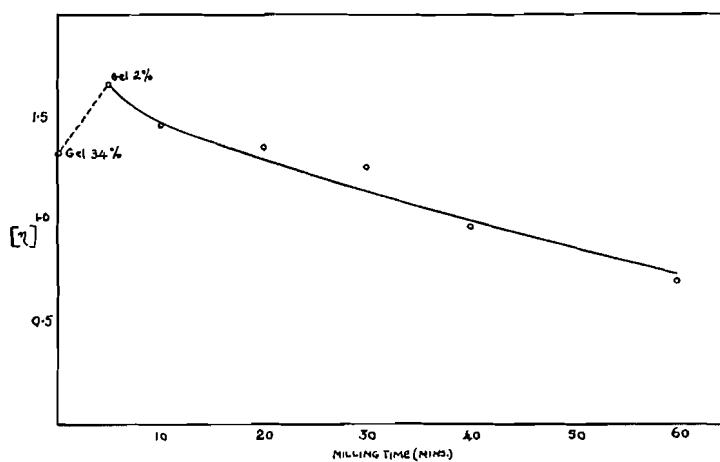


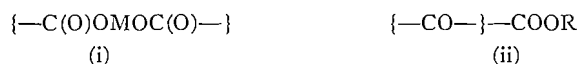
FIG. 3.

always gelled to a greater or lesser extent. This gel was broken down readily on milling, and, as with other acrylates (6), there was a steady fall in molecular weight with mastication (Fig. 3).

Cross-Linking Agents for Acrylate Copolymers

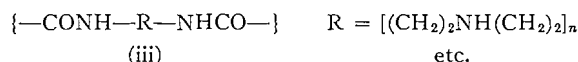
A variety of reagents have been used for cross-linking acrylate copolymers. Most of them attack the ester portions of the molecule and thus apply to all types, but some (e.g. hexamethylene tetramine (HMT) for copolymers with alkyl vinyl ketones) are more specific in their action. The more important substances used include the following:

(a) *Basic oxides and hydroxides* (e.g. lead oxide and calcium hydroxide) which form salt bridges between different chains (i). It has been suggested



that strong bases from monovalent metals (e.g. KOH) may form cross-links by an acetoacetic ester type condensation (ii) (12). This has not been proved, however, and will be discussed later.

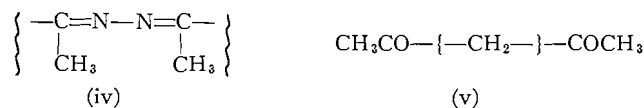
(b) *Polyamines*.—These presumably form amide bridges between the polymer chains (iii). Substances such as tetraethylenepentamine (TEP) and triethyl trimethylene triamine (Trimene Base) are the most commonly used.



(c) *Peroxides*.—Peroxides are used occasionally to effect cross-linking of polyacrylates. Abstraction of hydrogen atoms (probably skeletal hydrogen atoms adjacent to the carbonyl group) followed by dimerization of the radicals so formed is probably their mode of action. They are generally not very useful materials and tend to cause blowing.

(d) *Sulphur + zinc oxide*.—Pure polyacrylates will not cross-link with these reagents. The possession of halogen atoms, by incorporation, for example, of chloroethyl vinyl ether, or the presence of ketone groups renders them effective. This reaction is discussed in detail below.

(e) *Miscellaneous compounds*.—These include, for ketone copolymers, hydrazine (used as its organic salts in the presence of a base) which forms intermolecular azines (iv), hexamethylene tetramine + organic acids or para-formaldehyde which form interchain methylene bridges (v), trinitrobenzene + zinc oxide, and quinone dioxime + lead oxide. The mechanism by which the latter compounds react is not known.



Cross-linking by Sulphur + Zinc Oxide

Examination of vulcanizates from *n*-butyl acrylate and MVK quickly leads to the conclusion that rapid reaction occurs with sulphur and that concomitant

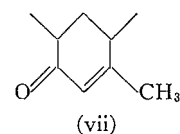
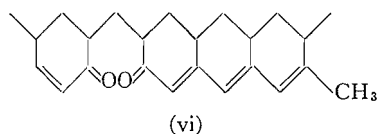
reactions associated with the polymer structure also occur. These latter reactions manifest themselves in greatly reduced heat-aging resistance of the copolymers. It is convenient, therefore, to discuss first the changes which occur on heating the copolymers alone.

(i) *Cyclization of MVK Polymers*

A feature of all compounded emulsion copolymers examined was a continuous and relatively large weight loss when heated above 100° C., accompanied by reduced swelling in a solvent such as benzene. This seemed to be in accordance with the view that the weight loss resulted from intermolecular condensation with consequent cross-linking and reduced swelling volume, until it was observed that weight loss – swelling volume measurements did not agree with estimates of cross-linking as judged from physical tests on cured slabs. This became further apparent when it was found that the pure gum copolymers themselves gave comparable weight loss and swelling volume curves but gave no sign of possessing a truly vulcanized structure. Furthermore, soluble copolymers (prepared by bulk or solution polymerization) when heated in the absence of air also lost weight. They became hard and resinous but, since they were completely soluble in methyl ethyl ketone and were thermoplastic, they were not cross-linked.

As a result of these observations, experiments were made on a solution copolymer containing 50–60% of MVK. (Initial monomer composition equimolar; for copolymer distribution curve see Fig. 2*a*.) On heating for 93 hr. at 160° C. in a sealed evacuated vessel, 5.1% of butanol and 4.0% of water were liberated. The polymer was transformed from a soft rubber to a hard resin, had a deep red-brown color, and was soluble in chloroform or methyl ethyl ketone. Titration showed the presence of 3.2% acid groups (calculated as acrylic acid).

Marvel and Levesque (10) studied the change in polymethyl vinyl ketone when heated at 270–360° C., and deduced the formation of polycyclic structures of the type (vi).



Infrared spectroscopic examination of the heated copolymer showed changes which were quite consistent with this type of structure (Fig. 4). Reduction of the intensities of the normal ketone absorption frequency and other associated bands was accompanied by new frequencies characteristic of $\alpha\beta$ unsaturated ketones; the ester carbonyl group remained essentially unchanged. It is clear therefore that reactions of the type described by Marvel occur quite rapidly at temperatures as low as 140°–160° C.² Calculation of the extent of this reaction by use of Wall's statistical theory for the isolation of carbonyl groups (15) in the copolymer shows that 6.1% of water would be eliminated;

²The ultraviolet spectra of the copolymers were rather featureless, but an appreciable increase in absorption intensity, particularly at higher frequencies, occurred after only 30 min. at 140° C.

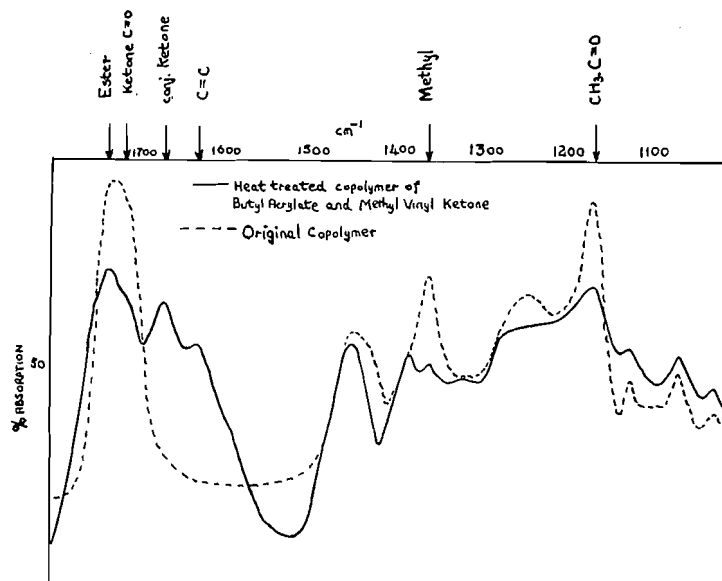


FIG. 4.

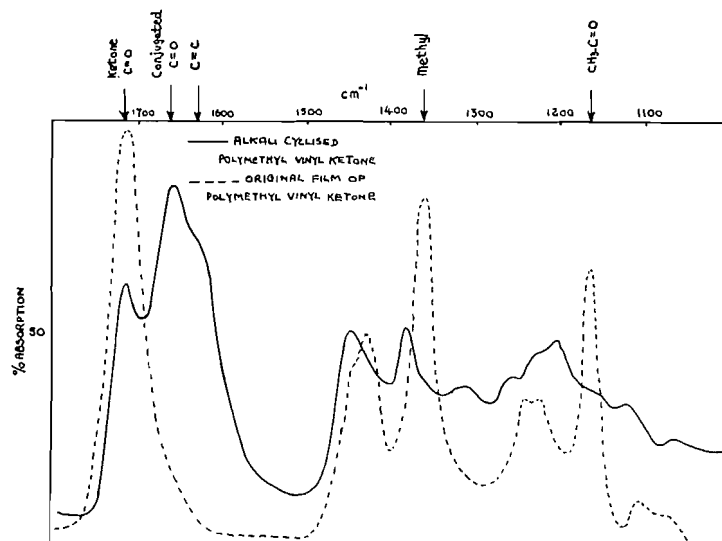


FIG. 5.

about two thirds of the residual carbonyl groups would be conjugated with ethylenic bonds. On the assumption that the monomer units were randomly distributed in the copolymer the experimental data show the reaction to have gone to about 80–85% completion.³ This estimate is in agreement with the intensity changes of bands in the infrared spectrum of the copolymer corresponding to carbonyl and methyl groups.

³The r_1, r_2 product for this system is not greatly different from unity; it follows that errors brought about by this assumption will not be great.

This condensation proceeds very slowly at temperatures below 100° C., but it has been found that polymethyl vinyl ketone and its copolymers rapidly give polyunsaturated ketones at room temperature on treatment with alkali. (Polymethyl vinyl ketone is transformed in a few seconds from a tough thermoplastic resin softening at about 50° C. to a hard brittle resin softening at 260–270° C. (5).) Under these conditions not a great deal of multiple ring closure occurs and mono-ring structures predominate (vii) (the infrared spectrum of the alkali cyclized polymer is shown in Fig. 5) and, as insoluble polymers are easily obtained, it is possible for some intermolecular condensation also to occur. It is obvious then that polymers containing methyl vinyl ketone can undergo rapid condensation reactions at room temperature in the presence of alkalies, or alone at vulcanization or heat aging temperatures. A further consequence of the cyclization reaction is the formation of carboxyl groups by hydrolysis of ester groups. In the presence of metallic oxides or hydroxides, this will result in many cross-links being formed.

The combined effect of these reactions undoubtedly results in continued cross-linking on heating and thus poor heat aging resistance. Confirmation of these views is found in the large amount of butanol liberated on heating a copolymer with lead oxide compared with that from pure poly *n*-butyl acrylate under the same conditions (Table I).

TABLE I

Polymer*	% Butanol	% Water	% Swelling volume in benzene
100% Butyl acrylate	1.27	0.08	1050
70 BA/30 MVK	7.44	0.66	150

*Heated at 140° C. in vacuo for 10 hr.

(ii) *Reaction of Sulphur with Acrylate-MVK Copolymers*

Hydrogen sulphide is evolved when a polymer containing methyl vinyl ketone is heated with sulphur, and some sulphur becomes combined with the polymer. Zinc oxide when present reacts with the hydrogen sulphide to give zinc sulphide. The amounts of sulphur combined and that liberated as hydrogen sulphide have been determined and the results are shown in Table II. It was found that approximately twice the amount of sulphur remained combined

TABLE II

Polymer	Curing system	% Swelling* volume	% Eliminated		% Sulphur			
			H ₂ O	<i>n</i> -BuOH	Init.	H ₂ S	Com- bined	Free
100 BA†	2% S, 10% ZnO	Dissolved	0.01	0.35	2.00	—	—	2.00
70 BA/30 MVK	2% S, 10% ZnO	760	1.08	1.28	1.98	0.57	0.87†	Neg.
	4% S	2210	0.71	0.45	3.97	0.44	0.94‡	2.40

*Benzene.

†BA = *n*-butyl acrylate.

‡Some sulphur was also present in odorous low molecular weight material extractable by benzene.

with the copolymer compared with that liberated as hydrogen sulphide, and that the reaction was substantially complete in about one hour; little hydrogen sulphide was liberated after this period.

As would be expected the amount of hydrogen sulphide evolved depended on the amount of MVK in the copolymer. This was determined for a number of high and low conversion copolymers and the results are summarized in Fig. 6.

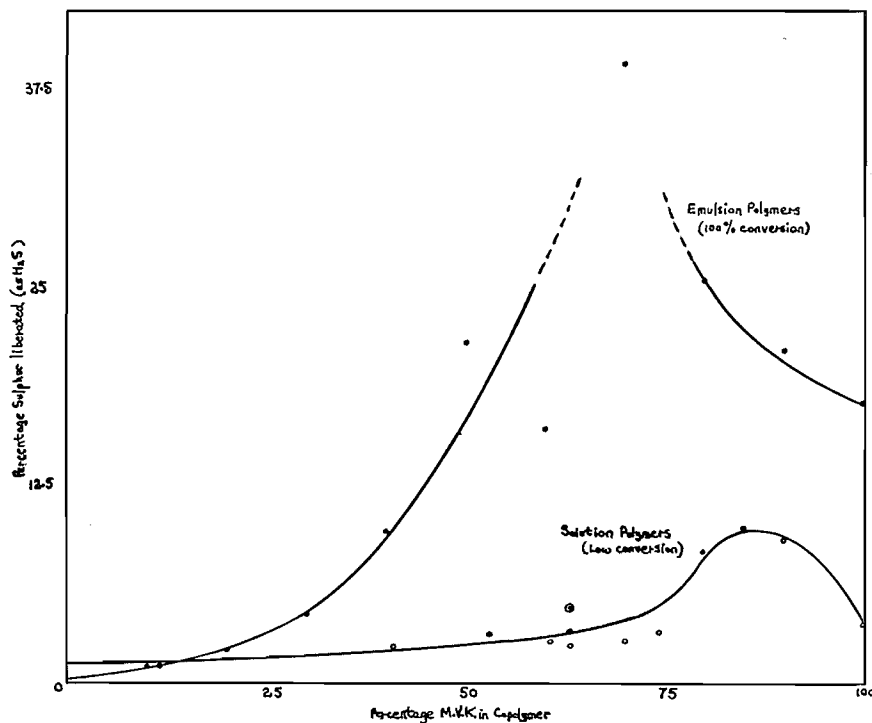


FIG. 6.

Two features are at once apparent, firstly that emulsion copolymers liberate much more hydrogen sulphide than those prepared in solution, and secondly that there is a maximum in the curve relating the amount of hydrogen sulphide liberated to the MVK content of the copolymer. With regard to the differences between emulsion and solution copolymers, it seemed possible that these may have arisen because of the different methods employed in incorporating the sulphur into the copolymers; in the case of emulsion polymers it was mixed on the mill while with solution polymers sulphur and polymer were dissolved in benzene and the solvent removed under vacuum. To test this point two 50/50 w/w copolymers were made, one in emulsion, the other in solution; both were taken to about 60% conversion. Sulphur (4%) was incorporated into both by milling and by use of a solvent. The hydrogen sulphide liberated on heating is given in Table III, together with the yields of volatiles liberated on heating the polymers alone at 150° C. It is apparent that a more intimate mixture of

TABLE III

Copolymer	% S liberated as H ₂ S*		Volatiles liberated on heating†	
	(a) Milled	(b) In solution	% H ₂ O	% Butanol
Emulsion	0.21	0.54	2.5	0.7
Solution	0.02	0.04	ca. 0.05	ca. 0.05

*Heating at 150° C. for three hours.

†At 150° C. for eight hours.

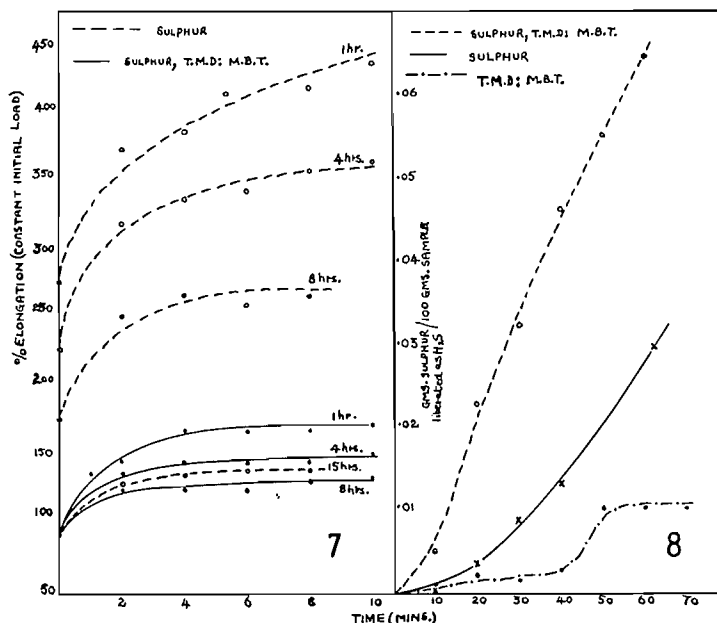
polymer and sulphur is obtained by the solution technique and that under both conditions the emulsion copolymer liberates much more hydrogen sulphide. This is accompanied by the ready loss of water, undoubtedly from cyclization, on heating. (Evidence to support the view that cyclization to give an $\alpha\beta$ unsaturated ketone is a prerequisite for attack by sulphur is presented below.) The reason for the susceptibility of emulsion copolymers to this reaction is not fully understood since spectroscopic examination of the unheated emulsion copolymer shows no evidence of prior cyclization. It follows that either the emulsion copolymers have different compositions (MVK is a water miscible monomer) or traces of reagents from the emulsion system accelerate the cyclization. The latter is the more probable, as no evidence of heterogeneity was observed on fractionating an emulsion copolymer from the latex. Furthermore the refractive indices of emulsion copolymers containing 70% or more of butyl acrylate were the same as those of the corresponding solution copolymers. Mixtures of the two homopolymers were not homogeneous and gave refractive index values substantially the same as polybutyl acrylate, irrespective of composition.

The explanation for the maxima in the curves relating the hydrogen sulphide liberated vs. polymer composition is even less obvious. The most probable cause is a reduction in solubility of sulphur in the higher ketone copolymers, particularly after some cyclization has occurred. It is also possible that a change occurs in the ratio of sulphur eliminated as hydrogen sulphide to that which combines with polymer.

That the attack of sulphur on the copolymers is a free radical reaction is shown by the fact that the rate of liberation of hydrogen sulphide is increased by the addition of the conventional rubber accelerators (MBT, TMD) as shown in Fig. 8. A study of the change in modulus of the polymer with heating time (Fig. 7) shows clearly the influence of accelerator on the rate of cure.

In these systems zinc oxide has the effect of taking up hydrogen sulphide, which causes blowing and some reversion by reducing disulphide cross-links, reacts with acid groups formed by hydrolysis of the ester (separate experiments on the pure polyacrylates showed zinc oxide alone to have a negligible cross-linking effect), and forms mercaptide cross-links by the reaction with thiol groups along the polymer chain.

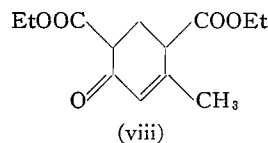
The above experiments show conclusively that sulphur reacts with MVK polymers and copolymers, and that cyclization with loss of water also occurs. The latter can be a major reaction and its effect, particularly in the presence of metallic oxides, can completely mask the influence of the sulphur.



FIGS. 7 AND 8.

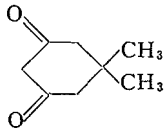
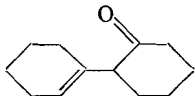
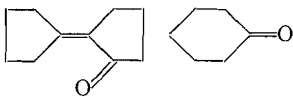
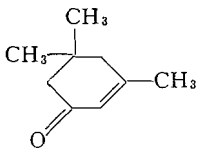
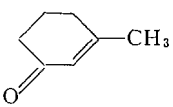
(iii) Mechanism of Sulphur-Copolymer Reaction

In order to decide the nature of the reaction a number of model compounds were heated with sulphur at 150° C. and the hydrogen sulphide evolution observed. The results are summarized in Table IV and show that the reaction of sulphur with ketones is not a general reaction. Stable aliphatic ketones do not react at the temperatures used in vulcanization of the copolymers, and it is interesting to note that those saturated ketones which do react possess two carbonyl groups in close proximity (e.g. acetyl acetone, dimethyl dihydroresorcinol), or can undergo condensation to give an unsaturated ketone. Thus cyclohexanone gives 2-(cyclohex-1'-enyl) cyclohexanone, 1,3-diacetyl diethyl glutarate can give 4,6-dicarboethoxy-3-methyl cyclohex-2-enone (viii), and, as already discussed, polymethyl vinyl ketone gives a cyclized polymer (v) on heating.



It appears that not all unsaturated ketones liberate hydrogen sulphide under these conditions, as shown by the cases of mesityl oxide and its higher homologue 5-methyl-4-hexen-3-one, which differ from the other unsaturated ketones examined in that they do not possess a secondary or tertiary hydrogen atom adjacent to the double bond. It follows from the behavior of 5-methyl-4-

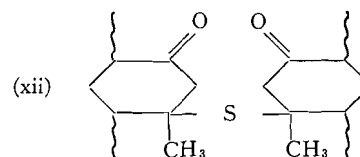
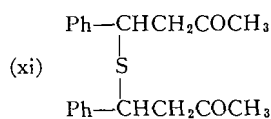
TABLE IV*

Hydrogen sulphide not liberated	Hydrogen sulphide liberated	
CH_3COCH_3	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	++++
$\text{CH}_3\text{COCH}(\text{CH}_3)_2$		+++
$\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}_3$	+
$\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$(\text{CH}_3\text{COCH}(\text{COOEt}))_2\text{CH}_2$	+
$\text{CH}_3\text{CO}(\text{CH}_2)_3\text{COOC}_4\text{H}_9$		++
$\text{CH}_3\text{COCH}=\text{C}(\text{CH}_3)_2$	$\text{—CH—CH}_2\text{—CH—}$ COCH_3 COCH_3	+++
$\text{CH}_3\text{CH}_2\text{COCH}=\text{C}(\text{CH}_3)_2$		+++
	 	++

*The ketones were heated at 150°C . for periods of 10–20 hr. In the case of those which liberated H_2S the speed of reaction is indicated by the + signs.

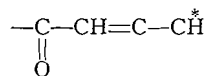
hexen-3-one, as with the saturated ketones, that the possession of a secondary hydrogen atom adjacent to the carbonyl group does not lead to the formation of hydrogen sulphide (unless of course it is instantly removed by rapid addition to the double bond—an unlikely possibility⁴).

⁴Hydrogen sulphide reacts readily with $\alpha\beta$ unsaturated ketones. Benzal acetone for example gives (xi) (2), and a comparable reaction with cyclized MVK would form (xii). This type of



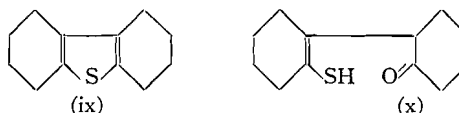
reaction seems sterically improbable however, in view of the ring structure elements and, of course, the ready evolution of hydrogen sulphide in the reaction is evidence against it.

It seems therefore that the following structure grouping is necessary, ab-



straction of hydrogen by sulphur occurring at the point marked by an asterisk.

The behavior of 2(cyclohex-1'-enyl) cyclohexanone is apparently anomalous, but it must be remembered that in this case the $\beta\gamma$ system is more than usually reactive.⁵ This compound when heated with sulphur forms 1,2,3,4,6,7,8,9-octahydrodibenzothiophen (ix), in good yield (3). The formation of this compound, however, is not directly relevant to the reaction in question. It can be



obtained directly from 2(cyclohex-1'-enyl) cyclohexanone (3) by addition of sulphur and loss of water, without any necessity of explaining the ready formation of hydrogen sulphide. A possible intermediate in the formation of (ix)

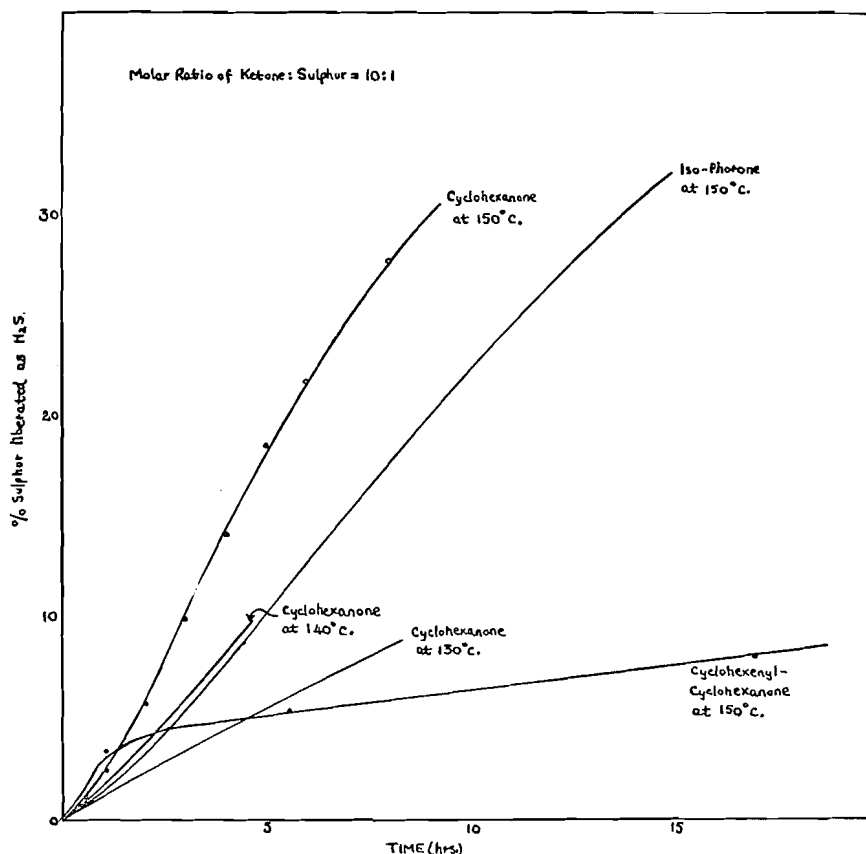
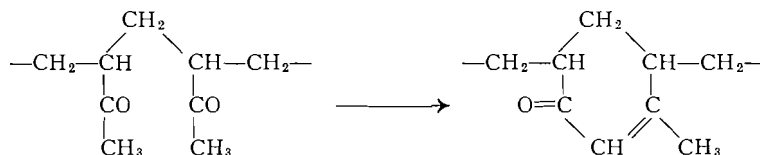


FIG. 9.

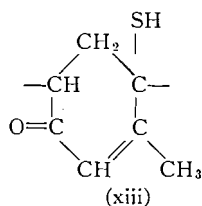
⁵This is apparent from its formation from cyclohexanone on heating instead of 2-cyclohexylidene cyclohexanone.

would be the thiol (x). Hydrogen sulphide, on the other hand, would be liberated after attack on the hydrogen atoms alpha to the double bond (positions 2', 6', or 1) giving complex sulphides (7). It is probable that such reactions may also occur since hydrogen sulphide is evolved continuously on heating (see Fig. 9) but in smaller amounts than from cyclohexanone.

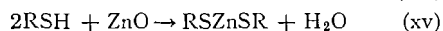
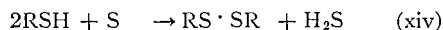
The following mechanism, which is supported by the above evidence, is that, initially, cyclization occurs between adjacent pairs or groups of MVK units.



The unsaturated structures are attacked by sulphur to give structure elements (xiii).



Oxidation of some of the thiol groups by sulphur could then occur with the formation of disulphide bridges and the liberation of hydrogen sulphide (xiv), while others would react with zinc oxide to form mercaptide cross-links (xv).



It is possible that this latter reaction is of some consequence in view of the necessity of using a combination of the zinc oxide and sulphur, which separately possess only weak cross-linking action under normal cure times and temperatures. The influence of the accelerator is presumably activation of the sulphur by opening the S₈ ring (8). The fact that, ultimately, vulcanizates of comparable state are obtained with or without accelerator, and that there is then no free sulphur available, supports this view.

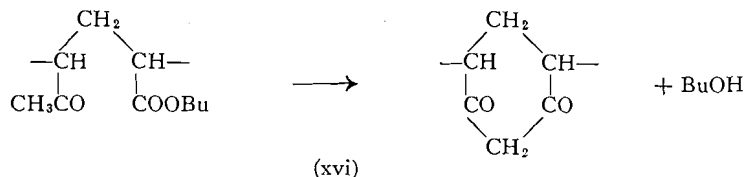
It may be concluded that the effect of the ketone monomer is only to provide, by condensation, unsaturated groups which can then react with sulphur.

(iv) Other Reactions

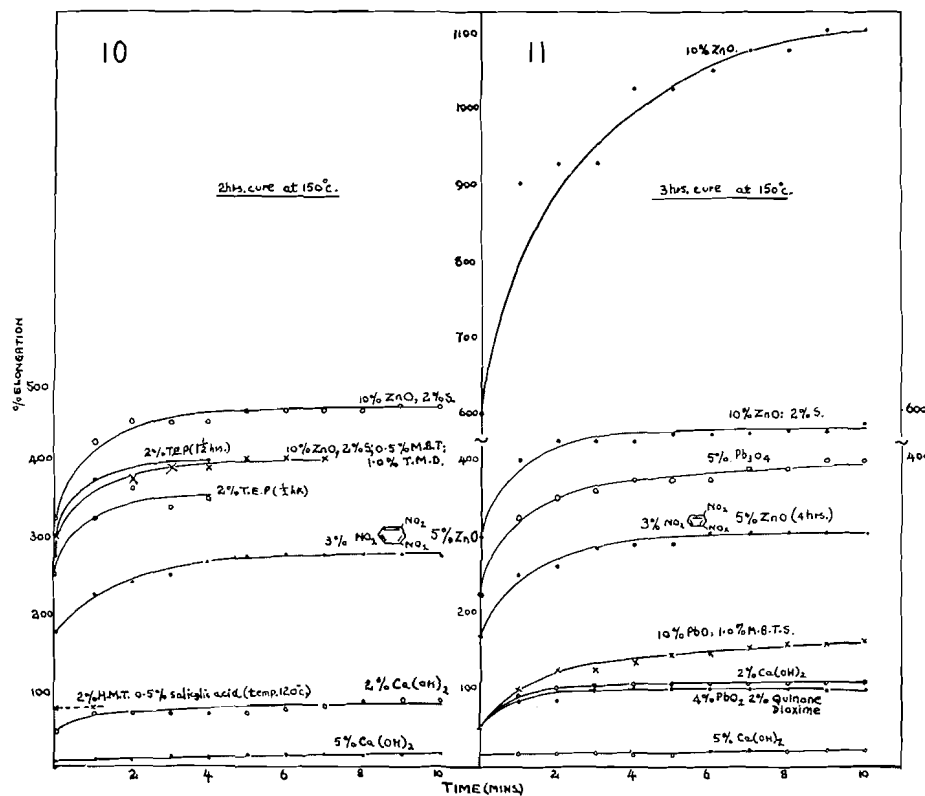
Semegen and Wakelin (12) in a study of the cross-linking of polyethyl acrylate suggest an acetoacetic ester mechanism for the reaction. The conditions they used, high temperatures (300° C.) and the presence of strong bases, are not comparable with those used in this work and it must be noted that alcohol is produced by thermal cracking of polyacrylates themselves. (The depolymerization of thermally unstable methacrylates cannot be regarded as supporting their theory.) It should be pointed out, however, that

as yet no alternative mechanism has been suggested for the cross-linking of polyacrylates by bases such as potassium hydroxide.

In view of this it is therefore desirable to consider the possibility of a reaction of the following type (xvi) occurring.



The model compound *n*-butyl 5-ketohexanoate was synthesized. Heating it alone or with sulphur at 150° C. produced no significant change, from which it may be inferred that there is no enhanced reactivity in the copolymer between adjacent MVK-acrylate units. On the other hand, heating with lead oxide at this temperature gave a fairly rapid reaction with liberation of butanol and the formation of a sticky solid soluble in chloroform, which proved to be mainly the lead salt of 5-ketohexanoic acid. No evidence was found for dimethyl dihydroresorcinol, and it must be concluded that this reaction does not take place at vulcanization temperatures. A point of interest was the speed of hydrolysis by lead oxide.



FIGS. 10 AND 11.

Comparison with Other Cross-linking Systems

It was thought desirable to compare the effect of the sulphur + zinc oxide system with some of the other compounds which may be used to cross-link polyacrylates.

Compounded samples were heated for various times and subsequently extended under constant initial load per unit area, and the elongation (instantaneous and after various periods of time) measured. A full program, varying the conditions of cure and using a combination of several curing agents, would be necessary to obtain the optimum properties in the vulcanizates. However, the results obtained show the general order of activity of the reagents used (Figs. 10 and 11).

It was found that calcium hydroxide and lead dioxide + quinone dioxime gave the fastest cures, but that the sulphur + zinc oxide combination gave the best formed vulcanizates. The latter were comparable to those obtained using polyamines, but had a lesser tendency to reversion on heating. Paraformaldehyde and HMT gave very rapid cures, the polymers not then altering on further heating. Paraformaldehyde gave highly blown products and is thus of little value, but HMT would appear to be suitable as a fugitive curing agent. In the case of most of the other systems, particularly those containing lead oxides, the hardening on heating is progressive, as shown by the data in Table V.

TABLE V

System	Elongation, %	
	1 hr. (at 150° C.)	7 hr.
Accelerated S, ZnO	450	310
Pb ₃ O ₄	400	200
PbO ₂ + QD	175	45
PbO	200	35
Ca(OH) ₂	80	—
HMT	85*	65
TEP	350†	400†

* $\frac{1}{2}$ hr.† $1\frac{1}{2}$ hr.

CONCLUSIONS

The effect of methyl vinyl ketone in promoting the cross-linking of its copolymers with *n*-butyl acrylate by alkaline reagents or by sulphur + zinc oxide appears to depend initially on the cyclization of adjacent ketone monomer units. These furnish water which, particularly in the presence of metallic oxides, enables hydrolysis to occur and thus form a three-dimensional network with metal salt bridges. In the presence of sulphur, attack occurs on the unsaturated ketone formed by the cyclization reaction with the formation of disulphide cross-linkages and zinc mercaptide cross-links. Zinc oxide also takes up the hydrogen sulphide formed in the reaction but has in itself only a weak cross-linking action. There is no evidence to support the view that direct attack occurs on the skeletal hydrogen atom adjacent to the carbonyl group.

No reaction occurs between sulphur and the ester part of the molecule, and nothing to suggest acetoacetic ester condensation reaction has been observed. Emulsion copolymers have been found to be much more readily cyclized than copolymers prepared in solution, probably because of the presence of traces of alkali. This influences both the ease with which they are cross-linked and the aging resistance of the copolymers.

APPENDIX

Analysis of MVK-Acrylate Copolymers

As stated in the text the satisfactory analysis of these copolymers proved to be a task of some difficulty. Several methods were tried with the following results:

1. *Hydrolysis*.—A solution of the copolymer in dioxan, aqueous alcohol, or dioxan-benzene gave homogeneous solutions with alcoholic potash in the cold. On heating, the polymer was wholly precipitated from solution (even when containing as little as 5–10% of combined ketone). Before heating, hydrolysis was clearly incomplete, whereas on boiling, the skin of polymer formed caused the results to be poorly reproducible. It was established that no alkali was associated with the insolubilized polymer, and, in fact, many of the results (consistent between themselves) gave high values for the acrylate content. It is possible that under the influence of the alkali a variable amount of oxidation to carboxylic acid occurred, and in some cases lower acrylate contents were found using a nitrogen atmosphere. Attempts to carry out the hydrolysis in sealed containers or pressure vessels at 100–120° C. gave less reproducible results and dark-brown precipitates of polymer were formed. The results obtained were broadly in agreement with those obtained by other methods, but the lack of reproducibility obtained at present between repeat determinations on the same polymer makes the method unreliable.

2. *Infrared spectroscopy*.—Films cast from chloroform on to rock salts show overlapping of the carbonyl frequencies (1720 and 1740 cm^{-1}) but here and with the 1440–1460 cm^{-1} , 1400 cm^{-1} , and 1070–1120 cm^{-1} bands, it was possible to carry out a determination of the ester contents with an accuracy of $\pm 5\%$.

3. *Refractive index measurements*.—In this method the basic assumption is that there is a linear relationship between refractive index and copolymer composition. It is possible that the relationship is curved but this cannot be verified until an absolute method has been obtained for determining the polymer composition. In fact, *a priori*, if Newton's law for the refractive index of mixtures holds, a linear relationship between molar composition and refractive index would be expected. A linear relationship between refractive index and weight composition has, of course, been found for butadiene-styrene copolymers (9), and, as it is reasonable to assume that there would be no interaction between adjacent ketone and ester groups, the deviation from linearity for the MVK copolymers should be small. Further evidence that refractive index measurements are satisfactory for copolymer analysis comes from the

fact that copolymers of ethyl vinyl ketone and methyl *isopropenyl* ketone, which can be analyzed accurately by oximation, give linear composition - refractive index changes (1). Refractive indices were measured on a series of low conversion (*ca.* 10%) copolymers. The polymerizations were carried out at 70° C. using a 50% solution of monomers in benzene and 0.25% benzoyl peroxide as initiator. Films were cast on glass plates and, after being thoroughly dried (at 10^{-2} mm. at 60-70° C.), were pressed directly on the upper prism of an Abbé refractometer. Those polymers containing 60% or more of MVK were warmed in order to obtain optical contact with the prism. Measurements were carried out at 25° C. using white light. Typical results obtained are shown in the following table. The accuracy of measurement was about 2×10^{-4} unit for the higher acrylate content polymer, and 5×10^{-4} unit for those of high ketone content. The values for the two pure polymers were obtained from a number of measurements carried out on polymers prepared in bulk, in emulsion, and in solution. In the examination of several

TABLE

Sample	Mole fr. MVK (monomer)	η_{25}	$\Delta n \times 10^4$	Mole fr. MVK (polymer)
1	1.000	1.5025	370	1.00
2	0.875	1.4981	326	0.93
3	0.725	1.4915	260	0.81
4	0.630	1.4875	220	0.73
5	0.535	1.4832	176	0.62
6	0.310	1.4750	95	0.39
7	0.250	1.4738	83	0.35
8	0.090	1.4679	24	0.11 (5)
9	0	1.4655	0	0.00

samples of polymethyl vinyl ketone it was observed that one, obtained from B.A.S.F. Germany, gave slightly yellow colored polymers possessing a higher refractive index than normal (η_{25} 1.5137). Attempts to prevent this discoloration by fractionation of the monomer were not successful, but it was observed that on keeping, a quantity of cross-linked "popcorn"-like polymer formed throughout the commercial product. MVK recovered from the partly polymerized mass then gave polymers of normal refractive index. The ultraviolet spectra of the colored polymers and copolymers showed them to possess considerably greater absorption over the range 250-400 $m\mu$ and no appreciable maximum (pure polymethyl vinyl ketone possesses a maximum at 280 $m\mu$ and negligible absorption above 330 $m\mu$). The cause of the differences has not yet been elucidated but is most probably due to copolymerization of impurities possessing two or more double bonds; the impurities would be concentrated in the low conversion copolymers examined.

Oximation

Quantitative oximation by a modification of the method of Trozzolo and Lieber (14) has been found to give satisfactory results with polymethyl *iso*-

propenyl ketone and polyethyl vinyl ketone, while polyethyl isopropenyl ketone does not react at all. MVK copolymers react readily but the tendency for the solutions to darken renders the end point difficult to observe and electrometric titration was employed. The main disadvantage of the method is the danger that a small amount of hydrolysis or oxamidation of the ester groups may occur. (It has been established, however, that no such reactions occur with polybutyl acrylate (1).)

Results obtained by the different methods on three copolymers are listed below. It can be seen that notwithstanding the scatter they are of the same order.

Polymer	Hydrolysis	% Butyl acrylate		Oxime
		Infrared	Refractive index	
A	24	20	19	25
B	28	25	22	—
C	47	40	43	43

Reaction of Copolymers with Sulphur

A series of low conversion solution polymers and high conversion emulsion polymers were made with varying proportions of MVK. The polymers were carefully dried under vacuum and sulphur (4%) incorporated by milling or in solution. Samples (0.2–2.0 gm. depending on ketone content) were placed in a thermostat at 150° C. and a gentle stream of nitrogen passed through. The gases were passed through ammoniacal cadmium acetate for three hours. At the end of this period excess iodine was added and the sulphide determined volumetrically.

Similar measurements on the simple ketones were made normally using a molar ratio of ketone to sulphur of 10:1. The greater amounts of hydrogen sulphide precluded the use of cadmium acetate as absorbent because of the formation of dense precipitates of sulphide, not readily soluble in iodine. It was found better to absorb the hydrogen sulphide in alkali and to estimate the sulphur gravimetrically after oxidation to sulphate. (Iodometric estimation of sulphide was not possible, since traces of ketone carried over by the gas stream reacted with iodine in alkaline solution.) In a typical experiment using 0.155 gm. of sulphur in 5 ml. of cyclohexanone at 150° C. hydrogen sulphide was liberated steadily; in seven hours 25% of the sulphur was eliminated as hydrogen sulphide. At 130° C. and 100° C. the corresponding amounts were 3.6% and 0.3% respectively.

The authors thank Mr. W. H. T. Davison and Mr. C. E. Kendall for spectroscopic examination of the copolymers and Miss R. K. Smith who carried out much of the analytical work. This paper is published by permission of the Dunlop Rubber Company Limited.

REFERENCES

1. CATTERALL, E. Unpublished work.
2. CHALLENGER, F. *Ind. Chemist*, 4: 315. 1928.
3. COOPER, W. *J. Chem. Soc.* 1386. 1955.
4. COOPER, W., BIRD, T. B., and CATTERALL, E. *Proc. 3rd Rubber Technol. Conf., London*, Paper 38. 1954.
5. COOPER, W. and CATTERALL, E. *Chemistry & Industry*, 1514. 1954.
6. DIETZ, T. J., MAST, W. C., DEAN, R. L., and FISHER, C. H. *Ind. Eng. Chem.* 38: 960. 1946.
7. FARMER, E. H. and SHIPLEY, F. W. *J. Polymer Sci.* 1: 293. 1946.
8. GORDON, M. *J. Polymer Sci.* 7: 485. 1951.
9. LEWIS, F. M., WALLING, C., CUMMINGS, W., BRIGGS, E. R., and WENISCH, W. J. *J. Am. Chem. Soc.* 70: 1527. 1948.
10. MARVEL, C. S. and LEVESQUE, C. L. *J. Am. Chem. Soc.* 60: 280. 1938.
11. MAST, W. C., REHBERG, C. E., and FISHER, C. H. *U.S. Patent No. 2,600,414*. 1952.
12. SEMEGEN, S. T. and WAKELIN, J. H. *Rubber Age (N.Y.)*, 71: 57. 1952.
13. SKEIST, I. *J. Am. Chem. Soc.* 68: 1781. 1946.
14. TROZZOLO, A. M. and LIEBER, E. *Anal. Chem.* 22: 764. 1950.
15. WALL, F. T. *J. Am. Chem. Soc.* 64: 269. 1942.