Vinyl Polymers Containing Acidic Ingredients

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production constantly changing here, as well as in many other regions around the world, evaluation and interpretation of these changes constitute a continuing challenge to the geographer.

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THE NATURE AND PROPERTIES OF TANNINS

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ABSTRACT

Tannins, amorphous substances found in special vacuoles in the cell sap of plants, are present in the roots, bark, stems, and seeds. They are soluble in water, colloidal in nature, and characterized by an astringent taste. The chemical nature of tannins has been investigated from both the standpoint of analysis and of synthesis. Reports of results were misleading because though workers referred to specific tannins they apparently were unaware that the term tannin should be used only generically. Tannins are very specific substances which are most accurately referred to by naming the exact source of the tannin as oak tannin, wattle tannin, or *Hypericum* tannin. Since the introduction of chromatographic technique in 1949, definite advances have been made in the study of tannins. Through this means it was discovered that tannins are polymeric mixtures and not polymeric molecules.

To demonstrate the nature of tannins as revealed by paper chromatography slides were shown of studies made of extracts from tropical plants. Two-dimensional chromatograms most clearly demonstrated the complex nature of tannins.

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VINYL POLYMERS CONTAINING ACIDIC INGREDIENTS
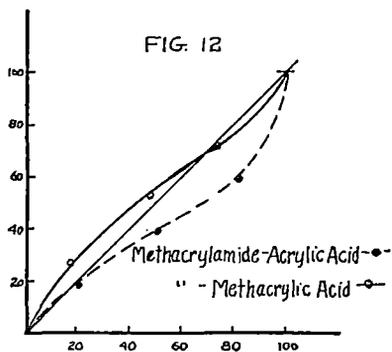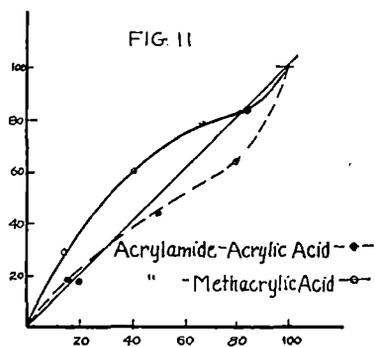
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The polymers observed in this research are typical products obtained by the free radical polymerization of active vinyl monomers. A monomer such as acrylic acid, $CH_2 = CHCOOH$, or more generally a vinyl monomer represented as $CH_2 = CHY$, has been shown to polymerize predominately in a head-to-tail fashion to give a macro molecule,—CH_2—CHY-CH_2-CHY-CH_2-CHY—. It is evident that head-to-head, tail-to-tail, and the mentioned head-to-tail mode of attachment might all occur, but polar factors rather than random distribution control the process to give the directed type of polymer pictured above. Other variations might be molecular weight distribution, chain branching, and similar factors which complicate the study of polymers.

Simultaneous polymerization of two different monomers creates more variables which must be considered. The simplest possibility would be the polymerization of the two monomers to give a product of uniform composition (even though of variable molecular weight) equal to the monomer charge. Such a polymerization is seldom encountered. It normally is true that the monomers enter the polymer in a ratio different from that of the monomer charge, thus giving rise to a polymeric product whose composition gradually changes during the polymerization. Much research has been conducted in this field of copolymerization to determine the tendency of monomers to copolymerize with one another and to determine the "monomer activity". In an excellent review, Mayo and Walling, 1950, develop the mathematical expression for the copolymerization equation. This gives the relationship of the instantaneous polymer in terms of monomer concentration and the monomer reactivity ratios. This mathematical analysis of copolymerization has led to a much better understanding of the copolymerization process. To a limited extent it allows prediction of the nature of the polymer which might be expected from two monomers whose reactivities are known.

Three extreme types of copolymerization are theoretically possible. The *ideal* type is that in which the relative reactivities of the two monomers are the same towards both free radicals based on the two monomers. Monomer units will be arranged at random along the polymer chain in relative amounts determined by the feed (but modified in practice by the relative reactivities of the two monomers, which usually differ from the ideal values). In the *alternating* copolymer, each radical prefers to react exclusively with the monomer of the other type and the monomer units alternate regularly along the chain. In general, known copolymerizations lie between these extremes; one monomer of a pair is more reactive than the other but there is also a tendency for the monomers to alternate to some extent. Lastly, *independent* polymerization represents the possibility that each type of radical will react preferentially only with the corresponding monomer. No true example of this type is yet known.

A great many monomer pairs have been reported in the literature and data are availabe to correlate the instantaneous polymer composition versus the monomer ratio. It is surprising that very few copolymers containing acidic ingredients have been studied. Figures 1-6 represent polymerization curves of a number of monomer pairs. The diagonal line represents the theoretical curve for polymers of the same composition as the monomers from which they were prepared. It is evident that the polymers differed appreciably from the composition of the corresponding charge.

Figure 1 gives the data of Fordyce and Ham, 1947, for the styrene-itaconic acid pair. It will be noted that the itaconic acid initially is very rich in the polymer. At a value of about 45 mole per cent of acid an "azeotrope" (so named because of the similarity to a distillation curve) is encountered at which the polymer should uniformly have

FIG. 7
Methy Acrylate-Acrylic Acid-•-
    " -Methacrylic Acid -○-

FIG. 8
Methyl Methacrylate-Acrylic A.-•-
    " -Methacrylic A.-○-

MOLE % ACID IN POLYMER

MOLE % ACID IN MONOMER

FIG. 9
Acrylonitrile-Acrylic Acid-•-
    " - Methacrylic Acid -○-

FIG. 10
Vinyl Acetate - Acrylic Acid-•-
    " -Methacrylic Acid-○-

FIG. 11
Acrylamide-Acrylic Acid-•-
    " -Methacrylic Acid-○-
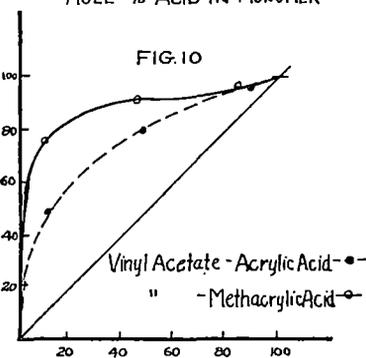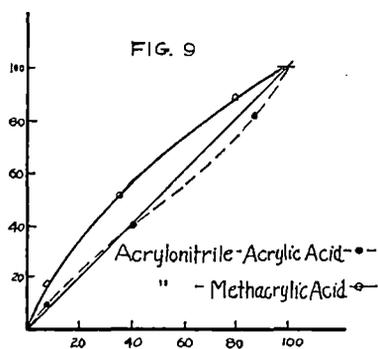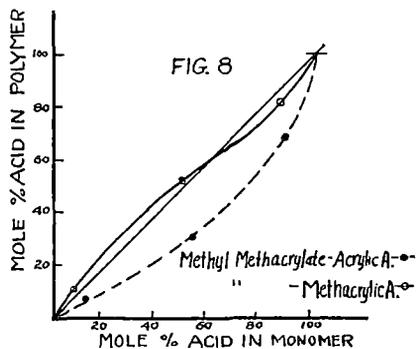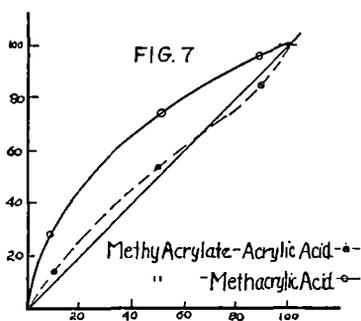
FIG. 12
Methacrylamide-Acrylic Acid-•-
    " - Methacrylic Acid -○-

the composition of the monomer mixture. At any monomer ratio other than the azeotrope value, the polymer evidently will vary in composition due to the shifting monomer composition.

Maleic anhydride frequently polymerizes in an alternating fashion to give the type of curve represented in Figure 2. This curve, with very little variation, has been reported for styrene-maleic anhydride by Alfrey and Lavin, 1945, for vinyl acetate-maleic anydride and isopropenyl acetate-maleic anhydride by Wilde and Smets, 1950, and for allyl acetate-maleic anhydride by Bartlett and Nozaki, 1953. However, maleic anhydride does not exclusively follow this alternating pattern as illustrated by polymers with methyl acrylate, methyl methacrylate, and vinyl chloride, respectively. Figure 3 represents the data recorded by Wilde and Smets, 1950, for these pairs.

The systems vinylidene chloride-crotonic acid, vinyl acetate-crotonic acid, and styrene-citraconic anhydride are shown in Figure 4. These data were observed by Chapin, Ham, and Mills, 1949. Very great diversity of behavior again is encountered.
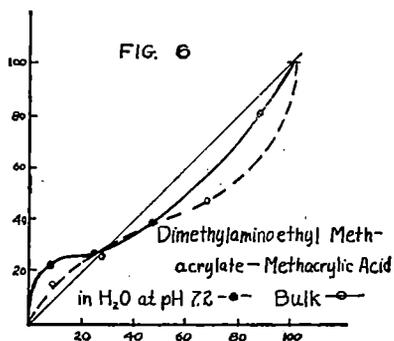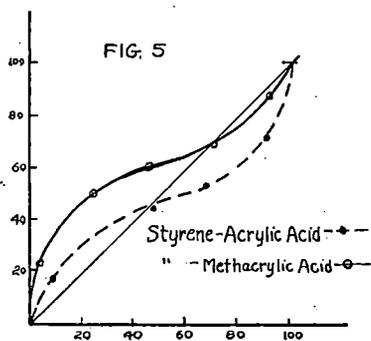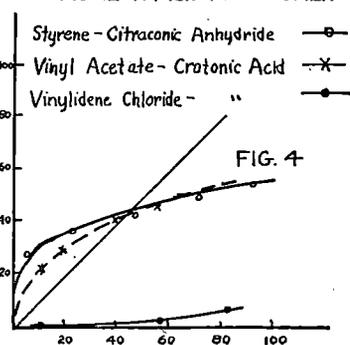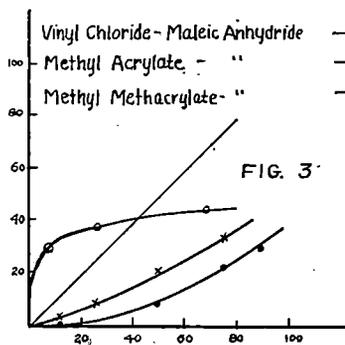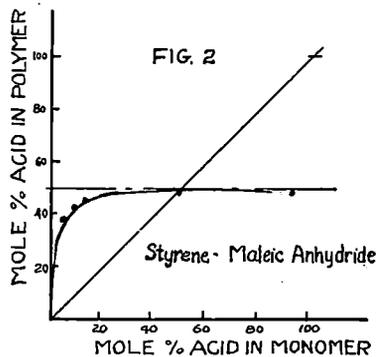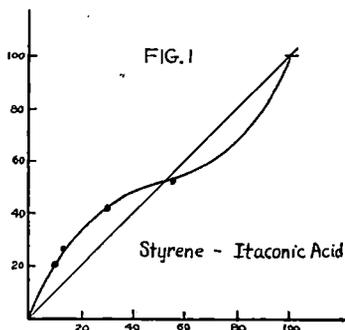
Styrene was copolymerized with acrylic acid and methacrylic acid, respectively, by Chapin, Ham and Mills, 1949, as represented in Figure 5. The similarity of the two acids is indicated here, and it will be noted that methacrylic acid in all instances enters the polymer much more rapidly than does acrylic acid.

The system dimethylaminoethyl methacrylate-methacrylic acid is interesting in that both acid and basic monomers are present. The pH of polymerization should alter the polymerization as was observed by Alfrey, Overberger, and Pinner, 1953. Figure 6 represents a part of their data and shows the effect of solvent variation.

In this research the acids were acrylic acid and methacrylic acid. These were independently polymerized with various monomers to give the data represented in Figures 7-12. Appreciable similarity to Figure 1 is shown in most of the curves.

Alkyl acrylates, $CH_2 = CHCOOR$, in which R varied from methyl through decyl, together with the acrylic acids polymerized according to Figure 7. These curves represent the data for methyl acrylate copolymers. It is striking that in all instances the methacrylic acid at all ratios entered the polymer in ratios much above the monomer compositions. The acrylic acid in the lower range of concentrations initially entered the polymer slightly above the monomer ratio, formed an azeotrope in the range of about 50-85% acid content, and then at very high acid concentration the acrylic acid entered the polymer somewhat more slowly than did the ester. Sufficient systems were run to suggest that these patterns will be encountered in most acrylate-acrylic acid and acrylate-methacrylic acid pairs.

If, for example, the original monomer mixture had 80% methyl arcylate and 20% acrylic acid, it is evident that the initial polymer would contain about 25% acid as seen from the curve. The residual monomer would gradually decrease in acid content and the polymer would, of course, have constantly changing composition. Finally only

FIG. 1 — Styrene – Itaconic Acid

FIG. 2 — Styrene - Maleic Anhydride

MOLE % ACID IN POLYMER

MOLE % ACID IN MONOMER

Vinyl Chloride - Maleic Anhydride —⊖—
Methyl Acrylate - " —✕—
Methyl Methacrylate - " —●—

FIG. 3

Styrene – Citraconic Anhydride —⊖—
Vinyl Acetate - Crotonic Acid —✕—
Vinylidene Chloride - " —●—

FIG. 4

FIG. 5
Styrene-Acrylic Acid - ◆ -
" - Methacrylic Acid -⊖-

FIG. 6
Dimethylaminoethyl Meth-
acrylate – Methacrylic Acid
in H₂0 at pH 7.2 -●- Bulk -⊖-

ester would remain and it would give a homopolymer. The overall polymer composition would equal 20% acid, but very few polymer chains actually would have this composition. More uniform polymer chains could be made by starting with about 16% acrylic acid in the monomer charge. The original polymer would then have about 20% acid. Acrylic acid would gradually be introduced as polymerization progressed in an attempt to maintain the monomer pair at 16% acid. This, obviously, would be hard to control. It is evident that the obtainment of a polymer of uniform composition would be difficult except for a monomer composition equal to the azeotropic value.

Figure 8 represent the acrylic acids with methyl methacrylate, $CH_2 = CH(CH_3)COOCH_3$. Similar results are obtained for esters up to about decyl methacrylate. The relative positions of acrylic acid and methacrylic acid remain the same as in Figure 7. However, now the methacrylic acid in the polymer is close to the diagonal and forms an azeotrope while in all instances the acrylic acid enters the polymers at a composition below its concentration in the monomer mixture. Were it desired to obtain a uniform polymer of 20% acrylic acid in this system, it would be necessary to start with a monomer mixture of about 40% acrylic acid and then add methyl methacrylate at such a rate that the monomer would have 40% acid. Again this would be difficult to accomplish in practice.

Figure 9 indicates that acrylonitrile polymerizes with the acrylic acids very similarly to the acrylate esters. The acrylic acid in the polymer is quite close to the diagonal and forms an azeotrope. In all instances the methacrylic acid enters the polymer above the diagonal line.

The curves of Figure 10 represent the copolymerization of vinyl acetate with the acrylic acids. Vinyl butyrate gives similar results. Both acids very readily enter the polymer, with the methacrylic acid again being the more reactive. It appears that the polymer would consist mainly of very high acid material plus essentially a homopolymer of the vinyl ester. It would be extremely difficult to obtain a homogeneous polymer of medium acid content.

Figures 11 and 12 represent the copolymerization data for the acrylic acids with acrylamide and methacrylamide, respectively. The relative positions of the curves for the two acids are very similar to those for the acrylate and methacrylate esters. The data indicate an azeotrope in each instance although this might be due to analytical error.

In practically all instances the composition of the polymer was determined by titration of a solution of the dry polymer. This is susceptible to possible error from residual monomer and solvent for it is known that complete removal of volatile contaminants is extremely difficult. The polymer is then dissolved in a suitable solvent, usually methanol or acetone. Titration with aqueous alkali to a permanent endpoint with phenolphthalein is then performed. Difficulty is sometimes encountered due to occasional precipitation of the polymer dur-

ing the titration. While it usually is possible to select a suitable solvent, on occasion it is very difficult to obtain a good solution. Any error encountered during the titration is reflected directly in the copolymerization curves. This error is especially significant when the polymer composition falls near the diagonal line for slight error in analysis can locate the curve either above or below the diagonal and thus be very misleading. Some of the data have been checked by the use of C^{14} tagged acrylic acid, which allowed a comparison of titration with counting procedure. The data checked quite closely, as will be reported in a subsequent paper.

Table I contains representative data obtained for several monomer pairs studied in this research. It is believed that they have a maximum error of about 5% and that for the most part they are considerably more accurate. Figures 7-12 have been prepared from the data in Table I.

TABLE I. — RELATIONSHIP OF MONOMER TO POLYMER COMPOSITION

	Mole Percent Acid in Monomer to Polymer	
	Acrylic Acid	Methacrylic Acid
Methyl acrylate*	12-16; 54-58; 92-89	10-29; 50-71; 90-95
Ethyl acrylate	13-16; 48-51; 93-91	11-35; 54-77; 92-94
-Chloroethyl acrylate	17-19; 65-64; 94-92	15-45; 61-78; 90-93
n-Butyl acrylate	17-19; 64-66; 94-93	14-45; 60-82; 91-91
Isoamyl acrylate	18-23; 64-71; 95-95	16-49; 62-83; 94-96
Methyl methacrylate	13-10; 58-32; 93-70	12-13; 54-55; 88-84
n-Butyl methacrylate	26-16; 66-39; 93-72	23-28; 63-62; 90-88
Acrylonitrile	8- 9; 42-41; 87-83	6-19; 38-54; 79-87
Vinyl acetate	12-48; 52-79; 92-94	12-77; 50-92; 86-95
Vinyl butyrate	15-59; 61-83; 94-96	15-80; 57-91; 89-94
Acrylamide	15-18; 50-42; 80-63	17-30; 45-62; 83-83
Methacrylamide	23-19; 54-38; 83-58	20-28; 50-54; 80-80

*A value of 12-16 means that monomer of 12 mole percent acid gave a polymer of 16 mole percent acid.

EXPERIMENTAL PROCEDURE

The copolymerization of methyl acrylate with acrylic acid is recorded to represent the experimental details of the polymerizations. The time of polymerization, the concentration of monomers, the solvent used for titration, and similar factors were varied with other monomer pairs as conditions dictated.

Into a clean test tube were placed 27 g. of freshly distilled methyl acrylate and 3 g. of glacial acrylic acid. Two drops of diacetyl (Agre, 1941) were added as catalyst and an atmosphere of natural gas was supplied. The corked tube was placed in a water bath at 40° C. and exposed at about 5 inches to a strong ultraviolet light source. After 70 minutes the solution remained clear and had become somewhat viscous. The polymer was precipitated by pouring the solution into purified ligroin. The granular polymer (initially a lump) was extracted well with ligroin for several days and then was dried at 50° C. for 4 days. The total yield was 0.7 g., which corresponds to a conversion of 2.3% to polymer. It is desired that conversion be low to give an in-

stantaneous polymer composition. A representative sample of the polymer (0.207 g.) was dissolved in 50 cc. of pure acetone to give a clear solution. Titration with 0.482 N aqueous sodium hydroxide required 0.78 cc. base, corrected by a blank. This corresponds to 13.1 weight per cent acrylic acid in the polymer or a mole per cent of 15.5% acid in this polymer prepared from an 11.7 mole per cent monomer charge.

SUMMARY

Acrylic acid and methacrylic acid have been copolymerized with a number of vinyl monomers to give the respective instantaneous polymers which were isolated, purified, and analyzed. In each instance, methacrylic acid has shown an appreciably greater tendency than acrylic acid to enter into the polymers. Except at the "azeotrope" point, it is evident that the polymer being formed changes in composition during the course of the polymerization.

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