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be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

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COPOLYMERS OF CHLOROPRENE WITH METHACRYLAMIDE, ACRYLONITRILE AND ACRYLIC ACID

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I. Introduction

In 1931 Carothers and his associates announced the preparation of chloroprene from vinyl acetylene;(8) its successful polymerization to a rubber-like material was revealed at the same time. The production of vinyl acetylene from acetylene had been demonstrated in the same year by Nieuwland and his co-workers.(28) In the years since these discoveries, polychloroprene or neoprene has developed to a highly useful commercial product; 50,000 long tons of neoprene were produced in 1950.

Neoprene is superior to natural rubber in many respects; it has superior resistance to deterioration by sunlight, ozone, heat, oils and solvents, and oxygen and is less permeable to gases. In many applications where these properties are important neoprene has replaced natural rubber. With regard to some properties, however, neoprene is surpassed by other elastomeric materials; for example, natural rubber has superior tensile strength and recovery; butyl rubber is less permeable to gases; GR-S possesses greater resistance to abrasion.

A number of investigators have explored chloroprene copolymerization, particularly in the last decade. Mighton(25) studied the copolymerization of chloroprene with alpha-unsaturated alpha-beta dicarboxylic acid esters and prepared polymers that exhibited outstanding freeze resistance combined with oil and solvent resistance. Mighton also obtained elastomers of improved stress-strain properties by the copolymerization of chloroprene with nitro alcohol esters of unsaturated dicarboxylic acids.(26) Superior copolymers of chloroprene, butadiene and vinyl compounds have been disclosed by Clifford and Wolfe.(10) Numerous other investigators have prepared improved elastomeric materials by copolymerization of chloroprene with a number of vinyl compounds.

It has been the object of this investigation to prepare and study new elastomeric materials of possible interest as erosion-resistant protective coatings. The need for such coatings has arisen with the increasing speed of military planes and the resultant failure of conventional coatings and of metal surfaces themselves on exposure to these speeds. In order to provide the protection required the coating system must be capable of absorbing the shock of impinging droplets without eroding or shattering; it must possess the necessary strength to withstand and recover from these impacts; moreover, it must be secured to the metal surface by a firm, durable bond. These requirements suggest that the coating sought should include a topcoat of high tensile strength and elongation and low permanent set, and a suitable primer system to bind this elastomer to the aluminum. This study has been concerned with the topcoat development.

Of the many available materials that have been tested as candidate topcoats, neoprene has come closest to fulfilling the requirements. As a result it appeared reasonable to seek improved topcoat materials among the copolymers of chloroprene.

Recent work in this laboratory has uncovered a new class of copolymers based on chloroprene and methacrylic acid(21) which have shown considerable promise as erosion-resistant coatings. Chloroprene was copolymerized in a persulfate-initiated emulsion system with methacrylic acid to yield polymers containing 12 percent of the acid at conversions of 55 percent to 60 percent. Vulcanization with magnesia or dithiocarbamate curing systems yielded a material with 7000 psi tensile strength, 700 percent elongation at break and an ASTM permanent set of 12 to 14 percent. This elastomer because of its high chloroprene content retained the excellent solvent resistance and superior aging characteristics of neoprene.

The success encountered with the chloroprene-methacrylic acid copolymer has encouraged the investigation of other chloroprene copolymers as erosion-resistant coatings. In this thesis, results of the copolymerization of chloroprene with acrylonitrile, acrylic acid, and methacrylamide are discussed. These monomers were chosen specifically for the purpose of achieving copolymers of high tensile strength and elongation and low permanent set. The reasons for this choice of monomers to obtain such an elastomer bears further discussion.

A. Structure Versus Polymer Properties

An elastomer is a mass of high molecular weight chains which in the unstressed condition exist in a coiled, tangled disorder. Inter-molecular attractions are relatively weak so that rapid Brownian movement of short chain segments is possible; however, the chains are long enough and sufficiently tangled so that overall movement between whole chains is impaired. It is this rapid internal Brownian movement and slow external Brownian movement that characterizes a rubber.

The degree of permanent set that results in an elastomer from an applied stress is determined by several factors. Under a sustained external stress mere length of chains and tangling is not enough to prevent slippage of whole chains past one another and a large permanent deformation results. To reduce this permanent set a series of fix points must be introduced, spaced far enough apart along the chains so that the segments in between are flexible enough to allow deformation. (30) Presumably these fix points can be established both by primary and secondary valence forces; reinforcement with fine particles of carbon black also generally provides weak fix points by irreversibly sorbing parts of the chain on their active surfaces. These considerationssuggest that in order to obtain an elastomeric material possessing a low permanent set it is necessary to choose a comonomer which contains groupings capable of forming primary valence links upon the introduction of an appropriate curing agent or one which contains highly polar groupings which are capable of establishing strong secondary valence forces between chains.

Similar factors are involved in the development of high tensile properties. Flory (13,14) has studied this subject in great detail. He postulates that the retractive force that exists when vulcanized rubber is deformed by stretching derives only from the so called principal chain segments. This term applies to those chain sections which extend between two points of crosslinkage as differentiated from the terminal chain sections which extend from a crosslink to an untied chain end. The latter, because of its loose end, relaxes and remains coiled despite the stress and does not contribute to the elastic resistance. The conclusion reached from these theories is that tensile strength depends not only on the degree of crosslinkage but also on the polymer molecular weight (before vulcanization): the shorter the original chains the larger is the proportion of inactive chain sections.

Another extremely important factor involved in the consideration of ultimate tensile strength is crystallization. Stretching results in crystallite formation with many polymeric materials; this is undoubtedly the result of increased orientation and closer packing of principal chain segments in the stretched state. Flory has shown that in the case of stress-crystallizable rubbers the ultimate tensile strength is a function of the fraction that is orientable under tension and upon the degree of crystallinity attained. It is worthy of note that carbon blacks interfere with crystallite formation and hence do not in general improve the ultimate tensile strength of stress-crystallizable rubbers.

Since cyrstallization depends upon the magnitude of the effective intermolecular forces it becomes apparent that the monomer requirements considered under permanent set also apply here; in addition high molecular weight is desirable.

It is appropriate now to consider briefly the means of obtaining the strong intermolecular attractions which have been indicated as desirable for the attainment of high tensile strength and low permanent set in an elastomer. Two major considerations are involved: (1) the intensity of the secondary valence forces, that is, the polarity of the structures on the chains together with the chain length; and (2) the distance between chains. It is well known that the magnitude of secondary valence forces decreases rapidly with increasing distance between active centers.(7) Hence increased chain symmetry and orientation enhance the intermolecular attraction. It is to be noted that any attempt at copolymerization (except where perfect alternation occurs) is detrimental to chain symmetry. Therefore, if any increase in intermolecular forces is to be attained by copolymerization the other contributing factors must be increased greatly. This is most effectively accomplished by increasing the polarity of the groupings on the chains. Two possibilities are immediately suggested: (1) the introduction of highly electronegative groups such as the cyano or nitro group; and (2) the use of groupings capable of forming hydrogen bonds such as $-\overset{O}{C}-OH$, $-\overset{O}{C}-NH_2$, $-OH$, $-NH_2$. Acrylonitrile, acrylic acid and methacrylamide are commercially available monomers which fulfill one or the other of the above requirements. It is to be noted that for two of the monomers chosen, acrylic acid and methacrylamide, the structure also suggests the possibility of achieving primary valence crosslinks with appropriate curing agents, a consideration which was discussed earlier.

B. Copolymerization

So far the possibility of attaining copolymerization of these selected monomers with chloroprene has not been considered.

Considerable insight into this problem is afforded by the monomer relative reactivity concept of Mayo and Lewis(23,24) and the Q and e values of Price.(4,29) Aside from steric hindrance, there are two important factors that determine monomer reactivities in copolymerization: (1) reduction of activation energy due to resonance stabilization in the transition state; and (2) polarity differences induced in both monomers and radicals by constituent groups. Price has considered these factors quantitatively for each monomer and has designated them Q and e values respectively. Copolymerization is more readily effected between monomers having comparable Q values and appreciable differences in polarity.

Reactivity ratios in the polymerization of a monomer pair are given by the equations:

$$r_1 = \frac{Q_1}{Q_2} \exp\left[-e_1(e_1 - e_2)\right]$$

$$r_2 = \frac{Q_2}{Q_1} \exp\left[-e_2(e_2 - e_1)\right]$$

In the case of chloroprene it has been found necessary to introduce a modification because of a difference in polarity induced in monomer and radical.(37) For chloroprene

$$r_1 = \frac{Q_1}{Q_2} \exp\left[-e_1^*(e_1 - e_2)\right]$$

where e* represents the e value for the radical.

The following Q-e data are available for the monomers concerned. No data has been published for methacrylamide.

Table I
Monomer Q and e Values

Monomers	Q	e	e*	Reference
Chloroprene	2.0	+0.9	-0.6	(37)
Acrylonitrile	.4	+0.9		(31)
Acrylic Acid	1.6	+1.0		(9)

Because of its conjugated structure methacrylamide would be expected to have a reasonably high Q value. It is likely that the e value would be zero to slightly positive considering the opposing effects of the methyl and amide groupings.

The bulk reactivity ratios for the systems under consideration have been calculated to be:

chloroprene-acrylonitrile	$r_C = 5.0$	$r_A = 0.2$
chloroprene-acrylic acid	$r_C = 1.25$	$r_A = .8$

Copolymerization occurs most readily between monomers when their reactivity ratios are of the same order of magnitude. Large differences in these quantities, however, do not prevent successful modification of one monomer with small percentages of the other. Thus polyacrylonitrile has been polymerized without too much difficulty with moderate amounts (8-12 percent) of vinyl acetate in order to improve its solubility; yet the reactivity ratios here are $r_A = 6.0$ and $r_{VAc} = .02$.(2)

In emulsion systems Wall has postulated that the relative reactivities of a copolymer system are altered by the distribution coefficient for the monomers between oil and aqueous phases.(36) These theories have been borne out by the work of Fordyce and Ham(16) and Fordyce and Chapin.(15) Although the necessary distribution coefficients are not available for the systems involved here, it becomes apparent even on a qualitative basis that the reactivity of acrylic acid with chloroprene will be greatly reduced because of the great difference in water solubility. The reactivity of the acrylonitrile in the chloroprene-acrylonitrile system will be reduced to some extent.

Lacking Q and e data for methacrylamide copolymerization predictions for the chloroprene methacrylamide system are difficult. It is reasonable to assume, however, that even though a reasonable reactivity might be predicted for methacrylamide on the basis of its conjugation, its high water solubility will greatly retard its copolymerization with chloroprene in emulsion.

In summary, therefore, it can be said that for the three copolymer systems considered chloroprene should dominate in the polymerization. Nevertheless sufficient copolymerization should be expected to achieve the modification desired.

II. Results and Discussion

Copolymers of chloroprene and acrylonitrile, chloroprene and acrylic acid, and chloroprene and methacrylamide have been prepared and studied. Polymerizations were carried out in a persulfate initiated emulsion system at 30° C. Elastomeric materials similar in appearance to polychloroprene were obtained for all three systems; investigations were confined to high diene levels.

In all three systems chloroprene was the more reactive monomer. Instananeous copolymer compositions drifted considerably over the course of the polymerization. Chains formed early in the reaction were predominant in chloroprene; not until the conversion approached the percentage of chloroprene charged did the second monomer enter the polymer to a large extent. Acrylic acid showed the lowest reactivity with chloroprene. All copolymers prepared have been analyzed and are described by an average composition. It should be borne in mind that the composition of individual chains must vary considerably.

With optimum cures these three copolymer systems surpassed commercial polychloroprene (Neoprene GR-M) in ultimate tensile strength and were roughly comparable to it in elongation at break and permanent set; the tensile strengths were below that of the chloroprene-methacrylic acid copolymer, however. An overall summary of polymer properties is presented in Table II. The effect of numerous variables upon the copolymer properties will be discussed in greater detail individually.

FIGURE I

LOW TEMPERATURE RETRACTION OF VULCANIZED ELASTOMERS

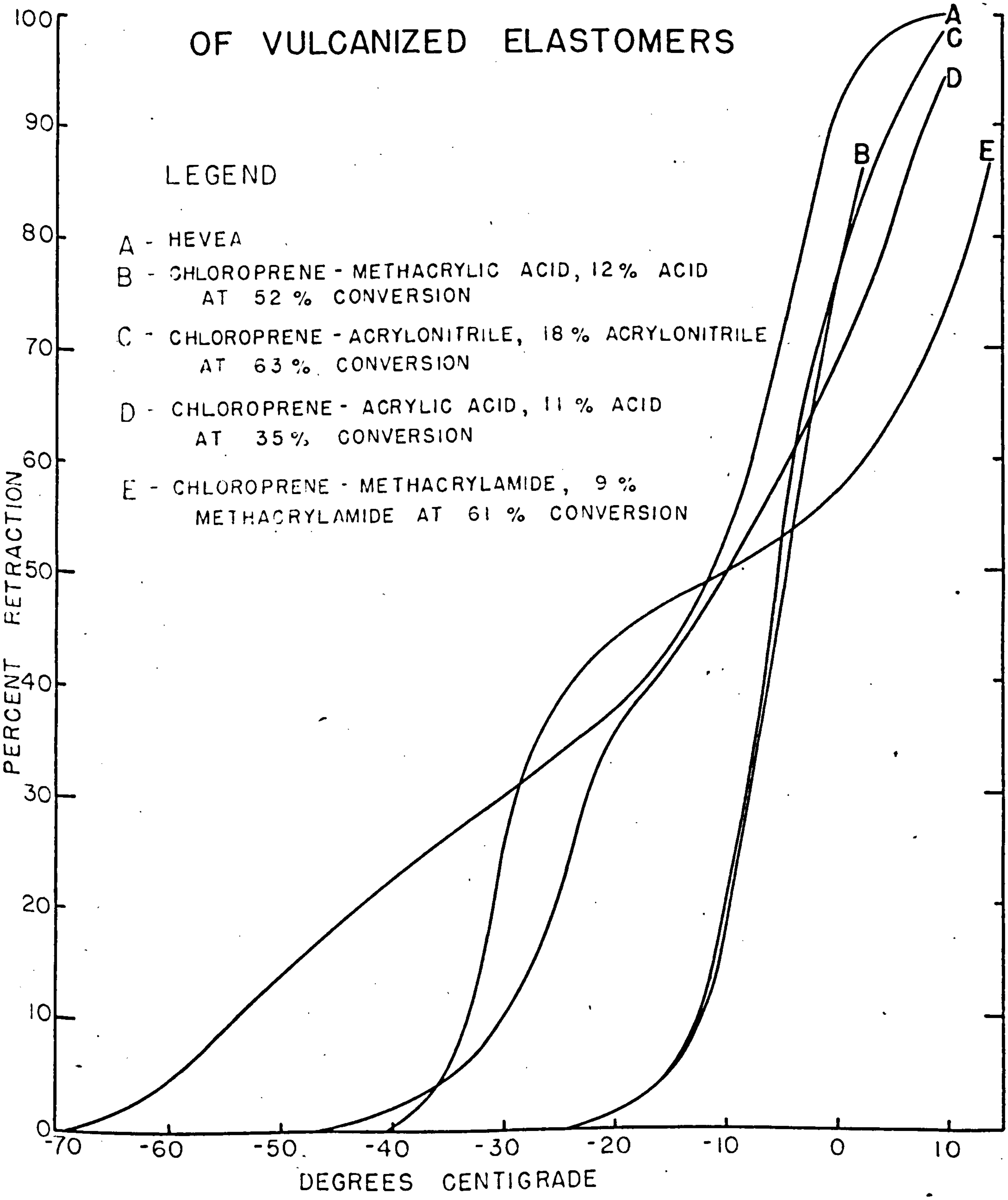


Table II
Physical Properties of Polymer Vulcanizates

Copolymer	Tensile Strength, psi	Elong. at Break %	ASTM Set
Polychloroprene	3500-4200	700	7-14
Chloroprene-methacrylic acid	7000	700	13
Chloroprene-acrylonitrile	4700	470	10
Chloroprene-methacrylamide	4800	760	7
Chloroprene-acrylic acid	5200	680	15

Copolymer	Agents	Cure
Polychloroprene	4 pts MgO, 5 pts ZnO (27 pts EPC black)	1/2 hr. at 144°C.
Chloroprene-methacrylic acid	5 pts. ZnO	14 days at room temperature
Chloroprene-acrylonitrile	4 pts MgO, 5 pts ZnO, 2 pts Et. Selenac (25 pts HPC black)	3 hrs. at 140°C.
Chloroprene-methacrylamide	6 pts Et.Zimate, 2 pts MgO, 2 pts S	2 hrs. at 120°C.
Chloroprene-acrylic acid	6 pts Et.Zimate, 2 pts MgO, 2 pts S	2 hrs. at 120°C.

Low temperature properties were examined using the retraction method of Smith, et al.(33) Vulcanized film strips elongated 250 percent were conditioned 10 minutes at -65°C. and their subsequent retraction measured as a function of temperature. The results are shown in Fig. 1. The cures employed were identical with those listed in Table II with the exception of the chloroprene-methacrylic acid polymer; the strips tested here were cured 2 hours at 120°C. with 1 part magnesia.

A comparison of TR values taken from the graph are listed in Table III; the TR values denote the temperatures at which 10, 30, 50, and 70 percent retraction has occurred.

Table III

Comparison of Copolymer Low Temperature Properties with Polychloroprene

Polymer	TR 10	TR 30	TR 50	TR 70
Hevea (33)	-54.2	-29.6	-11.1	-5.0
Polychloroprene (33)	-40.4	-35.2	-24.6	+3.6
Chloroprene-methacrylic acid	-12	- 8	- 5	-1
Chloroprene-acrylonitrile	-12	- 8	- 5	-1
Chloroprene-methacrylamide	-33	-29	-10	+9
Chloroprene-acrylic acid	-30	-22	-10	+1

The TR 10 value is influenced by viscoelastic effects and very little by crystallization and indicates the low temperature flexibility when considerable low temperature storage is not encountered. It is commonly used as a measure of low temperature flexibility for dynamic application. The TR 70 value is indicative of flexibility with low temperature storage and is influenced by both viscoelastic effects and crystallization; it provides a measure for flexibility under static stress.

In general, the copolymer TR values lie above those of neoprene indicating poorer low temperature flexibility. This is particularly true of the TR 10 values where particularly poor dynamic flexibility is indicated for both C-MA and chloroprene-acrylonitrile. It is interesting that both these polymers appear slightly superior with respect to flexibility under static stress. This indicates decreased crystallization tendencies. Although comonomers of high second order transition points would be expected to increase the crystallization, apparently the reduction in symmetry resulting from copolymerization has actually decreased the intermolecular attractions in these instances. It is interesting that the chloroprene-methacrylamide copolymer is not influenced in this manner but shows an increased tendency for crystallization; this was particularly true of the sample with no mercaptan modification.

These results indicate that the improved tensile strength of the chloroprene-methacrylamide may be due to a greater tendency for crystallization upon stretching as a result of stronger intermolecular attractions. Furthermore, carbon black reinforcement was found to have a detrimental effect upon tensile strength; this is characteristic of polymers that crystallize readily on stretch.(30)

The theory of carbon black reinforcement has been mentioned earlier; the small particles create weak fix points by irreversible sorption of parts of chain molecules. On the other hand these particles interfere with orientation and close packing of chains upon stretch and thus decrease crystallization tendencies. Thus in rubbers that show no stretch crystallization reinforcement increases tensile strength; in the crystallizable elastomers no improvement is realized.

There is further evidence for increased intermolecular attraction. Natural rubber possesses weak secondary valence forces between chains. Hence when released from a stretched state it snaps back because of the unrestrained internal Brownian movement of principal chain segments. Strong intermolecular forces restrain this internal Brownian movement and hinder the rapid return of the elastomer to the thermodynamically stable statistical coils. As a result, although the permanent set of these rubbers may be low they do not show the rapid rate of recovery characteristic of Hevea.

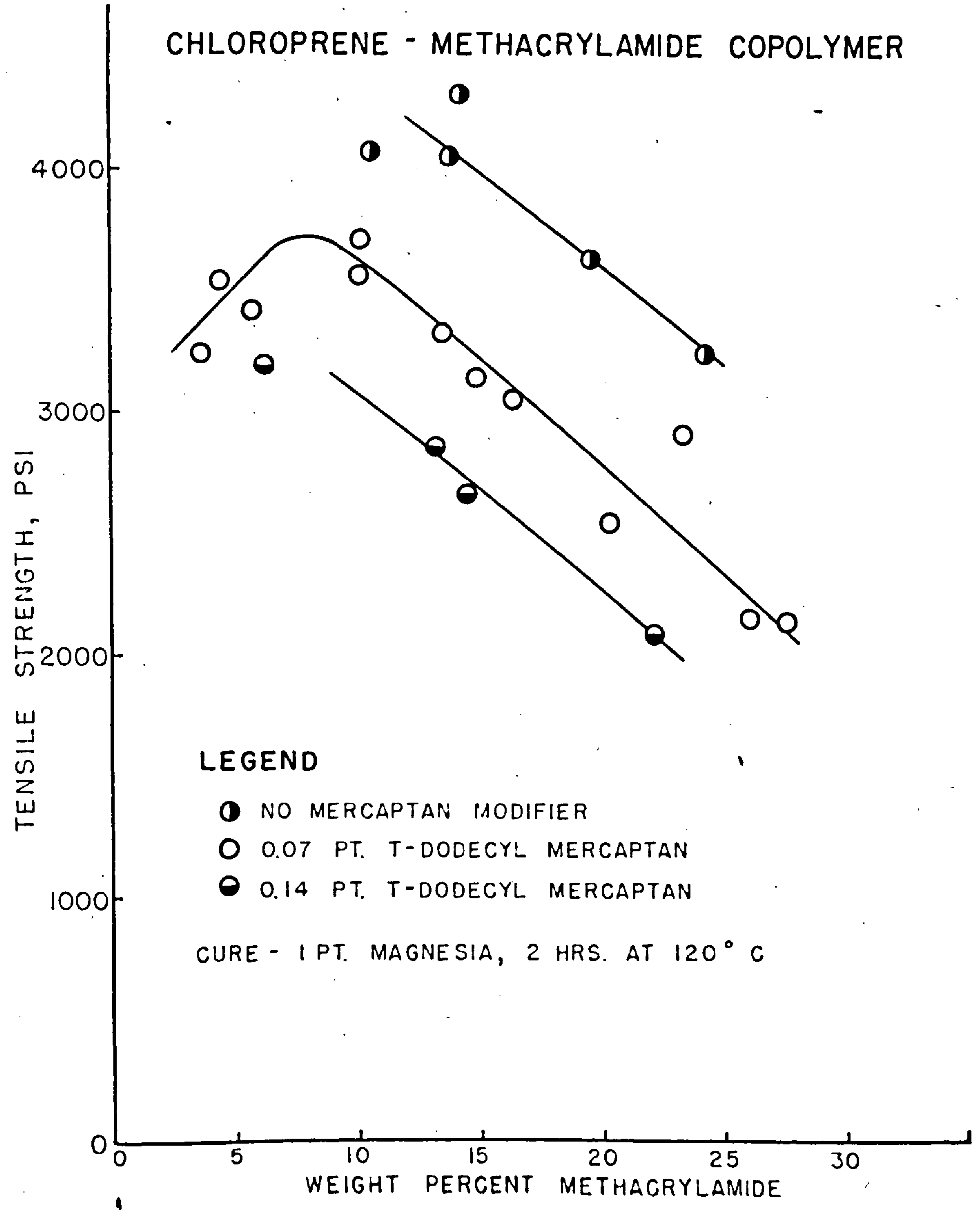
The chloroprene-methacrylamide copolymer possesses a slow recovery rate.

The high tensile strength of the C-MA copolymer may be the result of primary valence links through the carboxyl group. Several attempts to achieve a similar link between the amide groups of the methacrylamide copolymer with an appropriate curing agent were unsuccessful.

It also **appears** logical that the lower tensile strength of the chloroprene-acrylonitrile copolymer resulted from a lessened tendency for stretch crystallization. This polymer showed a marked improvement in strength with carbon reinforcement. In this copolymer intermolecular attractions are more likely of lower magnitude for several reasons: (1) acrylonitrile copolymerizes readily with chloroprene resulting in a more or less random copolymer with poor recurrence symmetry; and (2) dipole-dipole-interactions are weaker in magnitude than hydrogen bridges.

FIGURE 2

VARIATION OF TENSILE STRENGTH WITH COMPOSITION



A. Chloroprene Methacrylamide Copolymers

Copolymers of chloroprene and methacrylamide have been prepared containing from 0 to 30 percent methacrylamide. The following typical emulsion recipe was employed:

Redistilled Water	200 gms.
Triton X301* (emulsifier)	13 gms.
Sulfur (modifier)	0.229 gms
Potassium Persulfate (initiater)	0.6 gms.
Tertiary Dodecyl Mercaptan (modifier)	0.07 gms.
Monomers	100 gms.

Polymerization times at 30° were dependent on the monomer charge ratio varying from 3 hours to reach a 68 percent conversion from a 30 percent methacrylamide charge to 13 hours to attain a 65 percent conversion from a 50 percent charge. The system polymerizes readily throughout the pH range of 3 to 9. The best solvents for the polymers are cyclohexenone and toluene; dioxane, methyl isobutyl ketone, and butyl acetate are also suitable at most compositions and degrees of modification.

1. Variations of Properties with Composition and Conversion

Polymer properties are dependent upon polymer composition. The optimum polymer composition appears to be in the vicinity of 9 to 10 percent methacrylamide. Figure 2 shows the effect of methacrylamide content upon ultimate tensile strength for a fixed cure and degree of modification. The curve peaks at 10 percent methacrylamide and falls off rapidly above 15 percent. A similar trend exists in the permanent set data although it is not as clearly defined here. (Table IV) Elongation at break is less affected by

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* A 20 percent aqueous solution of an alkyl aryl polyether sulfate prepared by Rohm and Haas.

variations in composition in the range investigated; it is obvious, however, that if the diene content were decreased further the elongation would soon be reduced.

In so far as both ultimate tensile strength and permanent set are dependent upon the number of fix points, it is not surprising that they show similar trends with composition. The adverse effect of higher methacrylamide content upon these two properties can be explained by two factors: (1) the curing agent (Magnesia) employed in Fig. 2 (and also the others that have proved most effective in the system) crosslink the chloroprene group. Hence decreasing the frequency of these units in the chains will be evidenced in a decrease in number of primary valence links between chains; (2) some adverse effects may be becoming manifest as a result of decreasing chain symmetry.

Variation of cure has been shown to produce considerable shifts in this curve along the vertical axis as will be discussed subsequently. However, no shifts in optimum composition were evidenced. Considerable effort was directed to effecting auxiliary crosslinks between amide groups. These attempts proved unsuccessful; had such a cure been possible the optimum range probably could have been shifted.

Table IV
Effect of Composition Upon Elongation and Set for the Chloroprene-Methacrylamide Copolymer

% Methacrylamide in Polymer	% Elongation at Break	ASTM Set
6	1050	9
7	1010	10
10	980	9
11	1060	15
14	990	17
20	950	20

The effect of conversion independent of composition appears to have had little effect if any upon the physical properties of the vulcanizate. Two 11 percent methacrylamide copolymers polymerized from different charges to 51 and 65 percent conversion showed respectively tensile strengths of 3570 and 3460 psi, and elongations at break of 980 and 970 percent.

2. Effect of Modification and Milling

The effect of chain transfer agents upon physical properties was more apparent. Modifiers were introduced into the polymerization recipe to increase the solubility of the uncured polymer in appropriate solvents for possible lacquer applications. It was because of these possible lacquer applications that all physical test data was collected on free films poured from lacquer solutions. Hence two effects could be realized from polymer modification: (1) increase of lacquer uniformity and (2) decreased molecular weight.

Early studies were conducted without mercaptan modifications. These polymers provided high but poorly reproducible tensile results; lacquer gelatin was difficult to control and resulted in weak spots in the free films. Several levels of modification with dodecyl mercaptan were investigated. When cured with one part magnesia for 2 hours at 120°C. these polymers showed detrimental effects from modification even though the uniformity of the film was greatly improved. This effect is illustrated in Figure 2. The problem was ultimately solved with the development of a more efficient curing system; as a result it was possible to utilize the improved uniformity of the modified lacquers and subsequently cure to a high tensile strength with an appropriate curing system.

The effect of modification upon molecular weight is illustrated by the following intrinsic viscosity data for a 10 percent methacrylamide polymer at several levels of modification.

These tests were run after milling with tetramethyl thiuram disulfide; hence they do not show the characteristics of the polymer as polymerized but instead the characteristics of the polymer submitted to physical testing which are more pertinent. The observed gel contents were 55, 85 and 85 percent for levels of modification of none, 0.07 parts, and 0.14 parts mercaptan respectively. The corresponding intrinsic viscosities were 0.30, 0.39, and 0.35 at 25°C. Because of the gel content, these values do not provide an accurate reflection of the molecular weights.

The degree of milling also proved an important consideration in the attainment of improved physical properties. In addition to mercaptan modification, sulfur modification as described by Collins(11) and Youker(38) was also employed in all polymers.

The mechanism of sulfur modification of chloroprene has been investigated by Mochel and Peterson.(27) These investigators found that sulfur enters the polymer as a comonomer, not as an end group like the mercaptans; subsequent treatment with tetramethyl thiuram disulfide is believed to cleave chains at sulfur linkages. Increased solubility is achieved in this manner by reducing the average molecular weight below the critical value of gelation.

In the current investigation of chloroprene-methacrylamide copolymers it was found that a reasonable amount of milling was necessary to observe this increased solubility. With insufficient milling even these sulfur-modified polymers containing mercaptan produced gelled lacquers with corresponding lowered physical properties of the free films. Best results were obtained with 10 to 12 minutes milling through moderately tight rolls. Uniform gel-free lacquers were obtained by this procedure from polymers modified with both .07 and .14 parts dodecyl mercaptan. The effects of milling are illustrated in Table V for a 10 percent methacrylamide copolymer at 61 percent conversion modified with .07 part dodecyl mercaptan.

Table V
Effect of Milling Time on Solubility and Tensile Strength

Milling Time, min.	% Soluble in cyclohexanone	T.S. psi
4	63	3730
6	79	3600
8	84	3890
10	91	4330
12	99	4370

Milling produced no significant change in elongation at break or permanent set; for all of the above films the elongation was approximately 750 percent and the set 6 percent.

3. Curing

The most effective curing agents for the chloroprene-methacrylamide copolymers have been found to be metal oxides, dithio-carbamates, and polyhydroxy aromatics. All these are common neoprene vulcanizing agents and presumably effect a cure here through the chloroprene units. Ideally it should also be possible to create crosslinks between methacrylamide groups with such agents as formaldehyde; however, efforts to establish such crosslinks have met with little success.

Best results have been obtained with a combination of sulfur, magnesia and Ethyl Zimate (zinc diethyl dithiocarbemate) cured for two hours at 120°C. Table VI shows the variations in physical properties with several combinations of these curing agents for a 9 percent methacrylamide copolymer at 61 percent conversion modified with .07 parts dodecyl mercaptan. The amounts of Zimate and magnesia do not appear critical in the range of 3 to 12 parts for the Zimate and 2 to 8 parts for the magnesia. Sulfur shows a sharp maximum in tensile strength at 2 parts.

These results were obtained for a cure of 2 hours at 120°C. Variations in time and temperature of cure have shown that the time of cure at 120°C. is not critical; cures of one, two, and three hours at these temperatures evidenced no significant variations in physical properties. Longer times are required at lower temperatures to attain comparable results; at 100°C., a bake of 8 hours was found necessary.

Table VI

Effect of Variations of Zimate, Magnesia and Sulfur upon Physical Properties of Chloroprene-Methacrylamide Copolymers

Zimate	Parts Magnesia	Sulfur	T.S. psi	% Elong. at Break	ASTM Set
6	2	0	3730	890	10
"	"	2	4780	860	11
"	"	4	4130	780	11
"	"	6	3080	650	10
6	0	2	4240	1000	6
"	2	"	4780	860	11
"	4	"	4770	780	6
"	6	"	4500	750	6
"	8	"	4810	760	7
0	2	"	3410	890	9
3	"	"	4800	930	9
6	"	"	4780	860	11
9	"	"	4620	840	9
12	"	"	4670	740	11
15	"	"	4070	730	5

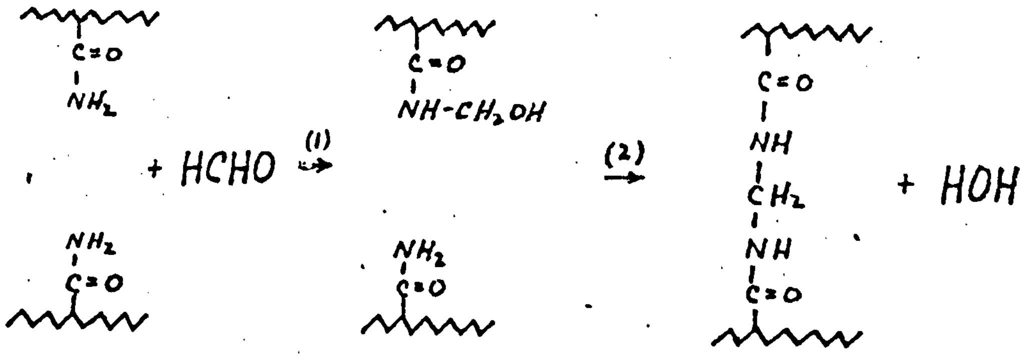
A large number of other curing systems were also tested. Some of the more important results of these studies are listed in Table VII. A standard cure of 2 hours at 120°C. was employed; the polymer contained 9 percent methacrylamide at 61 percent conversion and was modified with 0.07 parts dodecyl mercaptan.

Table VII
Effectiveness of Miscellaneous Curing Agents upon the Chloroprene-Methacrylamide Copolymer

Agent	Parts	TS, psi	Elong. %	ASTM Set
MgO	1	3930	1010	9
	2.5	4030	910	8
	4	3460	920	9
	6	3460	660	11
Catechol	8	4280	910	6
Pyrogallol	8	4110	640	5
Phloroglucinol	8	3890	530	5
MgO ZnO	2 3	3240	1130	10
MgO ZnO	4 5	3240	102	11
DMPC*	9	2850		
DMPC 622 Cure**	9	3000		
HCHO MgO	5 1	2690	830	9
HCHO MgO S	5 1 2.5	2280	820	9

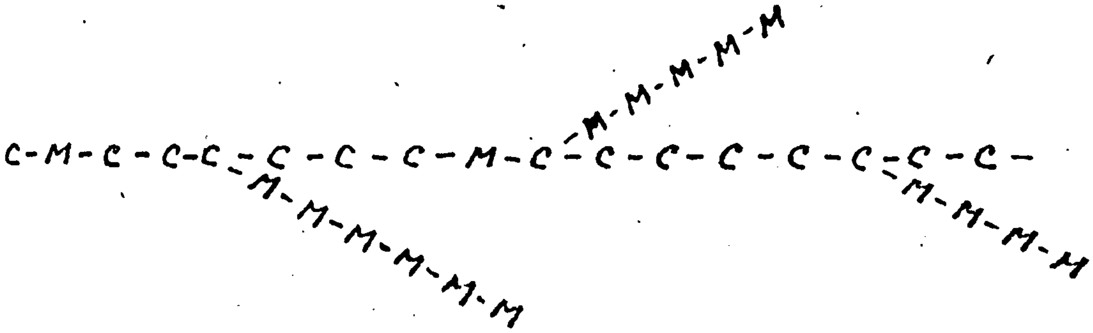
* - Condensation product of formaldehyde and para cresol.
** - 6 Zimate, 2 Sulfur, 2 Magnesia cure.

The work with formaldehyde and dimethylol para cresol (DMPC) are examples of the attempts made to effect a cure through the amide groups. It was hoped that formaldehyde would provide crosslinks in the following manner:



When these attempts with formaldehyde met with little success it was presumed that the formaldehyde was being lost by volatilization before step (1) could occur. Dimethylol para cresol was prepared by the condensation of formaldehyde with para cresol in basic solution;(17) it was hoped that because of its low volatility it would prove more effective than formaldehyde. This was not the case, however.

Subsequent work on the nature of the copolymer has indicated that a large portion of the methacrylamide is probably present as methacrylamide (m) chains grafted on to chloroprene (c) chains:



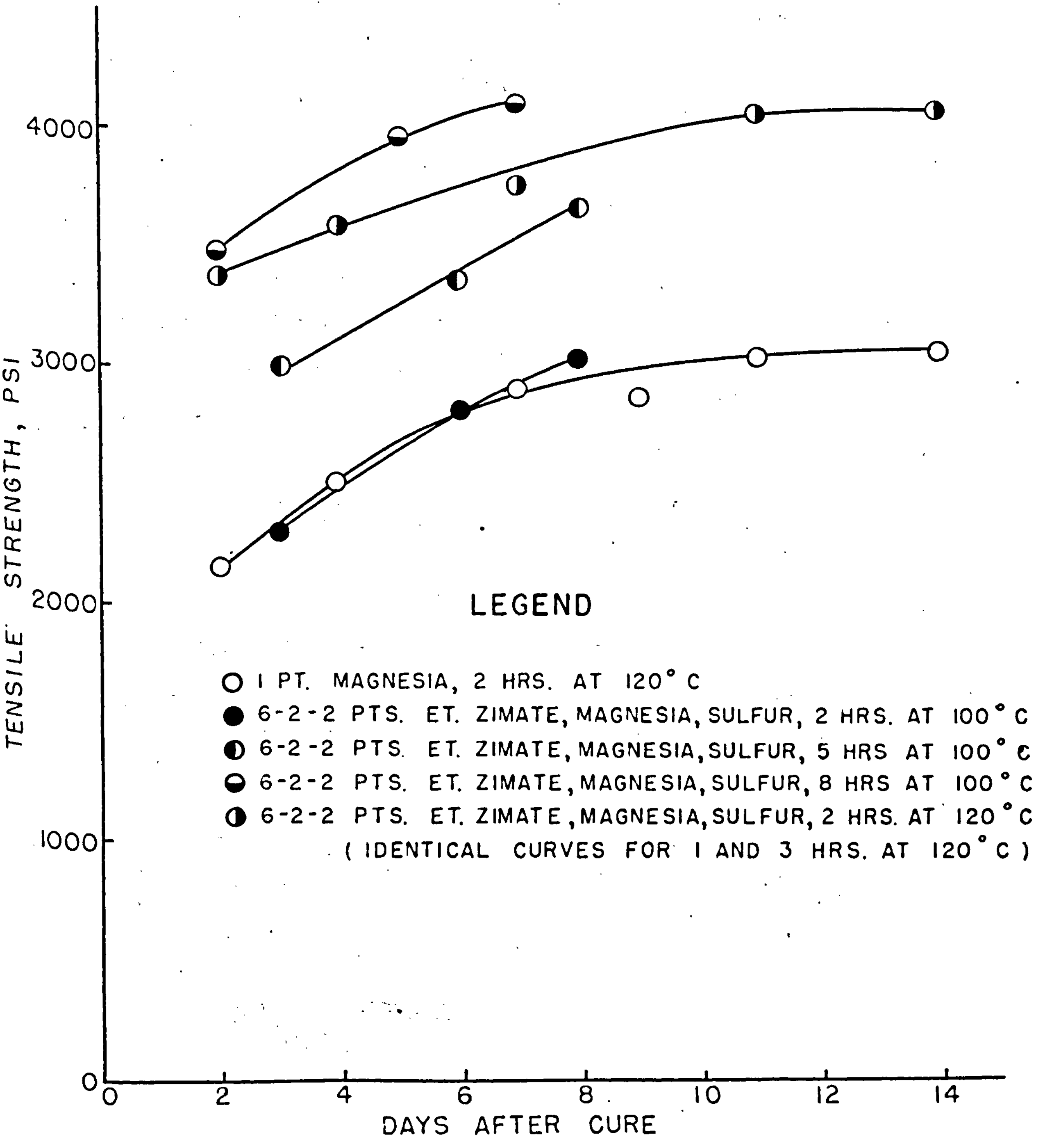
On the basis of this structure it is likely that condensation reactions occur between adjacent methacrylamide units with a lesser probability for interchain condensation. It this is true it could account for the failure of the formaldehyde type cures.

Regardless of the type of cure employed with the methacrylamide copolymer considerable time is required after baking before the maximum physical properties are attained; this could reasonably be the result of two effects: (1) the curing process proceeds at room temperature after being removed from the oven; and (2) minute quantities of the high-boiling cyclohexanone are trapped in the film and gradually diffuse out after stripping. Periods ranging from a week to over a month are required depending upon the nature of the curing agents and other variables. Time and temperature of cure appear to exert only a minor influence. These effects are illustrated

FIGURE 3

EFFECT OF TIME AFTER CURE UPON TENSILE STRENGTH

FOR CHLOROPRENE - METHACRYLAMIDE COPOLYMERS



in Figure 3 for a 1 part magnesia cure and a 6-2-2 zimate, magnesia, sulfur cure at several curing times and temperatures.

It will be noted that with the more efficient curing system the magnitude of the effect is less and the curve levels out more rapidly. The rate of increase is improved somewhat by decreasing the temperature of cure.

The foregoing results suggested that it might be possible to eliminate the bake entirely and cure the polymer by aging at room temperature. Although some degree of success has been realized in this endeavor, it has not been possible to duplicate the physical properties of higher temperature cures. The best room temperature cures were obtained with p-phenylene diamine as illustrated in Table VIII.

Table VIII
Effectiveness of Curing Agents in Room Temperature Cures for Chloroprene-Methacrylamide Copolymers

	Tensile Strength, psi, after	
Cure	10 days	20 days
6-2-2 Zimate, sulfur, magnesia	1900	2470
5 ZnO	2570	2650
5 MgO	2800	2900
5 ZnO + 8 Catechol	2240	2270
8 Pyrogallol	2680	2900
8 Phloroglucinol	2260	2280
8 Catechol	2600	3420
6 p-phenylene diamine	3570 (14 days)	

In the course of the curing studies it became of interest to examine the stability of the lacquer solutions. No signs of lacquer deterioration were apparent for periods exceeding three months. Lacquer systems containing curing systems remained usable up to a week after preparation; subsequently slight gelation was detected.

4. Reinforcement

The incorporation of carbon black and silica effected no improvement in physical properties; silica showed no effect while both Easy Processing Channel Black and Royal Spectra Black had a detrimental effect.

Table IX
Effect of Reinforcing Agents upon Physical Properties of Chloroprene-Methacrylamide Copolymers
(6-2-2 Zimate, Sulfur, Magnesia Cure)

Agent	Parts	T.S. psi	Elong %	ASTM Set
EPC	2	2850	960	10
	5	2670	930	12
	10	3030	940	10
	20	3020	920	12
Royal Spectra	2	2890	950	7
	5	2980	1030	8
	10	3030	970	12
	20	3280	900	21
Silica	2	4100	950	5
	5	4250	930	11
Control		4180	1010	10

As has been discussed, these results are in conformity with the stress induced crystallization tendency expected in the copolymer.

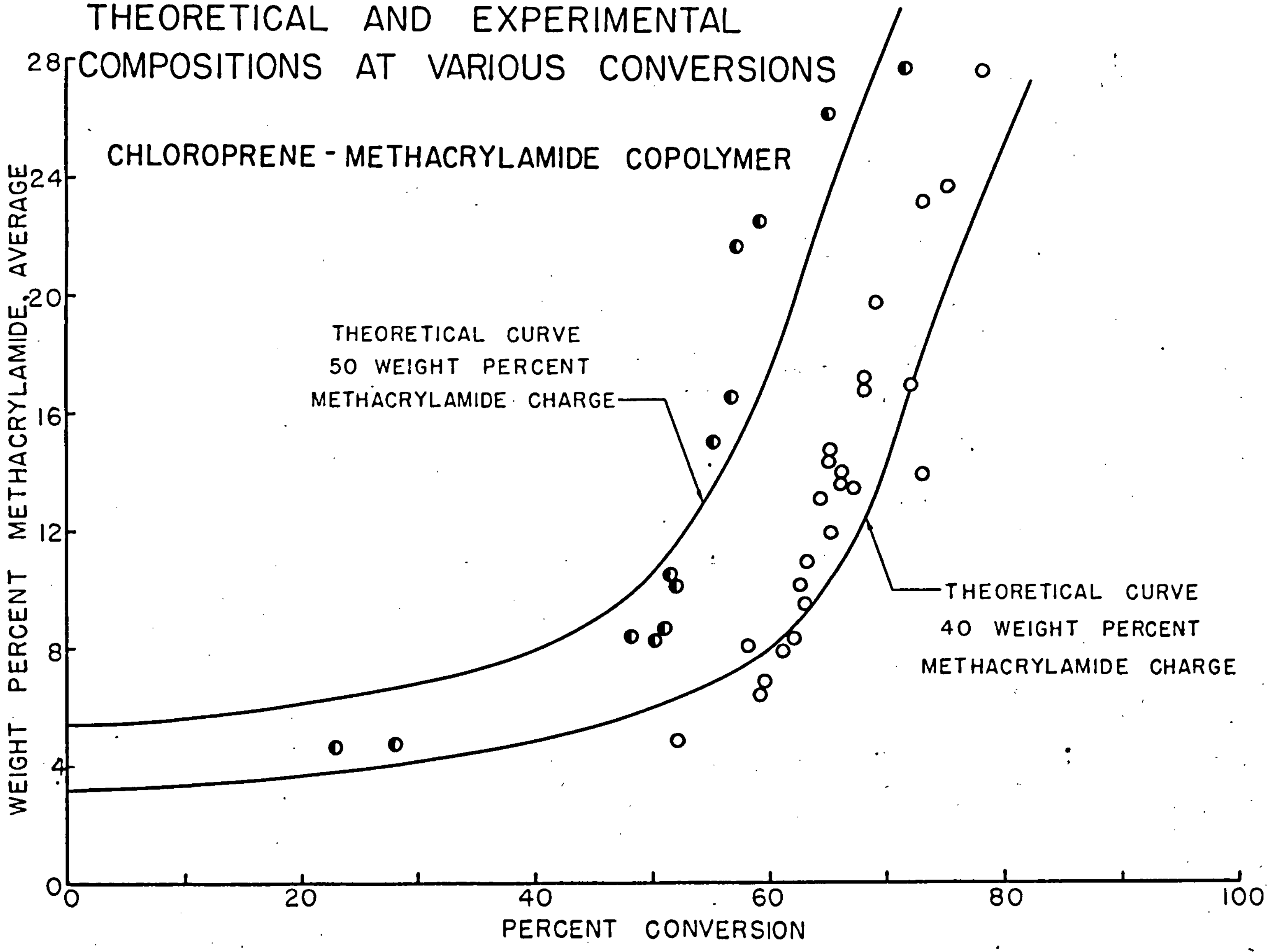
5. Nature of the Copolymer

Despite the great difference in reactivity between chloroprene and methacrylamide in emulsion it is believed that copolymerization is achieved. The bulk of the polymer chains contain at least 95 percent chloroprene with chains of high methacrylamide content being formed late in the polymerization. A certain degree of grafting of these high methacrylamide chains on the chains of high chloroprene content probably occurs. It is reasonably certain, however, that the polymer is more than a mere physical mixture of polychloroprene and polymethacrylamide.

FIGURE 4

THEORETICAL AND EXPERIMENTAL COMPOSITIONS AT VARIOUS CONVERSIONS

CHLOROPRENE - METHACRYLAMIDE COPOLYMER



Some insight into the nature of copolymer is afforded by a consideration of how the methacrylamide and chloroprene enter into the polymerization. Data on composition at various conversions for 40 and 50 weight percent methacrylamide charges have been plotted in Figure 4. It will be seen for both charges that the amide content remains low until practically all the chloroprene has been consumed and then rises abruptly. However, it is apparent even at 60 percent conversion for the 40 percent methacrylamide charge that polymer contains 5 to 8 percent methacrylamide. Similar results are apparent for the 50 percent charge. There is little doubt that the chloroprene does not polymerize 100 percent before some polymerization of the methacrylamide is initiated. There is some evidence to suggest that copolymerization has occurred from the beginning and that methacrylamide polymerization begins before the monomeric chloroprene concentration becomes low. If this were not the case, low conversion (below 30 to 35 percent) for both charges should contain 100 percent chloroprene. The results of several low conversion polymers are presented in Table X. It will be seen that they analyze considerably less than 100 percent chloroprene.

Table X
Composition of Low Conversion Copolymers of Chloroprene and Methacrylamide

Charge; Wt. % Methacrylamide	Conversion, %	Polymer Composition Wt. % Methacrylamide
40	21	4.7
40	34	4.9
50	23	4.6
50	28	4.9

The considerations involved here are more clearly demonstrated by mathematical treatment of the reactivity ratios of chloroprene and methacrylamide. For this purpose, these constants for the polymerizations have been determined for both solution and emulsion; the results were as follows: in solution at 50°C., $r_c = 5.5 \pm 0.5$, $r_m = 0.05 \pm 0.05$; in emulsion at 30°C., $r_c = 20 \pm 10$, $r_m = 0.03 \pm 0.03$.

In emulsion, these ratios were calculated from polymers at various charge ratios using the method of intersections developed by Mayo and Lewis.(24) Conversion was corrected for by the following equation which was also developed by these workers.

$$r_2 = \frac{\log M_2^\circ/M_2 - \frac{1}{p}\log\dfrac{1 - p\,M_1/M_2}{1 - p\,M_1^\circ/M_2^\circ}}{\log M_1^\circ/M_1 + \log\dfrac{1 - p\,M_1/M_2}{1 - p\,M_1^\circ/M_2^\circ}}$$

where $p = (1-r_1)/(1-r_2)$, M_1 and M_2 are the moles of monomers unpolymerized at the end of the reaction and M_1° and M_2° are the moles of monomers charged.

The data employed in these calculations is contained in Table XI.

Table XI
Composition-Conversion Data for Chloroprene Methacrylamide-Copolymers

Charge Wt. % Methacrylamide	Conversion %	Polymer Composition Wt. % Methacrylamide
15	68	2.5
25	68	2.6
30	68	3.7
40	34	4.9
40	61	7.9
50	51	10.5
70	31	17.4

Most of the data are in conformity with the reactivity of 20 for chloroprene and 0.03 for methacrylamide. The deviations are apparent in Figure 4 in which the curves represent the theoretical average composition for 40 and 50 weight percent methacrylamide charges based upon the above reactivity ratios. The largest deviations appear at the higher conversions. These inconsistencies will be discussed in greater detail later; suffice it to say here that the reactivity ratios presented are the most reasonable values available.

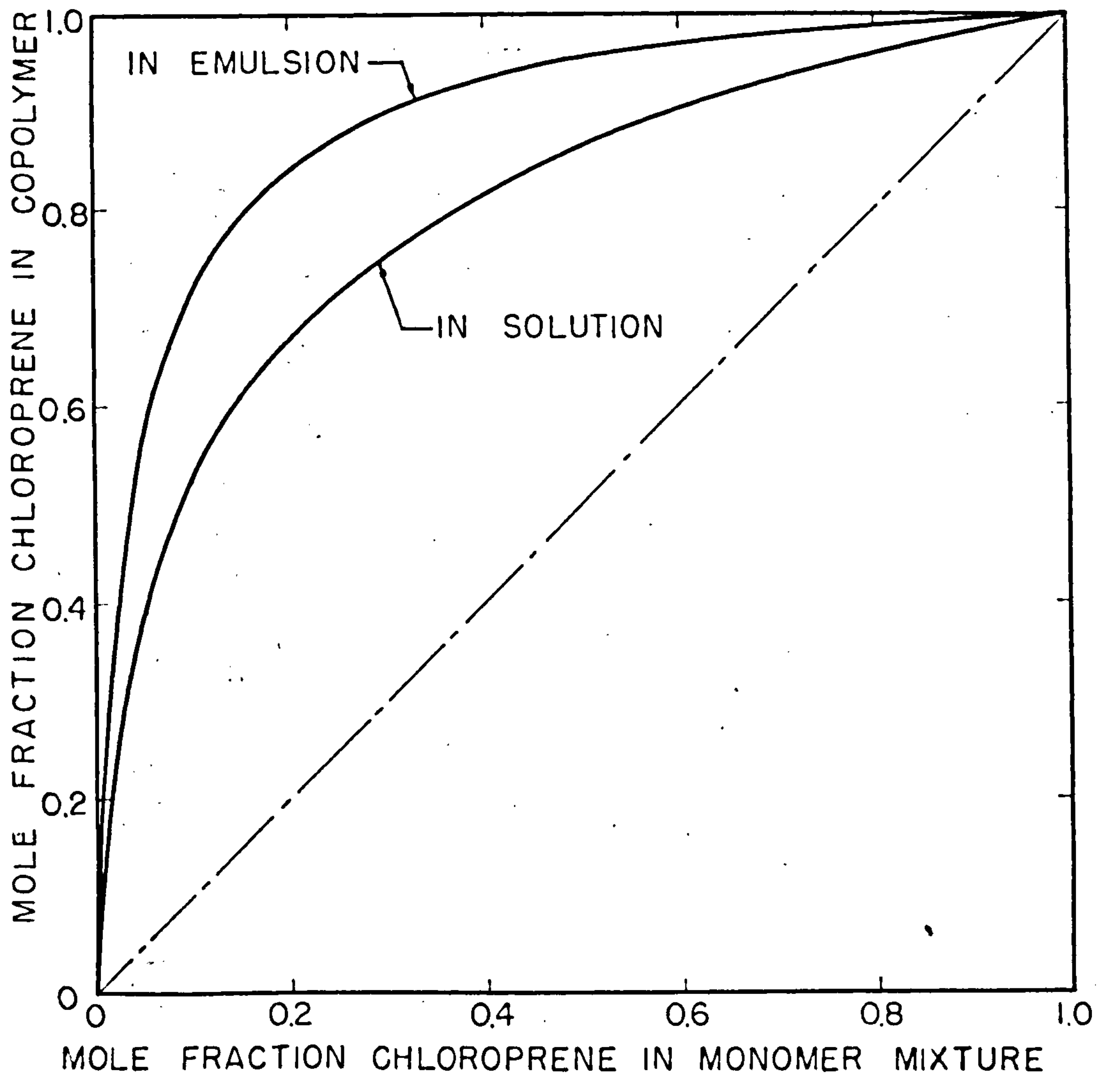
It should be noted that in this work reactivity ratios in emulsion have been interpreted following the treatment of Wall.(36) They differ from the corresponding ratios in bulk by the distribution coefficients of the monomers between the oil and aqueous phases and are consequently a function of the monomer-water charge ratio.

A determination of the bulk reactivity ratios was also undertaken. An obstacle was presented by the fact that methacrylamide is a solid, melting at 110°C. Bulk polymerization at high methacrylamide charges was not feasible.. Instead, the determination was made in solution in methyl ethyl ketone. No difference should exist between the values in bulk and in solution.(19,22) The choice of methyl ethyl ketone as solvent was dictated by solubility considerations. Considerable chain transfer with the solvent was probably involved; the polymers obtained were undoubtedly of lower molecular weight than emulsion analogs. However, chain transfer when not excessive has been shown to have little effect on relative reactivity of monomers.(5,34)

On the strength of the results obtained from this monomer

FIGURE 5

CHLOROPRENE - METHACRYLAMIDE
INSTANTANEOUS COMPOSITION CURVES



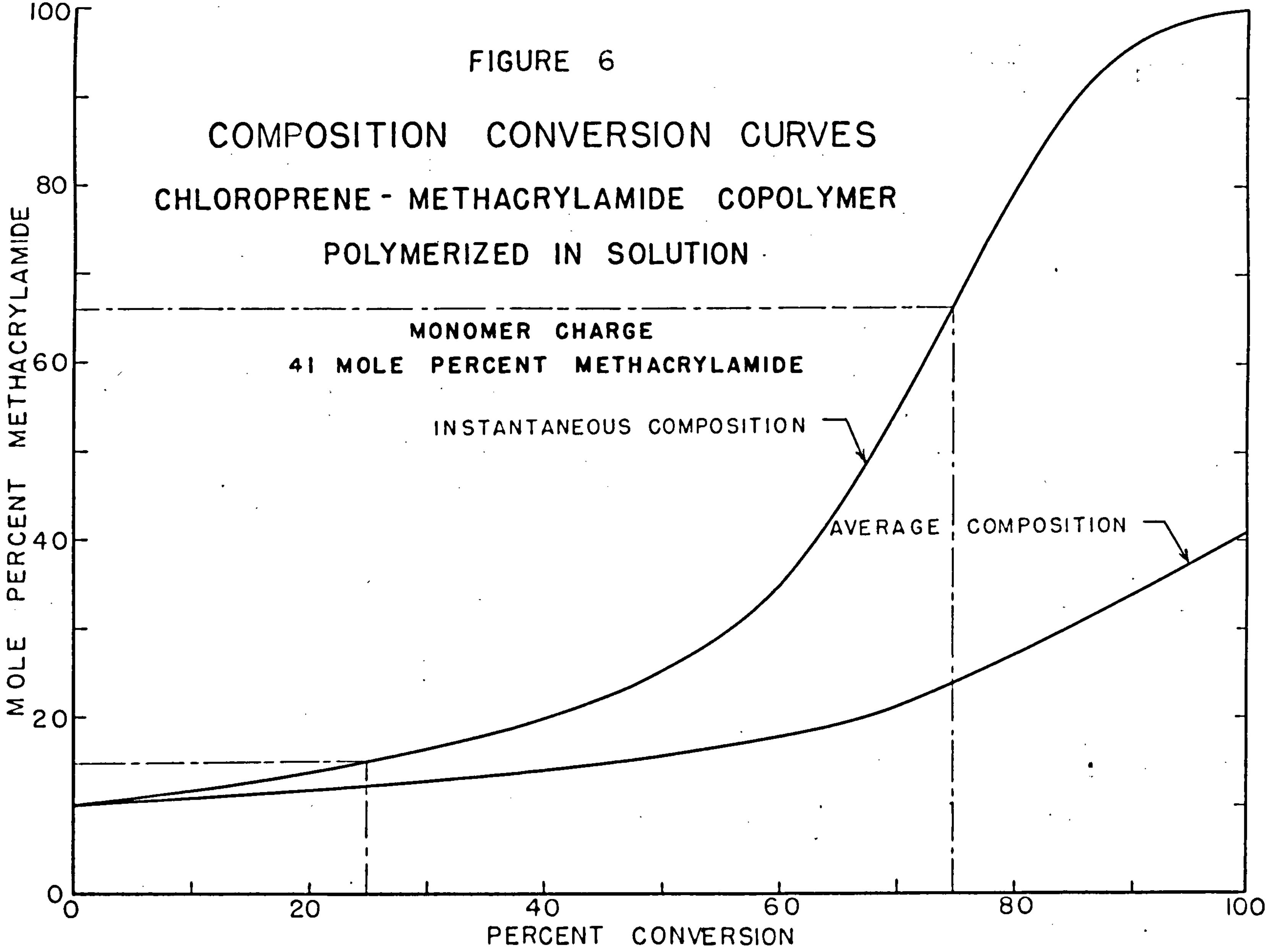


FIGURE 6

COMPOSITION CONVERSION CURVES

CHLOROPRENE - METHACRYLAMIDE COPOLYMER

POLYMERIZED IN SOLUTION

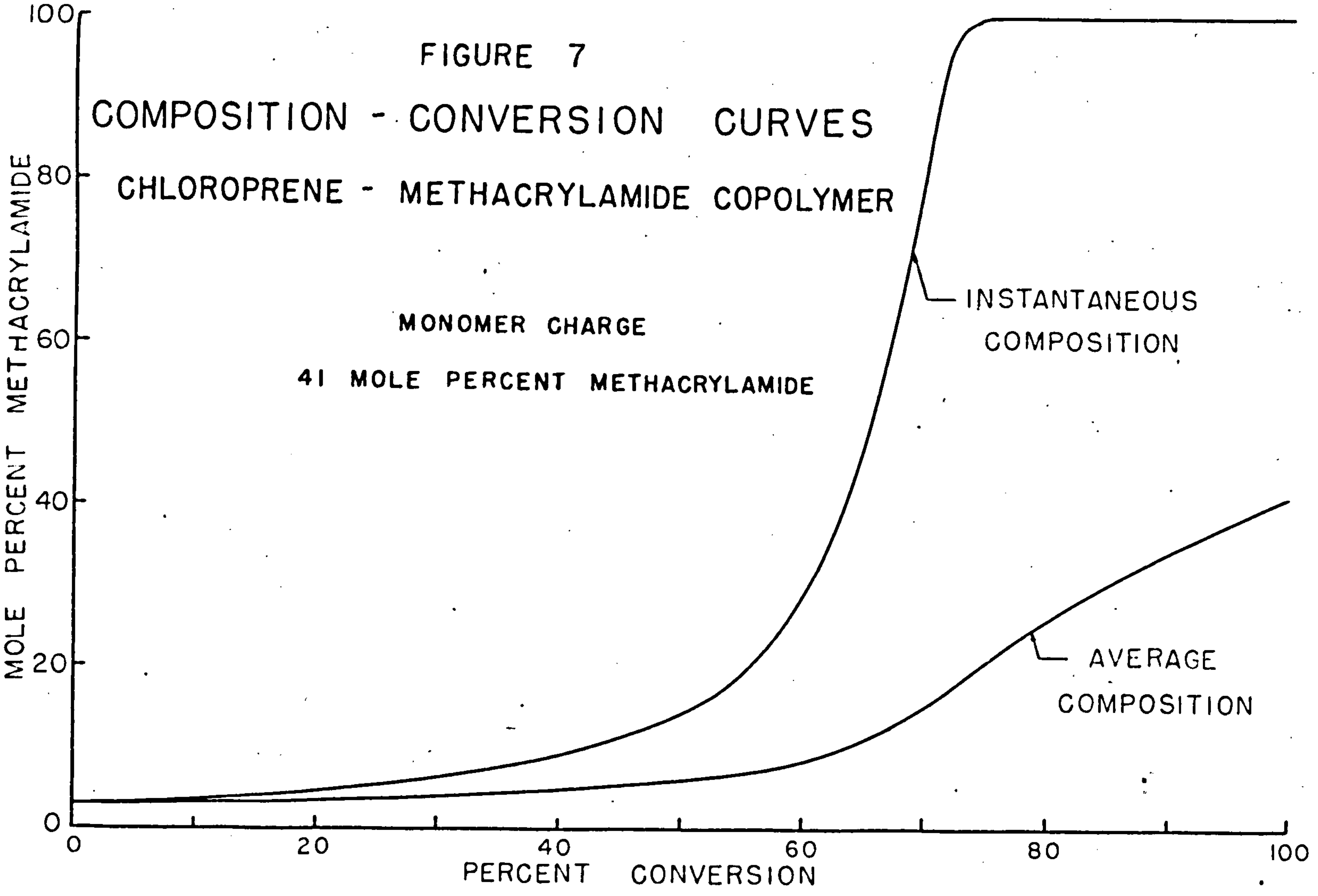


FIGURE 7

COMPOSITION - CONVERSION CURVES

CHLOROPRENE - METHACRYLAMIDE COPOLYMER

MONOMER CHARGE

41 MOLE PERCENT METHACRYLAMIDE

pair there is a considerably greater difference in reactivity in emulsion than in solution; this difference arises from the large water solubility of methacrylamide. In the comparison of the experimental results obtained it should be noted that part of the reactivity difference is due to the temperature difference; the low solubility of methacrylamide in methyl ethyl ketone at 30°C. prohibited investigation at this temperature in solution. Temperature effects have been discussed by Alfrey, et al;(3) increases in temperature have been shown to have a general levelling effect upon reactivity ratios.

The meaning of these reactivity ratios in terms of polymer compositions is described in the series of curves Figures 5-9. Figure 5 is a plot of mol fraction methacrylamide in the copolymer forming instantaneously as a function of mol fraction methacrylamide in the monomer. Both curves are typical reactivity curves for the case where one reactivity ratio is considerably more than unity and the other considerably less. No azeotropic composition exists.

In Figures 6 and 7 both instantaneous and average polymer compositions are plotted as a function of conversion. These curves aremore descriptive but are restricted to a particular monomer charge ratio. They were calculated from a charge ratio of 40 weight percent methacrylamide (41 mol percent) which was the charge most frequently employed. The curves of average copolymer composition versus conversion were calculated from the determined reactivity ratios using the following equations of Mayo and Lewis:

$$\frac{M_2}{M_2^\circ} = \left(\frac{M_1}{M_1^\circ}\right)^{\Omega} \qquad \Omega = \frac{r_2 \; M_2^\circ/M_1^\circ + 1}{r_1 + M_2^\circ/M_1^\circ}$$

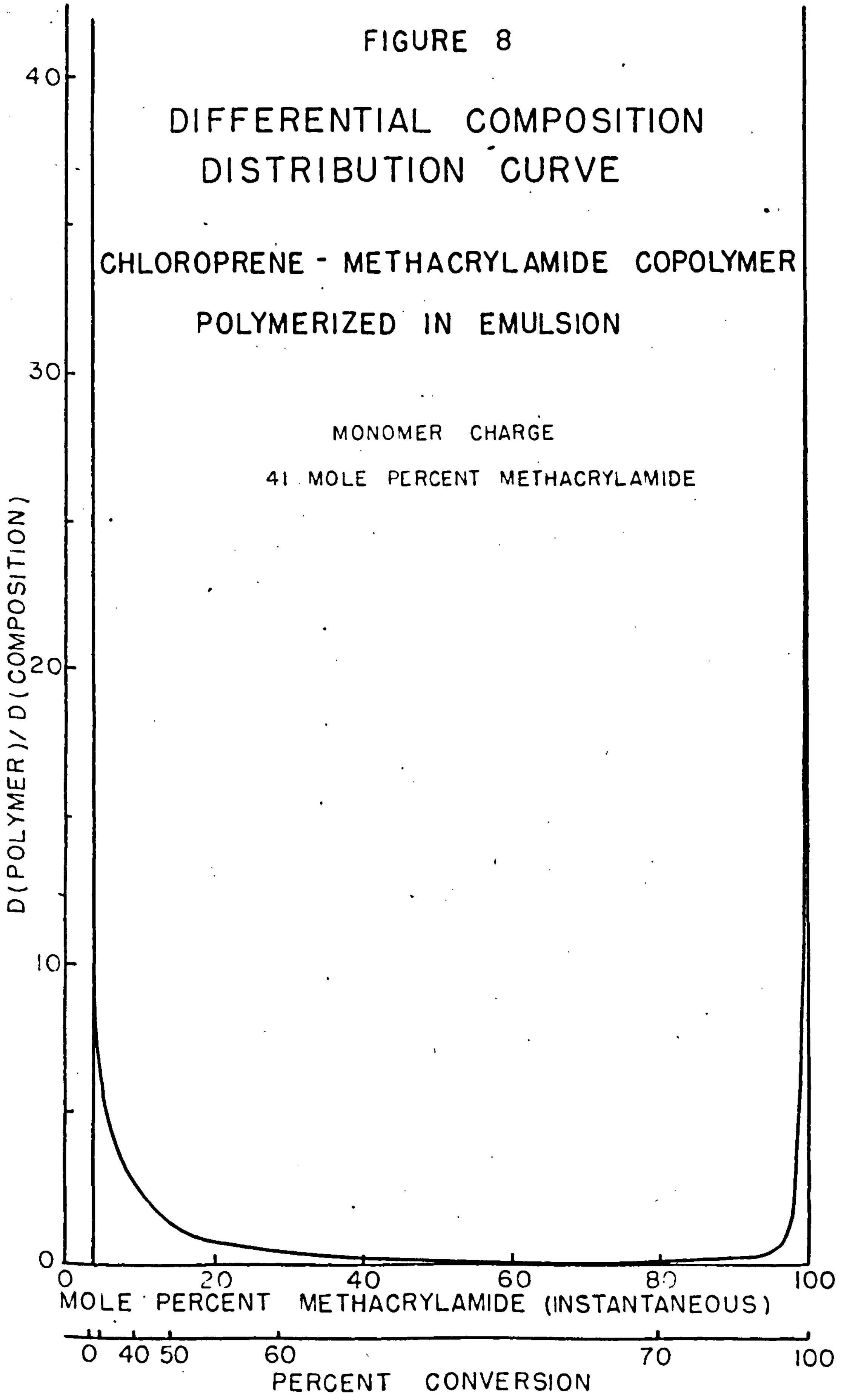


FIGURE 8

DIFFERENTIAL COMPOSITION DISTRIBUTION CURVE

CHLOROPRENE - METHACRYLAMIDE COPOLYMER POLYMERIZED IN EMULSION

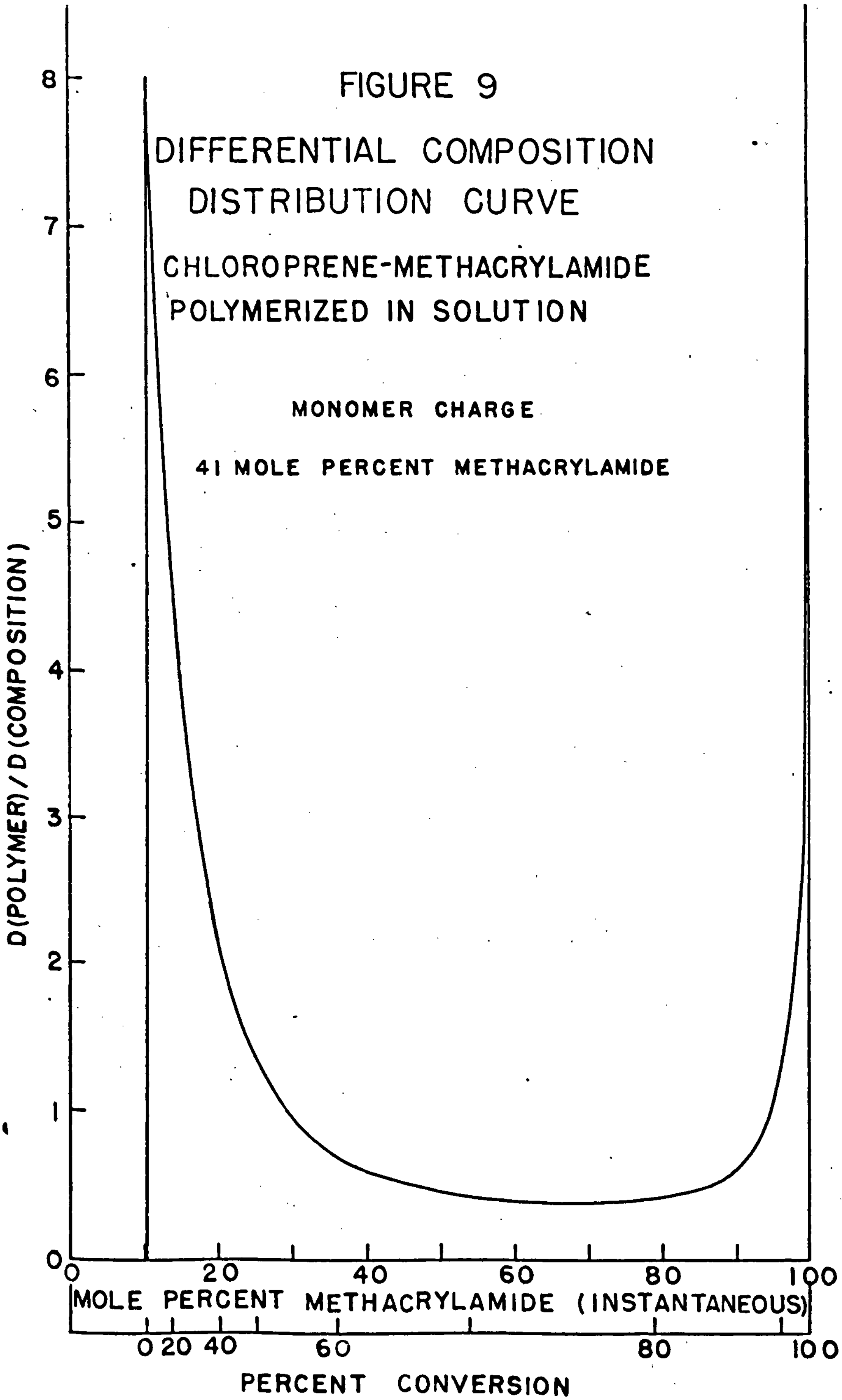


FIGURE 9

DIFFERENTIAL COMPOSITION DISTRIBUTION CURVE

CHLOROPRENE-METHACRYLAMIDE POLYMERIZED IN SOLUTION

In the case of the emulsion system this curve could have also been determined directly from experimental data.

The plot of composition of polymer forming instantaneously against conversion represents an integral distribution curve. It was found most expedient to determine this plot in the following manner. The data of the average composition curve can also be plotted in the form of moles of methacrylamide in the polymer (m_1) as a function of the moles of polymer ($m_1 + m_2$) for a given charge. The slope of this curve, $\frac{dm_1}{d(m_1 + m_2)}$ at any point represents the composition of the polymer forming instantaneously at the conversion corresponding to the abscissa of the point.

Integral distribution curves have been utilized by Skeist as an indication of copolymer heterogeneity.(32) The heavy dashed vertical lines indicate the portions of the curves that lie between 25 and 75 percent conversion. Skeist called the corresponding differences in copolymer composition the "interquartile ranges" and pointed out that they give a numerical measure of the dispersion of composition of the copolymer. This dispersion is poor in both cases; slightly better distribution is obtained in solution where the interquartile range is 15 to 66 compared with 5 to 99 in emulsion.

The distribution of composition is brought out more strikingly in the differential distribution curves, Figures 8 and 9. These are obtained by plotting the slopes of the integral distribution curves against instantaneous copolymer composition. The area under the differential distribution curve between any two instantaneous compositions represents the fraction of the monomer charge that has been converted to polymer of that composition range. For convenience, the corresponding conversion is plotted as an auxiliary axis. Like the integral distribution curves, these curves have also been plotted for a 41 mol percent methacrylamide charge. The distribution would be improved at higher methacrylamide charges.

The heterogeneity of the copolymer composition is also readily apparent in these curves. This is especially true for the emulsion copolymer where it will be seen that for a 60 percent conversion polymer roughly 1/3 of the polymer has a composition between 3 and 4-1/2 percent methacrylamide, another 1/3 between 4-1/2 and 9 percent, 1/6 between 9 and 14 percent, and the remaining 1/6 between 14 and 29 percent.

For further information on composition distribution it appeared reasonable to consider a fractional precipitation experiment. By proper choice of solvent and precipitant it was hoped that the polymer could be separated into fractions largely on a composition basis. The following data was obtained on the fractional precipitation of a 10 percent methacrylamide copolymer at 51 percent conversion prepared from a 50 weight percent methacrylamide charge. Out of 30 gms of polymer the following fractions were recovered:

Table XII
Fractional Precipitation Data for a Chloroprene-Methacrylamide Copolymer

Fraction No.	Weight	% Chloroprene by Titration	% Soluble	Intrinsic Viscosity
1	5.07	77.4	31	0.38
2	6.81	95.6	90	0.55
3	5.81	97.7	100	0.63
4	3.79	97.6	100	0.39
5	1.17	97.2	100	0.30

Relative reactivities for the chloroprene-acrylonitrile system have been published by Simha and Wall;(31) they list the following values which were found to hold in both bulk and emulsion:

$$r_C = 6.07 \pm 0.53 \qquad r_A = 0.01 \pm 0.01$$

Similar values but with a lower degree of precision were calculated from the emulsion polymers studied here. The values of $r_C = 5.0 \pm 1.0$ and $r_A = 0.02 \pm 0.02$ check within the limits of error of both sets of values.

Using the ratios experimentally obtained, integral and differential distribution curves were constructed by the procedures already discussed for a 40 weight percent acrylonitrile charge. Figures 12 and 13 show a composition distribution which is considerably better than the methacrylamide case. The polymer formed at the beginning of the reaction is believed to contain 15 mol percent acrylonitrile and an instantaneous composition of 100 percent is not indicated until 95 percent conversion. The indicated interquartile range is 24 to 75.

The differential distribution curve shows a reasonably good distribution up to about 50 percent conversion. A polymer at 60 percent conversion would be expected to have the following distributinn with composition; 1/3 of the polymer chains should be between 15-1/2 and 22 percent acrylonitrile; another 1/3 between 22 and 29; about 1/6 between 29 and 35; and the final 1/6 between 35 and 51 percent acrylonitrile.

The above data cannot be strictly compared to the differential distribution curve of Figure 8 which was plotted for a 40 weight percent methacrylamide charge; the corresponding 50 percent curve would have a slightly higher initial composition (4.8 percent) would contain 1/3 of the polymer between 4 and 5 percent methacrylamide and the high methacrylamide portion contains chains of higher methacrylamide content. The precipitation data indicated at least 35 percent of the polymer contains less than 3 percent methacrylamide. Although the titration results in general have not been considered to be accurate to more than ± 1 percent, it has been believed that the chloroprene contents have tended to be low rather than high. It is also true, however, that the chloroprene titration is the least accurate in the high chloroprene ranges so that the composition of fractions 3, 4 and 5 could all conceivably be between 95 and 96 rather than between 97 and 98 in which case the distribution would conform reasonably well with that predicted from relative reactivity considerations.

An alternative is to accept the precipitation data and re-examine the reactivity distribution and ratios. A considerably greater difference in monomer reactivity would be necessary to provide composition data conforming to the precipation data for the early portion of the polymerization; such ratios would be far from consistent with data at higher conversions. In other words it appears that the reactivity ratios shift during the course of the polymerization. At low conversion the chloroprene appears to be extremely reactive whereas the difference in reactivity appears to decrease as polymerization proceeds. This unusual shift in reactivity ratios may result from the shift in reaction locus.

At low conversion the micelles are considered to be the seat of reaction.(18) These micelles disappear before 20 percent conversion is attained; with their disappearance the locus of polymerization has shifted to the monomer polymer particles. This shift would occur gradually and would correspond roughly to the point where 1/3 of the polymer had been formed for a 50 percent conversion polymer. It is not inconceivable that the solubility of methacrylamide in the micelles would be less than in the monomer polymer particles. Hence as the locus shifts the emulsion reactivities could shift as a result of the change in distribution constant with the bulk reactivity still remaining constant.

$$r_{emulsion} = K_1 \, r_{bulk}$$

$$r_{emulsion} = K_2 \, r_{bulk}$$

Shifts of this type have been described by Wall in the polymerization of styrene with methyl methacrylamide.(36)

A further shift of polymerization locus may also occur when the chloroprene is nearly depleted. Some aqueous phase polymerization may occur early in the polymerization; it would be expected that the rate of polymerization here would be slow. As the chloroprene is consumed, the aqueous phase polymerization, although still of slow rate, could assume relative importance. The methacrylamide reactivity would be greater in the aqueous phase; another apparent shift in reactivity ratios could occur because a new distribution constant now applies. Some substantiation for this theory

Table XVI

Polymerization Data for Chloroprene-Acrylic Acid Copolymers

Wt % Acid Charged	Polym. Time, hrs.	Conversion	Wt % Acid in Polymer
33	8-1/2	57	5.8
	10-1/2	58	5.8
	12-1/2	60	6.5
37	8-1/2	56	---
	10-1/2	57	7.1
	12-1/2	57	7.7
45	6	49	3.1
	15	55	---
	23-1/2	55	10.0
55	6	42	---
	15	45	---
	23-1/2	45	11.5

Despite the inability to attain higher conversions in these recipes it was possible to exercise a limited degree of control over the polymer acid content by variation of charge ratio;polymers containing as much as 11.5 percent acrylic acid were obtained with a charge of 55 percent acid. It appears likely that most of this acid polymerizes later in the reaction; this is indicated by the significant difference in acid content, between the 49 and 55 percent conversions for the 45 percent acid charge.

Higher conversions and correspondingly higher acid contents are obtainable from these charges with the addition of 0.2 to 0.4 part of a reducing agent, sodium bisulfite, to the recipes described. Benefit can be gained from such a procedure, however, only if the additional conversion obtained is limited to a few percent; the instantaneous polymer composition is increasing rapidly in acrylic acid content in this range. If conversion is permitted to continue beyond this range, acrylic acid is polymerizing essentially by itself resulting in visibly heterogeneous polymers. The is provided by the observed large decrease in rate at the stage of the polymerization where most of the chloroprene should be consumed.

Although this solution polymer would at first contain some chloroprene content this polymer should be water soluble and not isolated from the emulsion by the usual coagulation techniques. It may well be that high conversion polymers are in reality polymers of higher conversions from which the high methacrylamide chains have been lost because of their water solubility. However, should some or all of these chains graft on to other polymer chains of considerable chloroprene content or if they crosslink between amide groups with the evolution of ammonia they should become a part of the coagulated polymer. A definite non-homogeneity of polymers of high conversion has been observed. In extreme cases this heterogeneous appearance is still detectable after milling. Small centers are apparent in the milled sheet which are only faintly rubbery; they do not appear to be pure methacrylamide (crosslinked) because of these slight but definite rubbery characteristics. Their presence and characteristics suggest grafting although the phase and manner in which this grafting occurs is not readily apparent.

On the basis of these discussions it appears that the chloroprene-methacrylamide copolymer is a heterogeneous mixture of chains of virtually no methacrylamide content formed early in the reaction of the micelles, chains of low methacrylamide content produced in the monomer-polymer particles, and chains of high methacrylamide content formed probably in the aqueous phase. In consideration of this description it becomes interesting to note whether a polymer of similar properties can be formed (1) by physical mixing of polymethacrylamide and polychloroprene, or (2) by grafting techniques. It was found that polychloroprene and polymethacrylamide are incompatible. Even prolonged milling leaves fine hard grains of polymethacrylamide scattered throughout the sheet. These grains have a crystalline appearance and do not resemble the slightly rubbery regions previously described in the high conversion copolymers.

Grafting, however produced polymers very similar to the copolymers. Methacrylamide contents of 3 to 9 were obtained after the addition of monomeric methacrylamide to a polychloroprene latex. The tensile strength, elongation and set of these grafted copolymers were the same as those exhibited by copolymers of the same composition. Grafting was not investigated extensively; reproducibility of conversions and composition appears more difficult by the grafting procedure.

B. Chloroprene-Acrylonitrile Copolymers

The chloroprene-acrylonitrile copolymers were studied in the composition range from 10 to 30 percent acrylonitrile. Polymerizations were conducted in emulsion at 30°C; the following is a typical recipe and is similar to that employed by Wagner:(35)

Redistilled water	150	gms
Triton X301 (emulsifier)	10	gms
Acetic acid	1	gms
Sulfur (modifier)	0.5	gms
Potassium persulfate (initiator)	0.6	gms
Monomers	100	gms

The acetic acid was incorporated in the recipe when it was observed experimentally that the rate of polymerization is faster in the acid range. In general the rate is slower than in the methacrylamide system and decreases with increasing acrylonitrile in the charge. Nine hours were required to attain a 64 percent conversion from a 27 percent acrylonitrile charge. Polymerization has been effected in the above recipe with the persulfate omitted but was considerably slower.

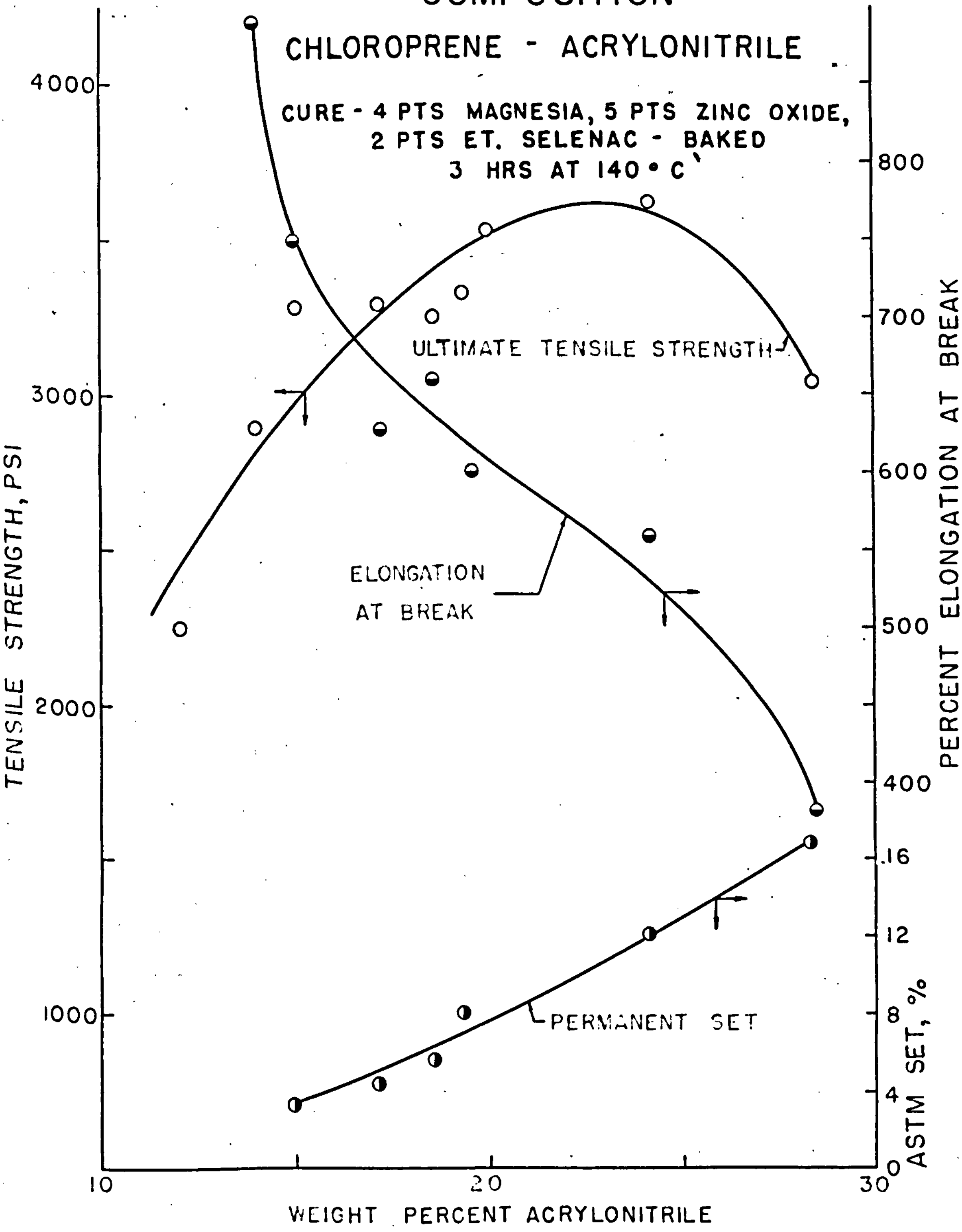
The best solvent for the polymer again proved to be cyclohexanone; methyl isobutyl ketone, chlorobenzene, butyl acetate, and toluene were also effective. In general these polymers were more rubbery than the chloroprene-methacrylamide copolymers and more soluble.

1. Variations of Physical Properties with Composition and Conversion

The free film physical properties of the chloroprene-acrylonitrile copolymers vary with both composition and conversion. Figure 10 shows the effect of composition upon tensile strength, elongation at break and permanent set. Tensile strength varies only

FIGURE 10

PHYSICAL PROPERTIES VERSUS COMPOSITION



slightly over the range of 15 to 25 percent acrylonitile with a possible peak at 24 percent. High acrylonitrile is definitely detrimental to both set and elongation. The permanent sets below 17 percent composition are very low but reach 17 percent at 28 percent acrylonitrile.

For a given monomer charge, conversion effects the composition and thereby the physical properties. With composition held constant and varying charge ratios, tensile strength increases with conversion within reasonable limits. This effect is illustrated in Table XIII.

Table XIII
Effect of Conversion upon Tensile Strength

% Acrylonitrile	Conversion, %	Tensile Strength, psi
14	38	1550
14	49	2170
14	68	2930
18	39	2140
18	49	2230
18	60	2480
18	70	2640

Elongation varies less significantly but permanent set rises abruptly at high (70 percent) conversions. The above polymers were all cured with 5 parts zinc oxide, 4 parts magnesia and 2 parts Ethyl Selenac and cured 3 hours at 140°C.

2. Effect of Modification and Milling

The chloroprene-acrylonitrile copolymers are sufficiently soluble with only sulfur modification, provided they are properly milled. These polymers form uniform, gel-free lacquers at 10 percent in cyclohexanone. A few polymers have been prepared employing 0.08 parts xylyl mercaptan in addition to the sulfur. A slight decrease in tensile strength was observed for these polymers for a 2.5 part mixed oxide cure (zinc and magnesium oxides).

Gel and intrinsic viscosity determinations were conducted on 17 percent acrylonitrile copolymers at several modification levels. As in the case of the chloroprene-methacrylamide copolymer these tests were run after milling with tetra methyl thiuram disulfide and show the characteristics of the polymer actually submitted to physical tests. Polymers modified with no mercaptan, 0.08 parts xylyl mercaptan and 0.16 part mercaptan all showed no gel and intrinsic viscosities at 25°C. of 1.04, 0.82 and 0.44 respectively.

3. Curing

The pure gum cholroprene-acrylonitrile copolymer baked without curing agent has a tensile strength less than 1000 psi at several compositions studied. Mixed oxide loadings ranging from 2 to 10 parts effect an increase of at most 400 psi. Considerable improvement is apparent, however, when an accelerator was added to the formulation. The following represent some of the result obtained with accelerated cures on a 19 percent acrylonitrile copolymer modified with 0.5 parts sulfur and 0.08 parts xylyl mercaptan; a bake of 3 hours at 140°C. was employed.

Table XIV
Accelerated Chloroprene-Acrylonitrile Cures

Oxide	Acc.	T.S.	Elong.	Set
Control	--	640	800	19
2.5 MgO 2.5 PbO	--	700	935	12
4 MgO 5 ZnO	1 Ethyl Zimate	2260	570	22
"	0.75 Cumate	2170	740	12
"	0.75 Cumate + 2.5 Sulfur	2570	720	16
"	1 Permalux	2190	510	21
" "	1 Permalux + 2.5 Sulfur	2480	680	13
"	2 Ethyl Selenac	2570	680	17

The Ethyl Selenac functioned as well with or without sulfur; Cumate and Permalux provided comparable results only with the addition of sulfur.

Polyhydroxy aromatics also proved to be effective curing agents, particularly phloroglucinol which exhibited a tensile strength of 3500 psi without black. The 6 parts Zimate, 2 parts magnesia, 2 parts sulfur cure previously discussed for the methacrylamide copolymer gave results roughly comparable to the Ethyl Selenac-mixed oxide cure.

4. Reinforcement

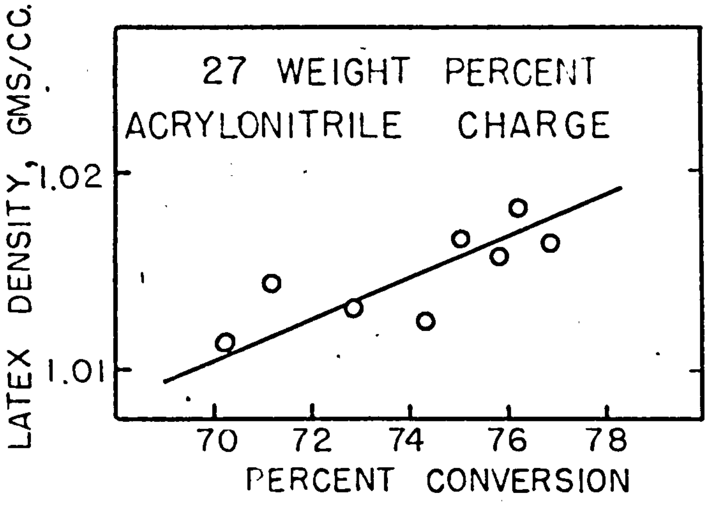
Reinforcement with carbon black adds to the tensile strength considerably; at high loadings it is detrimental to both elongation and set. This effect is well illustrated by the data of Table XV which was obtained for an 18.5 percent acrylonitrile copolymer at 63 percent conversion and modified only with 0.5 part sulfur. The curing agent employed was 8 parts phloroglucinol and the films were baked 2 hours at 120°C. The carbon black employed here was a hard processing channel black. These tensile strengths were the highest obtained with this copolymer.

FIGURE 11

DENSITY - CONVERSION CURVES

CHLOROPRENE - ACRYLONITRILE COPOLYMERS

30 ° C



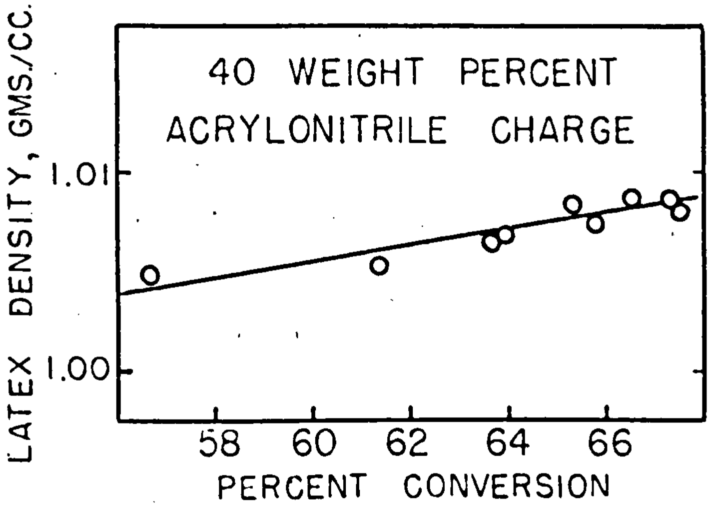


Table XV
Effect of Carbon Black Reinforcement upon Free Film Physical Properties

Parts Black	T.S. psi	Elong. %	Set
0	3130	650	5
2	3600	700	7
5	3740	700	7
10	3920	610	8
20	4650	580	10
25	4690	470	10

5. Density-Conversion Curves

Time alone is not a dependable standard for reproducing conversions from a given charge. The latices of the chloroprene-acrylonitrile copolymers are sufficiently free from precoagulation, however, that density and refractive index techniques are applicable. A typical density-conversion curve is shown in Figure 11 for a 40 percent acrylonitrile charge.

It is worthy of note that although a reasonable control of conversion is possible by this method complete control over composition is difficult to achieve. This difficulty arises from the nature of the polymerization: chloroprene polymerizes much more rapidly than acrylontrile so that the acrylonitrile content does not vary appreciably with conversion until most of the chloroprene has been polymerized. At conversions beyond this point a few percent difference in conversion represents an appreciable change in composition.

6. Nature of the Copolymer

Copolymer homogeneity was not investigated as extensively for the chloroprene-acrylonitrile copolymer as for the methacrylamide polymer. There is reason to believe that although the copolymer chains vary considerably in composition, the composition distribution is better than in the methacrylamide case.

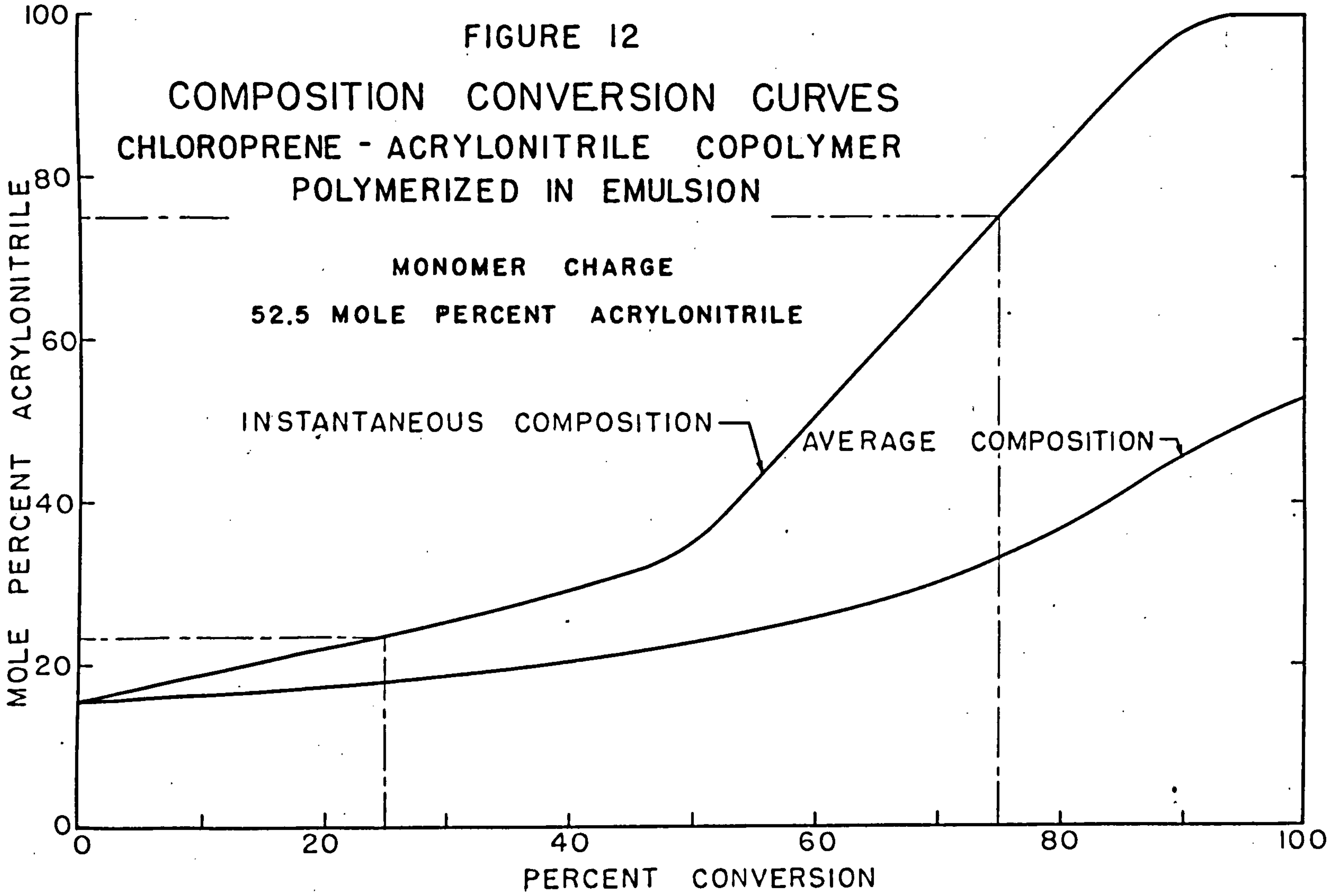


FIGURE 12

COMPOSITION CONVERSION CURVES
CHLOROPRENE - ACRYLONITRILE COPOLYMER
POLYMERIZED IN EMULSION

MONOMER CHARGE
52.5 MOLE PERCENT ACRYLONITRILE

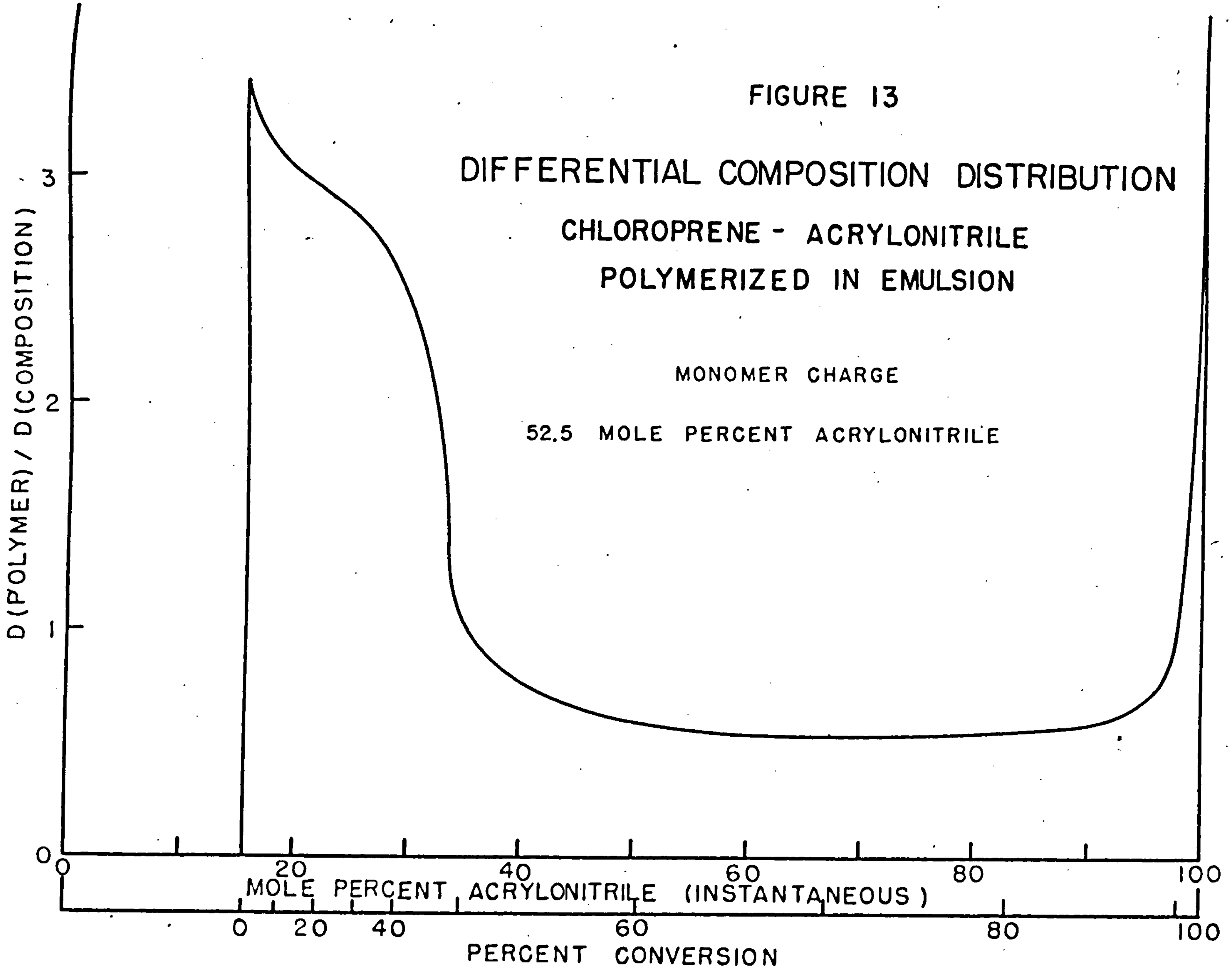
FIGURE 13

DIFFERENTIAL COMPOSITION DISTRIBUTION

CHLOROPRENE - ACRYLONITRILE
POLYMERIZED IN EMULSION

MONOMER CHARGE

52.5 MOLE PERCENT ACRYLONITRILE



Relative reactivities for the chloroprene-acrylonitrile system have been published by Simha and Wall;(31) they list the following values which were found to hold in both bulk and emulsion:

$$r_C = 6.07 \pm 0.53 \qquad r_A = 0.01 \pm 0.01$$

Similar values but with a lower degree of precision were calculated from the emulsion polymers studied here. The values of $r_C = 5.0 \pm 1.0$ and $r_A = 0.02 \pm 0.02$ check within the limits of error of both sets of values.

Using the ratios experimentally obtained, integral and differential distribution curves were constructed by the procedures already discussed for a 40 weight percent acrylonitrile charge. Figures 12 and 13 show a composition distribution which is considerably better than the methacrylamide case. The polymer formed at the beginning of the reaction is believed to contain 15 mol percent acrylonitrile and an instantaneous composition of 100 percent is not indicated until 95 percent conversion. The indicated interquartile range is 24 to 75.

The differential distribution curve shows a reasonably good distribution up to about 50 percent conversion. A polymer at 60 percent conversion would be expected to have the following distributinn with composition; 1/3 of the polymer chains should be between 15-1/2 and 22 percent acrylonitrile; another 1/3 between 22 and 29; about 1/6 between 29 and 35; and the final 1/6 between 35 and 51 percent acrylonitrile.

C. Chloroprene-Acrylic Acid Copolymers

The chloroprene-acrylic acid copolymer system was investigated to a limited extent only. Two factors were responsible for this: (1) the difficulty encountered in obtaining a homogeneous copolymer of reasonable acrylic acid content; and (2) the relative insolubility of the polymer. Whereas polymers have been prepared and studied over a wide range of composition, the product at higher acrylic acid levels was visible heterogeneous and of high gel content. A comprehensive study of polymerization and curing variables was not possible.

1. Polymerization Techniques

Polymerizations conducted using recipes similar to those employed with the other chloroprene copolymers were found to be limited in the conversions attainable. Charges of 33, 37, 45 and 55 weight percent acrylic acid were studied in the following recipe at 30°C:

Redistilled water	200 parts
Triton X301(emulsifier)	9.10 parts
Sulfur (modifier)	0.288 parts
Potassium persulfate (initiator)	.362 parts
Monomers	100 parts

In all cases conversion ceased at a point corresponding roughly to the percent chloroprene charged. This conversion was achieved in less than 6 hours; only a few percent was added to the conversion with extended polymerization times up to 24 hours.

Table XVI
Polymerization Data for Chloroprene-Acrylic Acid Copolymers

Wt % Acid Charged	Polym. Time, hrs.	Conversion	Wt % Acid in Polymer
33	8-1/2	57	5.8
	10-1/2	58	5.8
	12-1/2	60	6.5
37	8-1/2	56	---
	10-1/2	57	7.1
	12-1/2	57	7.7
45	6	49	3.1
	15	55	---
	23-1/2	55	10.0
55	6	42	---
	15	45	---
	23-1/2	45	11.5

Despite the inability to attain higher conversions in these recipes it was possible to exercise a limited degree of control over the polymer acid content by variation of charge ratio; polymers containing as much as 11.5 percent acrylic acid were obtained with a charge of 55 percent acid. It appears likely that most of this acid polymerizes later in the reaction; this is indicated by the significant difference in acid content, between the 49 and 55 percent conversions for the 45 percent acid charge.

Higher conversions and correspondingly higher acid contents are obtainable from these charges with the addition of 0.2 to 0.4 part of a reducing agent, sodium bisulfite, to the recipes described. Benefit can be gained from such a procedure, however, only if the additional conversion obtained is limited to a few percent; the instantaneous polymer composition is increasing rapidly in acrylic acid content in this range. If conversion is permitted to continue beyond this range, acrylic acid is polymerizing essentially by itself resulting in visibly heterogeneous polymers. The conversion control required is difficult to achieve because of the rapid polymerization rate in this critical region; for this reason the bisulfite technique is not considered practical.

Because of the apparent extreme reactivity difference between chloroprene and acrylic acid the only reasonable method of achieving a comparatively homogeneous copolymer is with an extremely high acrylic acid charge ratio. To circumvent the correspondingly low conversion that would be obtainable without bisulfite by such a procedure, step-wise addition of chloroprene has been employed. A moderate degree of success has been achieved with such techniques. Polymers up to 15 percent acrylic acid content have been obtained from initial charge ratios of 58 to 80 percent acrylic acid with the addition of chloroprene in additional portions at intervals of one to several hours. This technique, however, suffers from the disadvantage of rendering polymer duplication difficult.

Table XVII
Chloroprene-Acrylic Acid Copolymers Prepared with Step-wise Addition

	A	B	C	D	E
Parts chloroprene charged	20	25	20	20	15
Parts acrylic acid charged	42	35	42	50	55
1st chloroprene addition, parts	19@2 hrs.	20@1-1/2hrs.	38@2hrs.	40@2hrs.	15@4hrs.
2nd chloroprene addition, parts	19@3 hrs.	20@3 hrs.	--	--	15@8hrs.
Total time	6 hrs.	5	4	4	23
Conversion	61	66	57	35	47
% acid in polymer	15-1/2	10	10	11	15

2. Polymer Solubility

The chloroprene-acrylic acid copolymers showed an appreciable gel content. Cyclohexanone, dioxane, and toluene were found to be the best solvents for the polymer; even in these solvents gel-free solutions are difficult to obtain. Modification with dodecyl mercaptan in amounts up to 0.14 parts on the monomer is effective in reducing the gel but does not completely eliminate it except at low conversion. A copolymer polymerized with 0.07 part mercaptan was prepared from a total charge ratio of 50 weight percent acrylic acid using step-wise addition of chloroprene; at 35 percent conversion a neglible gel content was observed.

3. Physical Properties of Cured Polymers

It has not been possible to correlate polymer composition with physical properties because gel-free films have not been obtained at all compositions. By comparison with the optimum carboxyl content of the C-MA copolymers it has been calculated that the highest physical properties should be obtainable in the vicinity of 11.5 weight percent acid. The highest experimental properties were actually obtained at this composition but gel-free film data at other compositions were too sparse to verify this speculation or to establish a range of optimum composition. Table XVIII lists the film properties obtained at various compositions with a 1 part magnesia cure and a bake of 2 hours at 120°C.

Table XVIII
Chloroprene-Acrylic Acid Copolymer
Composition and Physical Properties

Wt % Acid in Polymer	Tensile Strength, psi	Elong. at Break, %	ASTM Set	Remarks
8	2560	940	20	Gel-free
10	2010	950	21	Gel particles
11	3500	850	14	Gel-free
12	2910	1000	12	Gel-free
13	2250	1190	21	Gel particles
14	1860	1170	20	Gel particles
15	1550	1010	20	Gel particles

The most effective cure has been shown to be 6 parts Ethyl Zimate, 2 parts magnesia, and 2 parts sulfur. A free film cured with this system and baked for 2 hours at 120°C. showed the following properties: tensile strength, 5230 psi; elongation at break, 680 percent; ASTM permanent set, 15 percent. This film was prepared from the 35 percent conversion, gel-free polymer described earlier; it was polymerized using 0.07 part dodecyl mercaptan with step-wise addition of chloroprene; the polymer acid content was 11 percent. The importance of gel-free films cannot be over-emphasized. The identical cure applied to a film containing visible gel produced a tensile strength of only 3290 psi; this polymer contained 14 percent acid at 85 percent conversion.

III. Experimental

A. Polymer Preparation

Monomeric chloroprene was obtained as a 50 percent xylene solution from E.I. du Pont de Nemours and Company; it was distilled at 220 to 280 mm pressure immediately before use. The acrylonitrile was an American Cyanimide product and was also distilled under vacuum before use. Rohm and Haas pilot plant methacrylamide monomer was received without inhibitor but was purified before charging by recrystallization from methyl ethyl ketone. The acrylic acid was also a Rohm and Haas product; it was obtained as a 60 percent aqueous solution and was fractionated before use. Because pure acrylic acid polymerizes readily even during vacuum distillation the product was collected as a 70 percent to 80 percent aqueous solution and titrated for actual acrylic acid content before charging.

Polymerizations were conducted in 6 ounce crown cap glass bottles fitted with screw caps. Components were charged in the following order: emulsifier solution prepared from redistilled water and Triton X301; acetic acid (chloroprene-acrylonitrile polymers only); vinyl monomer; chloroprene; mercaptan. Monomer charging was conducted at -10°C. to prevent chloroprene volatilization. The bottles were then warmed to polymerization temperature and sulfur and initiator added at zero time. For polymerization the bottles were rotated end-over-end at 30 rpm in a thermostatted water bath at 30°C. Where possible, conversions were followed from pre-determined latex density curves or latex refractive index curves.

Upon removal from the bath, the latices were short-stopped with an emulsion containing 5.8 parts hydroquinone, 5.8 parts tetramethyl thiuram disulfide, 5.3 parts Triton X301 and 100 parts distilled water; 1 cc was added for each 5 gms of monomer charged. Latices were coagulated with a saturated solution of sodium sulfate or sodium chloride, washed thoroughly with water at 40-50°C. and dried *in vacuo* at 40 to 50°C. to constant weight. Drying required 24 to 48 hours; the process was hastened by occasional passes through a rubber mill to expose fresh surface. Conversion was calculated from the dry polymer weight.

One part phenyl beta naphthylamine was added to the dry polymer on the rubber mill for stabilization; 0.5 to 2.5 parts tetramethyl thiuram disulfide was also added at the same time.

B. Free Film Preparation; Curing

Lacquers were prepared by ball milling with flint balls at 10 to 15 percent in cyclohexanone or mixed cyclohexanone and methyl isobutyl ketone. For the formaldehyde curing studies, toluene lacquer solutions were employed. Complete solution required from several days to several weeks depending upon the polymer composition and degree of modification.

The physical tests, tensile strength, elongation, and permanent set were conducted on free films from 3 to 5 mil s in thickness poured from these lacquers. Solid curing agents were dissolved in a minimum of appropriate solvent and added to the lacquers shortly before use. Metal oxides were prepared as 1 to 2 percent slurries in the same solvent as used in the lacquer. These were also prepared on the ball mill and were added to the lacquers immediately before use. To eliminate bubbles in the dried films, the lacquer solutions were placed under vacuum after stirring in order to remove the bubbles.

Films were poured on 3in x 6in carefully levelled glass plates and allowed to dry a minimum of 48 hours before curing by oven bake. After curing, the films were removed from the glass plates and cut into 1/4in strips for physical testing. Before test the strips were conditioned a minimum of 48 hours at 21°C. and 65 percent relative humidity.

C. Physical Testing

Ultimate tensile strength was determined with a Scott IP4 inclined plane tester and was computed from the measured cross-sectional film area before stress. Because of excessive film slippage, elongation at break could not be determined on this instrument; instead films were pulled to destruction by hand and the elongation at break checked visually with a steel rule. Permanent set was measured according to ASTM procedure (6) which specifies 10 minutes stretch at 300 percent elongation, and 10 minutes relaxation. The deformation expressed as a percent of the original length is defined as the permanent set. Ultimate tensile strengths were computed as the average strength of 10 individual strips; percent elongation at break and permanent set were each the average of four individual strip results.

D. Determination of Percent Gel and Intrinsic Viscosity

Percent gel was measured by placing 0.5 grams of polymer, accurately weighed and finely divided, upon 100 mesh stainless steel trays in 100 cc of distilled cyclohexanone.The solutions were circulated every 24 hours for five days. At the end of this period, a 10 cc sample was removed by a pipet tipped with cotton and the solids content of this aliquot determined by evaporation and drying *in vacuo*.

The percent gel, i.e. the percent insoluble, could be obtained in this manner.

The gel test solutions being of known concentration could be conveniently employed for intrinsic and inherent viscosity determination. Viscosities were measured at 30°C. with a #100 Ostwald viscometer. Intrinsic viscosity was then computed from the expression:

$$\eta = \lim_{c \to 0} \frac{1}{c}\left(\frac{t}{t_o} - 1\right)$$

where η is the intrinsic viscosity, c is the concentration in gms per 100 cc, t is the time observed from the polymer solution and t_o the observed time from the pure solvent in units consistent with t.

E. Polymer Analysis

In so far as chloroprene was a common monomer in all the copolymers prepared chlorine analysis was used as a convenient method for determination of composition. A finely divided .15 gm sample was fused in a Parr bomb with 15 gms sodium peroxide using 0.1 gm sucrose and 0.5 gm benzoic acid as initiator. Chloride was determined in the acidified fusion mass by the classical Volhard technique. It was found that complete fusions could be achieved by covering any protruding rubber pieces in the bomb charge with a layer of sodium peroxide and by resorting to flame ignition.

Titrations were observed to be consistently 2 percent low in chloroprene content; pure poly chloroprene prepared with no added short stop or antioxidident titrated only 98 percent chloroprene. Consistent errors in the elementary analysis of polymers are not unusual; for example, the nitrogen content of poly acrylonitrile is consistently found to be lower than expected.(1) To compensate for the consistent error in analysis here, 2 percent has been added to the titrated chloroprene content.

F. Fractional Precipitation

The fractional precipitation of the chloroprene-methacrylamide copolymer was conducted according to the conventional procedures.(12,20) Fifteen hundred milliliters of a 2 percent polymer solution in distilled cyclohexanone was prepared and a precipitant comprising a 1:1 toluene-methanol mixture was added slowly with stirring at room temperature. Addition was halted when a reasonable fraction had been precipitated as judged from the cloudiness of the solution. The mixture was then heated with stirring until solution was again complete and cooled slowly with stirring over 1 to 2 hours. After settling over night the mother liquor was decanted, the gel mass dissolved in fresh cyclohexanone, and precipitated by pouring into excess methyl alcohol. Fractions were dried to constant weight in vacuo at 40-50°C. In a similar manner, several cuts were obtained.

G. Low Temperature Flexibility

Free film strips of 1/4 inch width were stamped with 1 inch markings; stretched to 250 percent elongation, and clamped to a metal rule. The assembly was conditioned 10 minutes at -65°C. in a methanol dry ice bath in an unsilvered Dewar flask. The top clamp was then released and the temperature raised at the rate of 1 degree per minute. Temperature rise was controlled by the heat of an ordinary incandescent lamp. The length of the specimen was recorded at temperature intervals of 2 degrees.

IV. Summary

Copolymers of chloroprene and methacrylamide, chloroprene and acrylonitrile, and chloroprene and acrylic acid have been prepared in persulfate initiated emulsion systems at 30°C. Ketones, particularly cyclohexanone, are the best solvents for these systems. Vulcanizates of these copolymers have been shown to be superior to neoprene in ultimate tensile strength while possessing comparable elongation at break and permanent set. Neoprene shows better low temperature flexibility.

(1) Chloroprene-methacrylamide copolymers have been prepared over a range of composition from 0 to 30 percent methacrylamide; highest tensile strengths were observed in the vicinity of 10 percent. Modification with both sulfur and tertiary dodecyl mercaptan is necessary to obtain soluble polymers; satisfactory cures are obtainable with metal oxides, dithio-carbamates, or polyhydroxy aromatics. Highest results have been obtained with 6 parts Ethyl Zimate, 2 parts sulfur and 2 parts magnesia employing a bake of 2 hours at 120°C. Room temperature curing is also feasible. No improvement is effected with carbon black.

Relative reactivity ratios have been determined for this system as follows: in solution at 50°C., $r_c = 5.5 \pm 1.0$, $r_m = .05 \pm .05$; in emulsion at 30°C., $r_c = 20 \pm 10$, $r_m = .03 \pm .03$. The emulsion copolymer is heterogeneous in nature; the methacrylamide does not enter the polymer to an appreciable extent until late in the polymerization.

(2) The chloroprene-acrylontrile copolymers have been prepared in compositions from 10 to 30 percent acrylonitrile. Good solubility

can be obtained with sulfur modification alone. The most effective curing systems have been found to be polyhydroxy aromatics, or mixed oxides accelerated with dithiocarbamates. Highest tensile strengths are obtainable at 25 percent acrylontrile; considerable reinforcement can be effected with carbon black up to 25 parts.

The copolymer is considerably more homogeneous than the chloroprene-methacrylamide; chloroprene is still the more reactive monomer and predominates in the chains formed early in the reaction.

(3) The chloroprene-acrylic acid system has been investigated to a limited extent only. Polymers have been prepared containing from 0 to 60 percent acrylic acid; above 12 percent acid the polymers are visibly heterogeneous unless prepared with step-wise addition of chloroprene. High gel contents are observed except in the instances of low conversion polymers prepared with both sulfur and mercaptan modification. Effective cures are obtainable with metal oxides alone or with metal oxides in conjunction with sulfur and a dithiocarbamate accelerator.

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