

**A SURVEY OF METHACRYLIC ACID
AND ITS DERIVATIVES AS
SYNTHETIC RESINS**

VON DER
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HOCHSCHULE IN ZÜRICH
ZUR ERLANGUNG
DER WÜRDE EINES DOKTORS DER
TECHNISCHEN WISSENSCHAFTEN
GENEHMIGTE
PROMOTIONSARBEIT
VORGELEGT VON

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TO MY PARENTS

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I wish to state my thanks here to Prof. Dr.
H. E. Fierz-David for his interest in this work
carried out under his direction.

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INTRODUCTION

In the last few years the subject of resins and synthetic plastics has become increasingly important. In many places these products are replacing other substances heretofore in use. The production and demand for synthetic products of this kind has created a practically new industry. Among the literature is to be found a very interesting book, *Kunststoff-Wegweiser*, by G. Kränzlein and R. Lepsius, listing the synthetic plastics that are now being made in Germany. Other countries are producing these substances also in great quantity.

In the countries that are striving for self-sufficiency the importance of these products that can be made from materials found at home, to replace imports speaks for itself. In other countries, however, the importance is just as great. The world depression was partly to account for this new industry. Cheaper and better substitutes are always useful.

The use of various resins depends partly on their physical and chemical properties. For instance, if a resin is transparent, hard, insoluble, able to withstand temperature change and is not subject to cracking and splintering, it is a good substitute for glass. Methacrylate resins have found their place in windows for airplanes and for shatterproof windscreens for automobiles. If the resin can be colored during the process of its formation, it can find endless uses in common ways, such as drinking cups, automobile and electric fixtures, or penholders among others. The possibility of making eyeglass lenses, for cameras and scientific apparatus, of synthetic plastics is also present. This field is large with many interesting possibilities. Various other substitutions may be described here. In place of rubber, Plexigum,

a polymer of the acrylic acid series is used. For hard rubber, the polymers of methacrylic esters are used. Stone, horn, and wood, once replaced by bronze, iron and steel, can now in part be better replaced by synthetic resins. Examples are toothpaste tubes and "zinc" caps on wine bottles made from phenol derivatives, as styrene. Leather can be replaced by polymerized vinyl compounds. Casein from milk gives among other things artificial horn. Cork and asbestos can be replaced by synthetic resins also.⁽¹⁾

Methacrylic acid and its derivatives have been known a long time, as well as the fact that these tend to polymerize. Frankland and Duppa first prepared ethyl methacrylate in 1865.⁽²⁾ Fittig and Paul noted its tendency to polymerize in 1877.⁽³⁾ However, the production of synthetic resins from this series is comparatively new. The commercial possibilities of these products have been developed since 1930. Since that time much work has been carried out in this field, and today they are produced in many countries on a large scale. There are several methods available to produce the compounds of the methacrylic series, and it is the object of this paper to make a short survey of the various processes to find which is the best suited and economical for production on an industrial scale. A discussion of the various methods will be found below. Methacrylic acid is the alpha-methyl derivative of the more common acrylic acid, which with its derivatives is also polymerizable. The first work done in this direction was carried out by Röhm in 1904,⁽⁴⁾ but it was not until later that these became important as synthetic resins. Because the methacrylic series is newer, it was considered interesting to make a study of this part of the field.

(1) *Kunststoff-Wegweiser* 1937. G. Kränzlein and R. Lepsius Nov. '37. Verlag Chemie, G.M.B.H., Berlin.

(2) Frankland and Duppa. *Ann.* 136 12-13 (1865).

(3) Fittig and Paul. *Ann.* 188 54-55 (1877).

(4) *Neher. Ind. Eng. Chem.* 28 268 (1936).

THEORY

Preparation of Monomers

It has long been a known fact of chemistry that some compounds with an unsaturated carbon to carbon linkage, or double bond, can be polymerized. The simplest forms are perhaps the aldehydes and ketones. Another important polymerization is that of isoprene, a diolefin, to a resin which closely resembles rubber, and is probably related to it. As has been noted above, unsaturated compounds of other groups have been found to have the same tendency to polymerize. Acrolein, the aldehyde from which acrylic acid may be produced by oxidation, polymerizes so readily that it must be stored with an antioxidant present. When this grouping or double bond is present in other compounds, such as an acid or its esters, it is possible to polymerize these under certain conditions, chiefly in the presence of oxygen. The double bond is opened, and one molecule joins another many times over until the new molecule is many times the size of the original one, although of the same composition. It is considered that the chain is formed by a carbon to carbon linkage, hence the necessity of the double bond.

There are several known methods for the preparation of methacrylic acid and its derivatives. Not all of them are practical. Several of the methods were tried out in the laboratory and finally one chosen. The first method of importance is the dehydrohalogenation of halogen substituted

acids.⁽¹⁾ Another method is to produce the corresponding hydroxy acid and then eventual dehydration by means of various catalysts.⁽²⁾ The third method is the direct production from acetone cyanhydrin, hydroxy-isobutyric nitril, of the methacrylates.⁽³⁾

In theory the dehydrohalogenation of the halogen substituted acids or their derivatives would seem to be a very

-
- (1) Ber. Dsch. chem. Ges. *31* 3015-24 (1898).
Helv. chim. Acta *2* 144-61 (1919).
C. 1929 II 715; Bull. Soc. Chemie Belge *38* 133-45 (1929).
C. 1929 II 3251; E. P. 316,547 10/6/29.
C. 1935 II 1612; D.R.P. 607,483 29/12/34.
Ind. Eng. Chem. *28* 1160 (1936).
C. 1936 I 179; E.P. 428,223 6/6/35.
C. 1936 I 2439; A.P. 2,020,685 12/11/35.
C. 1936 I 3217; A.P. 2,013,648 10/9/35.
C. 1936 I 4075; F.P. 794,255 12/2/36.
C. 1936 II 866; A.P. 2,028,012 14/1/36.
C. 1937 I 1548; E.P. 452,658 24/9/36.
C. 1937 II 2072; D.R.P. 646,820 23/6/37.
C. 1938 I 3833; E.P. 479,690 3/8/37.
- (2) Frankland & Duppa. Ann. *136* 12-13 (1865).
Fittig & Paul. Ann. *138* 54-55 (1877).
Schryver, J. Chem. Soc. *18* 69 (1898).
Wagner-Jauregg, Helv. chim. Acta *12* 61 (1929).
C. 1930 I 740; E.P. 315,892 17/2/28.
C. 1933 I 3630; D.R.P. 573,724 27/2/30 (F.P. 797,154).
C. 1927 I 1741; Can. P. 263,186 3/8/26.
C. 1934 II 3182; E.P. 409,733 3/10/32 (E.P. 410,208).
J. Chem. Soc. London. 400-6; 714-7; 1054-61. (1935)
C. 1936 I 2440; E.P. 424,885 3/8/33.
C. 1937 I 429; F.P. 801,658 12/8/36.
C. 1937 II 3953; E.P. 466,504 24/6/37.
C.A. 1936 7587-5; A.P. 2,054,242 15/9/36.
C.A. 1937 3939-3; D.R.P. 639,953 24/12/36.
- (3) C. 1934 II 3182; E.P. 405,699 12/8/32.
C. 1935 II 3978; E.P. 427,810 30/5/35.
C.A. 1935 2547-5; E.P. 419,457 13/11/34.
C.A. 1936 4871-4; A.P. 2,041,820 26/5/36.
C. 1937 I 429; A.P. 2,042,458 2/6/36.
C. 1937 I 3061; Can.P. 358,936 1/12/34.

good process, but this proved not to be true in the laboratory. The acid is prepared by chlorinating isobutyric acid. The chlorination goes very smoothly in presence of light and a catalyst to give α -chlor-isobutyric acid. Substitutions of other halogens and other substitution positions give corresponding unsaturated compounds on dehydrohalogenation. Attempts, however, to remove a molecule of hydrogen chloride from the α -chlor-isobutyric molecule were not successful. Anhydrous ferric chloride was used as catalyst. Other catalysts may be used, but the cost of materials alone make the process of little commercial value.

The second method of importance is the preparation of the hydroxy acid or its derivatives. Rather than prepare these from the halogen substituted acid by replacement with the hydroxyl group, it is better to prepare the acid from the nitril, in this case acetone cyanohydrin. Several attempts were made without success to convert the cyanohydrin to the desired acid or its esters, using a mineral acid as the catalyst. The yields were poor and the process was considered to be of no value. Eventually, by careful control of the acid, water and alcohol content better results were obtained. This process necessitates the conversion of saturated hydroxy acid or ester to the unsaturated. The dehydration can be carried out by leading the substance through a tube containing as catalyst silicates or aluminium compounds at high temperature. Another procedure is to treat the saturated compound with phosphorous-oxychloride or similar compounds which have the ability to detach a water molecule.

The third method, which has proven to be the best, is the preparation of acetone cyanohydrin as above and separating a water molecule from it while converting the cyanide group to the acid or ester. In contrast to the other methods, this process has the advantage of being the cheapest and giving the highest yields.

Acetone cyanohydrin may be prepared in the laboratory in various ways.⁽¹⁾ One method is to treat acetone with liquid hydrogen cyanide, allowing them to react in the presence of a small amount of sodium or potassium carbonate, after which the carbonate is neutralized, as the cyanohydrin is unstable in the presence of alkali, and the excess hydrogen cyanide is boiled away. Another method, preferable to laboratory work, is the addition first of sodium bisulfite to the acetone, which gives a solid crystalline addition compound, precipitating in an excess of bisulfite solution, although it is soluble. By treating this compound with a saturated solution of potassium cyanide, a small amount of hydrogen cyanide is formed which reacts with the acetone, in equilibrium with the addition product. The equilibrium is thus upset, and as the reaction continues, more bisulfite is freed to give hydrogen cyanide to react with acetone. In this way only small amounts of the hydrogen cyanide gas are present, and the reaction goes to completion. The yield compares favorably with the former process. However, it would have no value on an industrial scale where treatment of the acetone with boiling or liquified hydrogen cyanide can be carried out more economically.

As noted above, acetone cyanohydrin is not stable in the presence of alkali. Therefore it is necessary to work with an acid catalyst. One hundred per cent sulfuric acid was selected as it acts not only as a catalyst, but at the same time removes a molecule of water from the compound, thus

⁽¹⁾Urech, *Ann.* 164 255 (1872).

C. 1903 I 1244; D.R.P. 141,509 13/5/03.

Bucher & Grolée, *Ber. Dsch. chem. Ges.* 39 1225 (1906).

Ultée, *Ibid.* 39 1857 (1906).

C. 1935 II 503; *Org. Syntheses* 15 1-2 (1935)

C. 1935 II 1445; E.P. 416,007 1/3/33.

C.A. 1936 2992-8; E.P. 439,054 28/11/35.

C. 1937 I 1547; E.P. 452,285 17/9/36.

C. 1937 I 1547; F.P. 804,124 6/10/36.

C. 1938 I 1660; A.P. 2,101,823 7/12/37.

going directly to the desired end product. By adding the cyanohydrin to the concentrated sulfuric acid and controlling the temperature, a white crystalline product is obtained, methacrylic acid amide.⁽¹⁾ However, if the reaction is not stopped there, but water is added without isolating the amide, the amide group is further saponified to give methacrylic acid. Again it is not necessary to isolate the product. Alcohol is added, and the ester of methacrylic acid is formed. Experiment has shown that it is necessary to add water first, as more than the amount present in the alcohol is needed for the reaction. In fact, an excess of the theoretical amount of water is apparently needed, as the best results are obtained with two mols of water to one mol of cyanohydrin. Due to the excess of water it is found that the esterification is somewhat hindered. The separation of the water molecule also does not go to completion. High temperature has a tendency to break down the molecule to acetone and carbon monoxide. Thus when the reaction is completed, there is a mixture of the unsaturated acid and ester as well as the saturated acid and ester and other impurities that are separated by fractionation. The acids may then be esterified, or in the case of the saturated products, a water molecule may be separated as described above. By controlling the conditions it is possible to direct the reaction in the desired course.

A modification of this method is to use alkyl sulfates, such as the methyl and ethyl esters of sulfuric acid.⁽²⁾ The alkyl group is thus brought directly into the molecule after saponification. This method was not tried out.

-
- (1) C.A. 1936 4180-3; E.P. 440,967 9/1/36.
C. 1937 II 858; E.P. 456,533 10/12/36.
C. 1937 I 185; E.P. 446,908 4/6/36.
C. 1937 II 4116; F.P. 815,908 26/7/37.
C. 1938 I 431; F.P. 813,844 9/6/37.
(2) C.A. 1936 8247-1; A.P. 2,056,771 6/10/36.
C. 1936 II 866; E.P. 437,197 20/4/34.

Another modification of the process is to prepare the methacrylic acid and to isolate it. It is then converted to the acid chloride or metallic salts which are in turn converted to the desired ester.⁽¹⁾

Two other preparations which have not been tried are the conversion of the cyanohydrin to the unsaturated nitril by means of a dehydrating agent, as phosphorous pentoxide,⁽²⁾ and the oxidation of methacrolein to methacrylic acid.⁽³⁾

The direct method described above has been found to be the most suitable and efficient. This reaction takes the following course. When cyanhydrin is added to one hundred per cent, sulfuric acid, the two substances react to give the acid amide, $(\text{CH}_3)_2\text{C}-(\text{OSO}_2\text{OH})\text{CONH}_2$. In addition to this reaction, the latter product goes partly to the saturated ester on the addition of water and alcohol, and, which is more harmful, the saturated acid breaks down to acetone, alcohol, and carbon monoxide. By increasing the amount of sulfuric acid, and keeping the temperature not too high, it has been found possible to decrease the tendency of the molecule to break down and to increase the yield of the desired products. Sodium sulfate was added to prevent the break down, and to bring the reaction to completion by upsetting the equilibrium between ester and acid, but the process was not successful. As has been said, a certain amount of water is necessary for the completion of the reaction, and by controlling this factor the yield was improved. The reaction goes to completion by splitting off ammonium sulfate which is water soluble. The acid is then esterified with the alcohol that is added.

Due to the tendency to polymerize exhibited by the acid and its esters, especially during heating, it was found neces-

(1) C. 1933 I 2608; D.R.P. 570,955 30/1/31.

(2) C. 1935 I 1216; J. Am. Chem. Soc. 66 2710 (1934).

C. 1936 II 2022; Cong. chim. Ind., Bruxelles 870-74 (1935).

(3) C. 1937 I 4871; F.P. 807,222 7/1/37.

sary to have some anti-oxidant present during the reaction.⁽¹⁾ Copper or sulfur may be used, but the best reagent was found to be hydroquinone. This is a polyhydroxy compound containing two hydroxyl groups which are readily oxidised, giving quinone. Copper shavings or powder may be used, and are converted to black copper oxide.

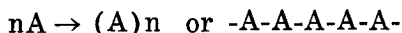
⁽¹⁾C. 1937 I 2259; E.P. 456,147 3/3/35.
C. 1938 I 4534; A.P. 2,105,284 11/1/38.
C. 1938 II 965; F.P. 819,045 8/10/37.

PREPARATION OF POLYMERS

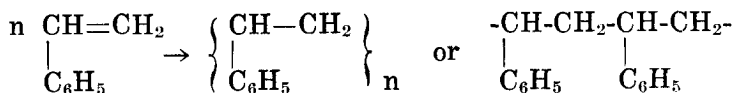
A resin may be defined as a semi-solid or solid, complex amorphous mixture of organic substances, with no definite melting point and having no tendency to crystalize. Characteristic physical properties are a typical luster and conchoidal fracture rather than a definite chemical composition.⁽¹⁾

To prepare resinous compounds it is necessary to start with substances of low molecular weight. The transformation of these low weight compounds to complex derivatives is called polymerization. In polymerization two distinct types of reaction take place, namely polymerization proper and condensation. In the former, the type of polymerization studied in this paper, the polymer retains the percentage composition of the monomer, or in other words, the final product is simply a multiple of the monomer. In condensation on the contrary, the formula of the final condensate is to be found by first subtracting the sum of the simple compounds which have been liberated during the condensation. The term polymerization then will be used in the sense of macropolymerization, as distinct from condensation.

Additive or homopolymerization is a kind of polymerization in which the polymer is built up by the additive combination of the monomer. Represented schematically:

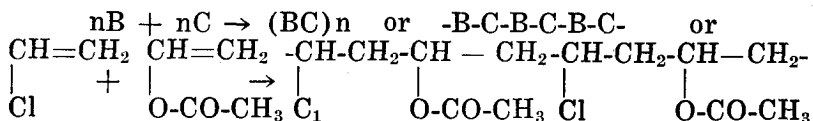


where n is the number of monomeric groups of A , the monomeric unit. An example of this is the polymerization of styrene:

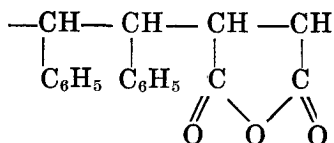


⁽¹⁾Ellis, "Chemistry of Synthetic Resins."

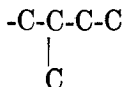
Co-polymerization is the term used when two or more substances polymerize at the same time to yield a product which is not necessarily a mixture of polymers, its properties differing from those of either polymer alone.



Hetero-polymerization is a special case of additive co-polymerization which involves a readily polymerizable substance and another substance which is also unsaturated, but which by itself is not readily polymerizable. An example is maleic anhydride which alone does not ordinarily polymerize, yet readily polymerizes with stilbene in boiling xylene to give a white amorphous heteropolymer. The structure is as follows:



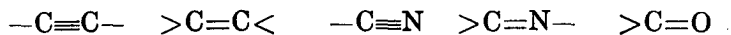
Both chemical and physical concepts of the molecule have been used to account for the ease of additive polymerization. If, for instance, a molecule contains groups which tend to destroy its symmetry, this factor favors resin formation⁽¹⁾. Boeknoogen has noted that in nature the following unsymmetrical arrangement of carbons is found many times in natural gums, resins, and rubber:⁽²⁾.



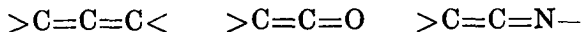
(1) Vorländer, C.A. (1922) 16 2800; Z. angew Chem. (1922) 35 249.

(2) Boeknoogen, C.A. (1932) 26 4600; Verfkroniek (1932) 25 617

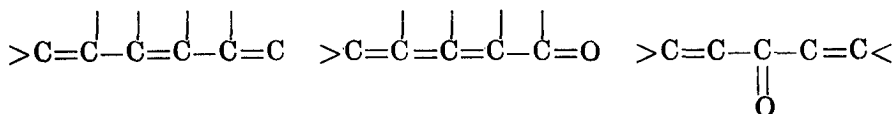
It appears as if nature had a special preference for this grouping in building up highly polymerized substances. However, the presence of certain unsaturated groups seems also necessary, polymerization potential groups, similar to chromophores in dyestuffs. The presence of these groups in a molecule do not mean that the compound is a resin, but that under certain conditions it may be possible to convert the substance to a resin. Roughly speaking, any unsaturated grouping is a polymerizing factor:



External factors, especially light and heat and catalyst, play a very great part as well as grouping. If all unsaturation is on one atom,



the tendency for polymerization is greater. Conjugation,



lays even more stress upon the polymerization tendency⁽¹⁾

A negative group attached to the vinyl radical, such as the benzene ring, in styrene shows an influence on the molecule of forming polymers of high degree. Such negative groups are the carboxyl, aldehyde, acetyl, acetoxy, ethoxy, and chloride. Other groups have the opposite effect. A methyl group on the ethylene grouping greatly hinders the polymerization. The ethylene group may exist in a ring and

(1) Ind. Eng. Chem., Neher, (1936) 267-71.

Ibid, (1936) 635-6.

J. Am. Chem. Soc. (1937) 241-53.

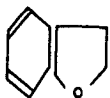
Ind. Eng. Chem. (1936) 1060-63.

Ibid, (1937) 595-9.

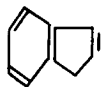
J. Chem. Soc. London, (1938) 11-19.

maintain its ability to polymerize, although not to build giant molecules, as in:

Cumarone



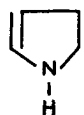
Indene



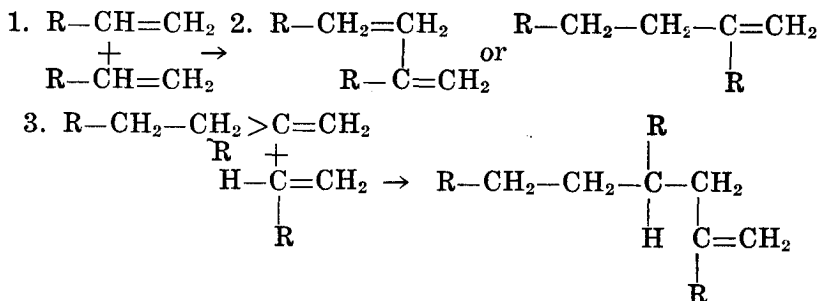
Cyclopentadiene



Pyrrole



The reaction mechanism of addition polymerization is shown by the change on position of an hydrogen atom.



As this reaction continues the unsaturated molecules of the monomer and polymer are combined to give eventually a long chain molecule or macromolecule. The reaction of one molecule joining another takes place apparently instantly.

Catalysts have a definite effect on polymerization processes, but this effect is not very well understood. The more important catalysts are strong inorganic acids, anhydrous inorganic halides, certain oxygenated bodies, such as benzoyl peroxide, and highly absorbent materials.⁽¹⁾ The effect of the catalyst is aided by heat to a certain degree, depending on the stability of the polymer at any given temperature. A catalyst lowers the limit of stability, and thus styrene polymerizes in the cold with stannic chloride and not until 27° with heat alone.⁽²⁾

(1) Staudinger, Ber. Dsch. chem. Ges. 59 3031 (1926).

(2) Staudinger and Bruson Ann. 447 110 (1926).

It may be noted that after the polymerization reaction is completed the two end members of the chain of molecules which make up the large polymer molecule are theoretically unsaturated. Several suggestions have been put forward to solve this problem.⁽¹⁾ The free radicals may be oxidized or otherwise converted to saturated groups, or the ends may combine with solvent molecules. It is possible that the ends combine with each other, but this view finds opposition. The ring thus formed would be so large that ring closure, the last step in the reaction, would be made impossible. The suggestion that the ends are eventually chemically converted and thus saturated seems to be the most logical conclusion.⁽²⁾

The experimental work in the laboratory has been carried out with the purpose of finding the best conditions, temperature, catalyst, and time necessary, for the polymerization of the various monomers that have been prepared. There are three general methods for carrying out the polymerization. The first is casting, or heating the monomer alone with a small amount of catalyst,⁽³⁾ or heating and stirring the monomer,⁽⁴⁾ or centrifuging the monomer.⁽⁵⁾ Of these processes, heating the monomer alone with a small amount of catalyst was the method carried out in the laboratory. The second method consists of the solution of the monomer in a solvent in which is soluble, but in which the polymer precipitates out,⁽⁶⁾ and the third method is to form an emulsion by mixing the monomer with a substance in which it is not soluble.⁽⁷⁾ The polymerization products obtained by the second and third methods are spongy masses or kernels, which can be ground up and subsequently used as molding powders.⁽⁸⁾ In the laboratory it was found that the lower esters of the methacrylic series give the best polymers. The molding process was not carried out.

(1) C. 1938 I 3603; Agnew, chem. 50 767-73 25/9/37.

(2) W. H. Carothers. Chem. Reviews. (1937) 8 379.

- (3) C. 1934 II 672; E.P. 401,653 14/12/33.
C. 1935 I 3725; E.P. 417,999 12/10/34.
II 766; E.P. 423,790 4/2/35.
II 2889; F.P. 781,493 16/5/35.
II 3840; A.P. 2,008,719 23/7/35.
C. 1936 I 201; F.P. 785,506 12/8/35.
C. 1937 I 211; F.P. 803,009 21/9/36.
I 446; Schw.P. 181,818 16/3/36.
I 447; A.P. 2,045,651 30/6/36.
I 447; A.P. 2,045,660 30/6/36.
I 1806; A. P. 2,057,673 20/10/36.
A.P. 2,057,674.
I 4435; E.P. 460,241 18/2/37.
I 4436; A.P. 2,063,315 8/12/36.
C. 1938 I 196; Can.P. 364,561 9/3/37.
I 1467; E.P. 474,001 18/11/37.
I 2072; E.P. 474,242 25/11/37.
I 2073; F.P. 821, 383 3/12/37.
I 3978; F.P. 821,382 3/12/37.
II 1684; A.P. 2,118,063 31/5/38.
A.P. 2,118,864.
A.P. 2,118,945.
A.P. 2,118,946.
(4) C. 1938 I 441; E.P. 471,755 7/10/37.
I 2072; A.P. 2,097,586 2/11/37.
I 3120; D.R.P. 656,134 29/1/38.
I 3544; F.P. 820,749 17/11/37.
I 3978; A.P. 2,104,760 11/1/38.
II 2355; A. P. 2,122,886 5/7/38.
(5) C. 1938 I 2073; It.P. 348,320 16/2/37.
I 2962; E.P. 475,552 16/12/37.
(6) C. 1929 II 3069; E.P. 663,711 24/8/29.
C. 1934 I 2982; F.P. 753,045 5/10/33.
C. 1935 I 3991; E.P. 422,697 14/6/35.
C. 1936 I 2452; E.P. 437,271 28/10/35.
I 3585; E.P. 437,284 2/11/35.
C. 1937 I 447; Can.P. 353,925 5/11/35.
I 735; E.P. 453,521 8/10/36.
I 753; E.P. 453,578 14/9/36.
I 2475; F.P. 804,048 14/10/36.
I 4436; A.P. 2,067,234 12/1/37.

- C. 1938 I 440; E.P. 465,789 10/6/37.
 I 441; Can.P. 362,013 24/11/36.
 I 2453; A.P. 2,099,047 16/11/37.
 I 2964; A.P. 2,101,107 7/12/37.
 I 3120; E.P. 470,397 9/9/37.
 I 3396; E.P. 470,503 16/9/37.
 II 194; Russ.P. 51,154 30/6/37.
 II 965; A.P. 2,109,595 1/3/38.
 II 2355; A.P. 2,121,839 28/6/38.
 II 3326; A.P. 2,125,885 9/8/38.
 II 3469; E.P. 487,593 21/7/38.
- (7)C. 1931 II 3278; E.P. 709,991 25/6/31.
- C. 1935 I 3991; E.P. 419,357 2/11/34.
 II 2889; F.P. 780,204 20/4/35.
- C. 1937 I 447; F.P. 797,686 1/5/36.
 I 1806; F.P. 803,171 24/9/36.
 I 4436; E.P. 459,720 11/1/37.
 II 4117; Can.P. 362,232 1/12/36.
- C. 1938 I 2963; F.P. 818,741 2/10/37.
 II 3327; F.P. 829,311 8/7/38.
- (8)C. 1935 I 1628; E.P. 411,860 12/7/34.
- C. 1938 I 441; F.P. 817,854 13/9/37.
 I 1476; A.P. 2,097,274 26/10/37.
 II 1140; E.P. 482,836 5/5/38.
 II 1684; A.P. 2,120,006 7/6/38.
 II 1867; E.P. 484,343 2/6/38.

It is advantageous to give the polymers colour. This may be done during or before the polymerization by adding soluble or insoluble dyestuffs. The latter can also be added during the molding process.⁽⁹⁾ Softeners, to give a more pliable resin,⁽¹⁰⁾ and fillers⁽¹¹⁾ may be also added during the polymerization reaction or during the molding. The molding is carried out by filling a form with the polymer in powder or granular form and heating and pressing. The subject of mixed polymers,⁽¹²⁾ has been discussed above. Examples and results are noted below.

-
- (9)C. 1935 II 2889; E.P. 427,194 16/5/35.
 C. 1937 I 211; F.P. 803,169 24/9/36.
 II 2910; A.P. 2,084,399 22/6/37.
 C. 1938 I 441; Can.P. 362,023 24/11/36.

- (10) C. 1933 II 1261; F.P. 745,085 2/5/33.
C. 1938 I 1009; Can.P. 366,496 1/6/37.
II 430; E.P. 478,822 24/2/38.
II 431; F.P. 823,816 27/1/38.
II 1139; D.R.P. 656,642 27/4/38.
- (11) C. 1934 II 673; E.P. 401,653 30/11/33.
C. 1936 I 3226; E.P. 436,084 31/10/35.
- (12) C. 1934 II 672; Can.P. 314,116 11/8/31.
C. 1935 II 3840; F.P. 784,095 22/7/35.
C. 1936 I 1484; E.P. 420,159 27/12/36.
C. 1937 I 2475; F.P. 806,325 12/12/36.
I 3076; A.P. 2,090,596 17/8/37.
I 4435; E.P. 459,056 28/1/37.
II 3088; E.P. 467,492 11/6/37.
II 3088; E.P. 467,402 11/6/37.
II 3242; A.P. 2,087,468 20/7/37.
A.P. 2,087,469 20/7/37.
II 3824; F.P. 816,267 4/8/37.
- C. 1938 I 2962; F.P. 818,740 2/10/37.
I 2073; E.P. 467,900 22/7/37.
I 2963; A.P. 2,101,061 7/12/37.
I 2964; E.P. 475,131 9/12/37.
I 2964; E.P. 475,132 9/12/37.
I 3545; E.P. 822,263 24/12/37.
I 3546; E.P. 475,570 23/12/37.
I 3979; E.P. 476,244 30/12/37.
II 3327; E.P. 489,311 18/8/38.
II 3327; Belg.P. 422,123 21/12/37.

The last reaction of interest is the conversion of the polymer to the monomer. This is done by heating the polymer to temperatures above its softening point with sand.⁽¹³⁾

In concluding the theory of polymerization, it has been found that the methacrylic esters give the best polymers, and that the methyl ester is the best of the series. The results will be found in a table below. The polymer of methyl methacrylate is an unusual resin. It has a unique clarity, high softening point, good dielectric properties, good impact and tensile strength, low specific gravity and excellent light stability. It is unattacked by most of the inorganic reagents and insoluble in many of the

organic solvents. It can be easily molded, and the molded form can be worked; sawed, drilled, turned, ground, and sanded. It is softer than glass, but it is very surface resistant. The original brilliance can be returned to the scratched polymer by rapid polishing. The transparency of the polymer allows it to be dyed in light shades and also suggests its use as a glass substitute. Its uses are many and varied in different fields, and include the replacement of formerly used resins.

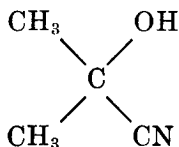
However, from experiments carried out and described below, it is apparent that the tiglic acid series of compounds are not as useful for polymerization as the methacrylic acid series. The advantages of the methacrylates, hard, clear polymers, are lacking in the tiglic ester polymers. The tiglates are not so readily polymerized as the methacrylates.

(13) C. 1937 I 4872; E.P. 460,009 19/1/37.

EXPERIMENTS

Preparation of Monomers

1. Acetone Cyanohydrin

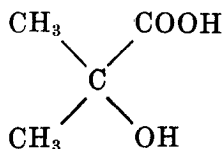


1 mol of hydrogen cyanide, 27 g., or a slight excess, in liquid form, are added to 1 mol. 58 g., of acetone, in the presence of a small amount of K_2CO_3 which acts as catalyst. The liquid hydrogen cyanide is obtained by reacting concentrated sulfuric acid with a concentrated solution of potassium cyanide, and cooling with ice and salt. The liquid hydrogen cyanide is added to the acetone with cooling and stirring. After the reaction is complete, the K_2CO_3 is neutralized with concentrated H_2SO_4 . The excess hydrogen cyanide is boiled away, and the product is fractionated under vacuum. The yield is 60% pure acetone cyanohydrin, boiling at 71° at 12 mm. of mercury.

2. Acetone Cyanohydrin

1 mol of acetone, 58 g., are added slowly with cooling and stirring, to 1 mol of sodium bisulfite, 102 g., a concentrated solution. After the addition is completed, 1 mol of potassium cyanide, 67 g., a concentrated solution, is added, cooling and stirring. An oily liquid, acetone cyanohydrin, separates from the solution. It is collected and fractionated, after adding 3 or 4 ccm. of concentrated H_2SO_4 to acidify the solution. The yield is 65-70% pure acetone cyanohydrin, boiling at $70-71^\circ$ at 12 mm. of mercury.

3. α -Hydroxyisobutyric Acid



1 mol. of acetone cyanohydrin, 85 g., 72g. of water, 200 g. of concentrated hydrochloric acid are boiled together for 12 hours. The α -hydroxyisobutyric acid is then extracted with ether. It is a white crystalline solid, crystallized from benzene. The yield is 4%, the melting point 79°.

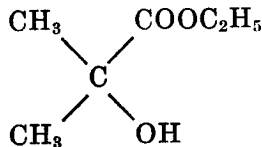
4. α -Hydroxyisobutyric Acid

1 mol of acetone cyanohydrin, 85 g., 144 g. of water, and 400 g. of concentrated H_2SO_4 are boiled together for 12 hours. The product is extracted with ether and crystallized from benzene. The yield is 11%, the melting point 79°.

5. Methyl- α -Hydroxyisobutyrate

1 mol of acetone cyanohydrin, 85 g., 320 g. of methyl alcohol, and 96 g. of concentrated H_2SO_4 are boiled together for 12 hours. The product is extracted with ether and fractionated. The yield is 6%; the ester boils at 137°.

6. Ethyl- α -Hydroxyisobutyrate



1 mol of acetone cyanohydrin, 85 g., 368 g. of ethyl alcohol, and 200 g. of concentrated H_2SO_4 are boiled to-

gether for 12 hours. The product is extracted with ether and fractionated. The yield is 4%. The boiling point is 150°.

7. Ethyl- α -Hydroxyisobutyrate

1 mol of acetone cyanhydrin, 85 g., 368 g. of ethyl alcohol and 300 g. of concentrated H₂SO₄ are boiled together for 12 hours. The product is extracted with ether and fractionated. The yield is 17%, the boiling point 150°

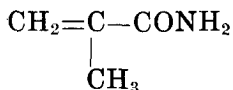
8. Methyl- α -Hydroxyisobutyrate

85 g. of acetone cyanhydrin, 56 g. of methyl alcohol and 13 g. of water are mixed and heated to 55°. To this solution are added 180 g. of a mixture composed of 58 g. of concentrated hydrochloric acid and 77 g. of ethyl alcohol. The hydrogen chloride is thus 23.6% of the mixture. The second mixture is added to the first, cooling if necessary to keep the temperature below 70°, and stirring. Ammonium chloride separates out as it is formed. When the addition is complete, the mixture is heated to 85° for three hours. The product is then filtered and fractionated. The yield is 14%, boiling at 137°.

9. Ethyl- α -Hydroxyisobutyrate

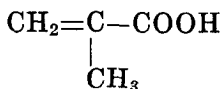
85 g. of acetone cyanhydrin, 60 g. of methyl alcohol and 13 g. of water are heated to 55°. To this solution are added 180 g. of 23.6% alcoholic hydrogen chloride, stirring and cooling if necessary to keep the temperature below 70°. When the addition is complete, the mixture is heated to 85° for three hours. The product is then filtered and fractionated. The yield is 16%. The boiling point is 80° at 14 mm. of mercury.

10. Methacrylic Acid Amide



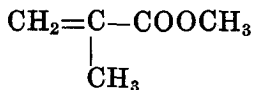
85 g. of acetone cyanohydrin are dropped slowly into 150 g. of 100% sulfuric acid, stirring and cooling to 80°. When the addition is complete, the mixture is heated for an hour at 130°. The product is then diluted with five times its weight of water, and neutralized with calcium carbonate. The calcium sulfate that is formed is filtered off, and the product is obtained by extracting with ether or by evaporating the solution and collecting the amide. The yield is 40%. The product is a white crystalline solid, melting at 105°.

11. Methacrylic Acid



85 g. of acetone cyanohydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling to 80°. When the addition is complete, the mixture is refluxed for an hour at 130°. The mixture is then allowed to cool somewhat and 36 g. of water are added. The mixture is then refluxed for three hours at 125°. To prevent polymerization, it is necessary to add 5% by weight of hydroquinone at the time the water is added. The acid is then extracted with ether and fractionated. The yield is 63%; the boiling point is 60° at 10 mm. of mercury.

12. Methyl Methacrylate



85 g. of acetone cyanohydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling at 80°. When the addition is complete the mixture is refluxed at

130° for an hour. The mixture is then allowed to cool somewhat, and 36 g. of water are added. The mixture is then refluxed for three hours at 125°. 5% by weight is added at this time. The mixture is then cooled to 60°, and 64 g. of methyl alcohol are added. The mixture is then refluxed for two hours at 100° with stirring. The ester is extracted after neutralizing the solution with sodium carbonate solution, and fractionated. The first fraction to distill over is a mixture of alcohol and acetone. The second fraction distills over at 70-80°. This fraction contains the methyl ester and water. The ester is separated mechanically. The ester then distills over at 100°. The yield is 48%. On further fractionation, methyl- α -hydroxyisobutyrate is obtained.

13. Methyl Methacrylate

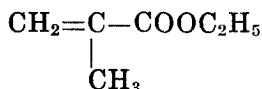
85 g. of acetone cyanhydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling to 80°. When the addition is complete, the mixture is heated for an hour at 130°. The mixture is allowed to cool to about 60°, and 64 g. of methyl alcohol are added slowly. The mixture is then refluxed at 100° for two hours. The product is extracted with ether and fractionated. The yield is 6%, the boiling point 100°.

14. Methyl Methacrylate

17 g. of acetone cyanohydrin are added dropwise to 40 g. of 100% sulfuric acid, stirring and cooling to 80°. When the addition is complete, the mixture is heated for an hour at 130°. The mixture is allowed to cool somewhat, and 9 g. of water are added. The mixture is refluxed for three hours at 125°. The mixture is then allowed to cool to about 60°, and 13 g. of methyl alcohol and 12 g. of waterfree sodium sulfate are added. The mixture is then refluxed at 100° for three hours. After

cooling, the liquid is filtered from the sodium sulfate, and the methyl methacrylate is extracted with ether and fractionated. The yield is 35% of ester which boils at 100°.

15. Ethyl Methacrylate

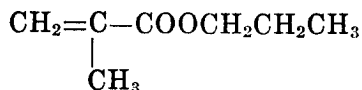


85 g. of acetone cyanohydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling to 80°. The mixture is then heated at 130° for an hour. The mixture is allowed to cool somewhat and 36 g. of water are added. The mixture is refluxed for three hours at 125°. The mixture is then cooled to 60°, and 92 g. of ethyl alcohol are added. The mixture is then refluxed at 100° for two hours. The product is extracted with ether and fractionated. The yield is 43%. The boiling point is 116.7°.

16. Ethyl Methacrylate

One-half mol. 77 g. of phosphorous-oxychloride are added to 1 mol of ethyl hydroxyisobutyrate, 122 g. The mixture is refluxed for three hours at 90-100°, and the hydrogen chloride is boiled away. The mixture is then diluted with water and fractionated. The yield of ethyl methacrylate is 53%. The boiling point is 116°.

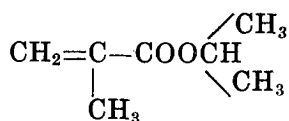
17. Normal Propyl Methacrylate



85 g. of acetone cyanohydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling to 80°. The mixture is then heated to 130° for an hour. After allowing the mixture to cool somewhat, 36 g. of water are added, and the mixture is refluxed for three hours at

125°. The mixture is cooled to about 65°, and 120 g. of n-propyl alcohol are added. The mixture is then refluxed for two hours at 110°. The product is extracted with ether and fractionated. The yield is 40%. The boiling point is 141°.

18. Iso-Propyl Methacrylate

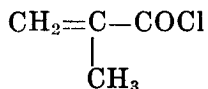


85 g. of acetone cyanohydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling to 80°. The mixture is then heated to 130° for an hour. After allowing the mixture to cool somewhat, 36 g. of water are slowly added. The mixture is then refluxed for three hours at 125°. The mixture is then cooled to about 65°, and 120 g. of iso-propyl alcohol are added. The mixture is refluxed for two hours at 110°. The product is extracted with ether, and fractionated. The yield is 40%. The boiling point is 125°.

19. Isopropyl Methacrylate

85 g. of acetone cyanohydrin are added dropwise to 150 g. of 100% sulfuric acid, stirring and cooling to 80°. The mixture is then heated to 130° for an hour. After allowing the mixture to cool somewhat, 120 g. of iso-propyl alcohol are added and the mixture is refluxed for two hours. 30 g. of sodium sulfate, water free, are added and the mixture is distilled while stirring, the temperature of the bath being taken to 225°. The distillate is then fractionated. The yield of isopropyl methacrylate is 10%. The boiling point is 125°.

20. Methacrylic Acid Chloride

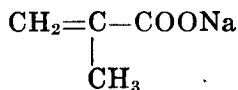


6 mol of thionyl chloride, 720 g. are added slowly to 1 mol of methacrylic acid, 86 g. The mixture is refluxed for two hours, to allow the hydrogen chloride to boil away, and then fractionated. The excess thionyl chloride is distilled over first, and then the methacrylic acid chloride is collected. The yield is 90%. The boiling point of the product is 90°.

21. Methyl Methacrylate

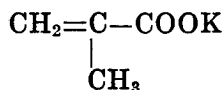
48 g. of methyl alcohol are added to 160 g. of pyridine. To this mixture is added one mol of methacrylic acid chloride, 104 g. The mixture is stirred for eight hours at room temperature. The pyridine is then neutralized by adding the solution to dilute hydrochloric acid. The product is then extracted and fractionated. The yield of methyl methacrylate is 31%. The boiling point is 100°.

22. Sodium Methacrylate



One half mol (37 g.) of methacrylic acid is added to 300 ccm. of sodium hydroxide, 41° Bé. On cooling and stirring the sodium salt separates out of the solution. It is washed and dried. The yield is 74%.

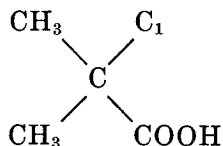
23. Potassium Methacrylate



One half mol (37 g.) of methacrylic acid is added to 300 ccm. of potassium hydroxide, 41° Be. On cooling

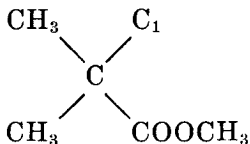
and stirring, the potassium salt precipitates out of solution. It is washed and dried. The yield is 76%.

24. *α*-Chlor-Isobutyric Acid



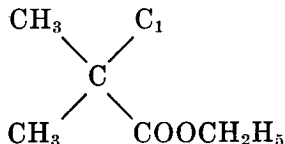
1 mol of isobutyric acid, 88 g. is chlorinated, heating the reaction to about 100°, with 5% sulfur as catalyst, until the weight has increased by 40 g. 10% of the theory. The product is then fractionated. The yield is 41%. The *α*-chlorisobutyric acid boils at 147-50° or at 87-93° at 13 mm. of mercury.

25. *α*-Chlorisobutyric Acid Methyl Ester



1 mol of *α*-chlorisobutyric acid, 122 g. 50 g. of concentrated hydrochloric acid, and 80 g. of methyl alcohol are refluxed for five hours. The product is then fractionated. The yield of the methyl ester is 63%. The boiling point is 133°.

26. *α*-Chlor-Isobutyric Acid Ethyl Ester



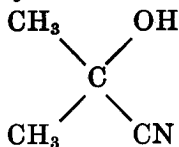
122 g. of *α*-chlor-isobutyric acid, 115 g. of ethyl alcohol, and 50 g. of concentrated hydrochloric acid are refluxed for five hours. The product is then fractionated.

The yield of the ethyl ester is 48%. The boiling point is 149° or 46-48° at 14 mm. of mercury.

27. Methyl Methacrylate

1 mol of methyl α -chlor-isobutyrate, 137 g. is heated with 13.7 g. of water free iron chloride for three hours, allowing all the hydrogen chloride that is formed to boil off, at 100°. The product is extracted and fractionated. The yield is 35% of the theory. The boiling point is 100°.

28. Methyl Ethyl Ketone Cyanohydrin



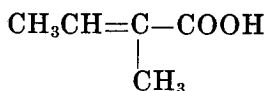
1 mol of hydrogen cyanide, 27 g. is added to 1 mol of methyl ethyl ketone, 72 g. or a slight excess, in liquid form, in the presence of a small amount of K_2CO_3 which acts as catalyst. The liquid hydrogen cyanide is obtained by treating a concentrated solution of potassium cyanide with concentrated sulfuric acid, cooling the gas with ice and salt to the liquid form. The liquid hydrogen cyanide is added to the ketone with cooling and stirring. After the addition is complete, the K_2CO_3 is neutralized with a measured amount of concentrated sulfuric acid. The excess hydrogen cyanide is boiled away, and the product is fractionated under vacuum. The yield is 60%. The boiling point is 81° at 12 mm. of mercury.

29. Methyl Ethyl Ketone Cyanohydrin

1 mol of ethyl methyl ketone, 72 g. is added to 1 mol of sodium bisulfite, 102 g. in concentrated solution, slowly, cooling and stirring. After the addition is complete, 1 mol of potassium cyanide, 67 g., in concentrated solution, is

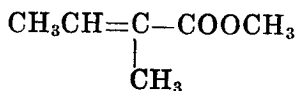
added, stirring and cooling. An oily liquid, the cyanohydrin, separates from the mixture. It is collected and fractionated from the solution, which has been slightly acidified with concentrated sulfuric acid. The yield is 40% pure methyl ethyl ketone cyanohydrin, boiling at 81° at 12 mm. of mercury.

30. Tiglic Acid



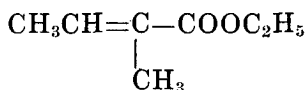
1 mol of methyl-ethyl-ketone cyanohydrin, 99 g. is added slowly with stirring and cooling to 80° to 160 g. of 100% sulfuric acid. After the addition is complete, the mixture is heated to 140° for an hour. The mixture is then allowed to cool somewhat, and 32 g. of water are added. The mixture is then refluxed for three hours at 135°. It is then diluted with water, extracted with ether, and fractionated. The acid boils at 100-105° at 13 mm. of mercury. It is a white solid, crystallized out of water. The melting point is 63°. The yield is 34%.

31. Methyl Tiglate



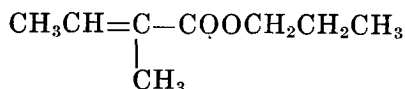
1 mol of methyl-ethyl-ketone cyanohydrin is slowly added with stirring and cooling to 80°, to 160 g. of 100% sulfuric acid. The mixture is then heated for an hour at 140°. After allowing the mixture to cool somewhat, 32 g. of water are added, and the mixture is then refluxed for two hours at 135°. The mixture is then cooled to about 60° and 64 g. of methyl alcohol are added, and the mixture refluxed for three hours at 100°. The product is diluted with water, and extracted with ether. The ester is obtained by fractionating; it boils at 131°. The yield is 35%.

32. Ethyl Tiglate



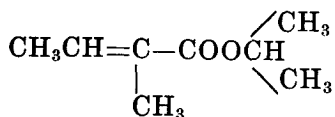
1 mol of methyl ethyl ketone cyanohydrin is slowly added with stirring and cooling to 80°, to 160 g. of 100% sulfuric acid. The mixture is then heated for an hour at 140°. After allowing the mixture to cool somewhat, 32 g. of water are added, and the mixture is then heated to 135° for two hours. The mixture is then cooled to 60°, and 92 g. of ethyl alcohol are added, and the mixture refluxed at 110° for three hours. The mixture is diluted, the product extracted and fractionated. The yield is 30% of the ethyl ester, boiling at 141°.

33. N-Propyl Tiglate



1 mol of methyl-ethyl-ketone cyanohydrin is slowly added to 160 g. of sulfuric acid, 100%, with stirring and cooling to 80°. After the addition is complete, the mixture is heated to 140° for an hour. It is then allowed to cool somewhat, and 32 g. of water are added. The mixture is then refluxed at 135° for three hours. The mixture is cooled to 60°, 120 g. of n-propyl alcohol are added, and the mixture is refluxed for two hours at 110°. The mixture is diluted, the ester extracted with ether and fractionated. The yield is 30% of ester, boiling at 66° at 14 mm. of mercury.

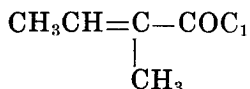
34. Iso-Propyl Tiglate



1 mol of methyl-ethyl-ketone cyanohydrin is slowly added to 160 g. of 100% sulfuric acid, stirring and cool-

ing to 80°. After the addition is complete, the mixture is heated to 140° for an hour. It is then allowed to cool somewhat, and 32 g. of water are added. The mixture is then refluxed at 135° for three hours. The mixture is cooled to 60°, 120 g. of iso-propyl alcohol are added, and the mixture is refluxed for two hours at 110°. The mixture is diluted, the ester extracted with ether, and fractionated. It boils at 63° with 22 mm. of mercury. The yield is 21%.

35. Tiglic Acid Chloride



1 mol of tiglic acid, 100 g. are treated with 1.5 mol of thionyl chloride, the latter being added slowly, and the reaction is allowed to go to completion, the substances refluxing from the heat of reaction for three hours. The excess thionyl chloride is boiled off, and the acid chloride is fractionated under vacuum. The boiling point is 41° at 13 mm. of mercury. The yield is 90%.

36. Methyl Tiglate

42 g. of methyl alcohol are dissolved in 160 g. of pyridine. To this mixture is added 1 mol of tiglic acid chloride, 139 g. The reaction is stirred at room temperature and then allowed to stand for several hours. The pyridine is neutralized by adding the mixture to dilute hydrochloric acid, and the ester is obtained by extracting with ether and fractionation. The yield is 70% of ester, which boils at 131°.

PREPARATION OF POLYMERS

1. Benzoyl Peroxide

One seventh mol benzoyl chloride, 20 g. dissolved in 40 g. acetone, is added to, with stirring and cooling, 8 g. sodium peroxide dissolved in 80 ccm. of ice water. The mixture is stirred until the benzoyl peroxide has completely precipitated out. It is filtered, washed with alcohol, and kept moist to prevent decomposition. The yield is 12 g. 70% of the theory.

2. Methyl Methacrylate Polymer

10 g. of methyl methacrylate, 10 g. of acetone and 1 g. of 30% hydrogen peroxide are boiled together for 20 hours. The acetone is distilled off, and the polymer is found on the bottom of the flask as white crystals. It is washed and dried.

3. Methyl Methacrylate Polymer

10 g. of methyl methacrylate, 90 g. of acetone, and 1 g. of 30% hydrogen peroxide are refluxed with stirring at 70-90° for 24 hours. The acetone is then distilled off, and a thick, syrupy form of the polymer is found. This is placed between two glass plates, and heated at 100° for two hours, without pressure. The result is a shatterproof glass, the polymer acting as adhesive.

4. Methyl Methacrylate Polymer

10 ccm. of methyl methacrylate, 37 ccm. of methyl alcohol, 53 ccm. of water and 1 g. 30% hydrogen

peroxide are heated at 100° for two hours. The polymer is a soft spongy mass. It is washed with alcohol and water, dried and ground to a powder. The resulting molding powder is very fine, and white.

5. Ethyl Methacrylate Polymer

10 ccm. of ethyl methacrylate, 40 ccm. of methyl alcohol, 50 ccm. of water and 1 g. 30% hydrogen peroxide are heated for 20 hours at 100°. The polymer separates out from the solution, a hard brittle mass, partly adhering to the flask. It is washed, dried, and ground to a powder.

6. Methacrylic Methyl Ester Polymer

4.5 g. of methyl methacrylate, 45 ccm. of methyl alcohol, and 0.5 g. benzoyl peroxide are refluxed at 100° for five hours. The polymer is found on cooling the mixture to have precipitated out. It is a spongy mass. It is filtered, washed with alcohol and water, dried, and ground to a powder. The powder is white in color, fine and granular.

7. Methyl Methacrylate Polymer

4.5 ccm. of methyl methacrylate, 30 ccm. of water, and 0.5 g. of benzoyl peroxide are refluxed at 110° for three hours. The polymer is found as a brittle white mass, adhering to the sides of the flask. It is broken up, washed with alcohol and water, dried, and ground to a powder. The powder is white in color.

8. Methyl Methacrylate Polymer

10 g. of methyl methacrylate and 1 g. of 30% hydrogen peroxide are boiled together for 12 hours. The polymer is bound to be a hard, colorless mass, full of cracks, in the bottom of the flask. The under side is very smooth, following the line of the flask.

9. Methyl Methacrylate Polymer

5 g. methyl methacrylate and 0.5 g. 30% hydrogen peroxide are heated for 20 hours at 65-70°. The polymer is a hard, colorless resin, but it is not clear due to bubbles formed during the heating.

10. Methyl Methacrylate Polymer

5 g. methyl methacrylate and 0.5 g. hydrogen peroxide are heated for eight hours at 75°. The polymerization is only partly completed, as the polymer is hard in the center, but on the surface is spongy, and has the odor of the monomer.

11. Methyl Methacrylate Polymer

5 g. methyl methacrylate, and 0.5 g. hydrogen peroxide, 30%, are alternately heated to 75° and cooled to 20°. After three hours, the polymerization begins. The temperature is then maintained at 60° to prevent bubble formation. The polymer is a hard, colorless substance, but not entirely clear due to bubbles that have been formed.

12. Methyl Methacrylate Polymer

5 g. methyl methacrylate, and 0.5 g. of hydrogen peroxide are heated for 20 hours at 60°. The polymer is a hard colorless substance, which is comparatively bubble free.

13. Ethyl Methacrylate Polymer

5 g. of ethyl methacrylate, and 0.5 g. of hydrogen peroxide are heated at 60° for 69 hours. The polymer is a hard colorless substance, but it is not clear and bubble free.

14. Methyl and Ethyl Methacrylate Polymer

5 g. of methyl—, 5 g. of ethyl methacrylate, and 0.5 g. of 30% hydrogen peroxide are heated for 72 hours at 60°. The polymer, a hard, colorless mass is washed and dried. The differences of a polymer composed of one or more monomers are not noticeable.

15. Methyl Methacrylate Polymer

5 g. methyl methacrylate and 0.1 g. benzoyl peroxide are mixed, filtered, and heated for 21 hours at 60°. The resulting polymer is a hard, colorless, clear resin. It is transparent, with no trace of bubbles due to escaping oxygen from the catalyst. The polymer is very elastic and can be worked; sawed, drilled and turned.

16. Ethyl Methacrylate Polymer

5 g. ethyl methacrylate and 0.1 g. benzoyl peroxide are mixed, filtered, and heated for 21 hours at 60°. The resulting polymer is a hard, clear, transparent resin. The properties are similar to those of the methyl polymer.

17. Normal Propyl Polymer

5 g. of n-propyl methacrylate and 0.1 g. benzoyl peroxide are heated for 27 hours at 60°, after being mixed and filtered. The resulting polymer is a hard, clear, transparent resin. The properties are similar to the methyl polymer.

18. Iso Propyl Polymer

5 g. of isopropyl methacrylate and 0.1 g. of benzoyl peroxide are mixed, filtered, and heated at 60° for 46 hours. The resulting polymer is hard, clear, and transparent, but is very slightly yellow in color. Otherwise the properties are similar to those of the methyl polymer.

19. Colored Polymers

5 g. each of methyl, ethyl and n-propyl and iso-propyl alcohol are mixed with 0.1 g. benzoyl peroxide and 0.1 g. of soluble dyestuff, filtered, and heated at 60° for 41, 27, 65, and 24 hours respectively. The dyes are orange, red, red and brown. They are fluorine compounds, and though they have no apparent free reducing properties, it has been noted that the rate of polymerization is slowed down by their presence. The resulting polymers are hard, clear, transparent colored resins. The properties of the polymers are not changed due to the dyestuffs, which are diffused equally throughout.

20. Mixed Polymers

5 g. each of mixtures of equal parts of methyl-and ethyl methacrylate, methyl-and n-propyl methacrylate, methyl and iso-propyl methacrylate, ethyl-and n-propyl methacrylate, ethyl and iso-propyl methacrylate, and n-propyl and iso-propyl methacrylate are mixed with 0.1 g. of benzoyl peroxide, filtered, and heated at 60° for 27, 45, 45, 18, 21, and 18 hours respectively. The monomers are all equally miscible in this proportion. The resulting polymers are clear, hard resins, completely homogeneous. The properties are the same as those of the polymers from single monomers.

21. Polymerization at Higher Temperature

5 g. each of methyl, ethyl and n-propyl methacrylate are mixed with 0.1 g. of benzoyl peroxide, filtered, and heated at 75° for two, two and four hours respectively. The methyl and ethyl polymers are full of cracks and bubbles, are partly spongy and brittle. The n-propyl polymer is fairly hard and clear. It is thus apparently better to heat the lower esters at a lower temperature for a longer time to produce polymers of the desired properties.

22. Methyl Tiglate Polymer

5 g. of methyl tiglate and 0.5 g. of 30% hydrogen peroxide are heated at 75° continuously for seven days. The polymerization after that time is partly complete, giving a syrupy liquid. The temperature is raised to 100°, and the substance is heated for two days longer. The result is a colorless soft polymer.

23. Mixed Polymer

5 g. methyl tiglate, 5 g. ethyl methacrylate and 0.5 g. 30% hydrogen peroxide are heated together at 100° for seven days continuously. The resulting polymer is colorless, but soft and full of bubbles.

24. Normal Propyl Tiglate Polymer

10 ccm. n-propyl tiglate, 40 ccm. ethyl alcohol, 50 ccm. water, and 0.5 g. benzoyl peroxide are heated together with refluxing for four hours. The monomer does not polymerize.

25. Methyl Tiglate Polymer

10 ccm. of methyl tiglate, 40 ccm. of methyl alcohol, and 0.5 g. of benzoyl peroxide are heated together with refluxing for eight hours. The polymer precipitates out, a soft, colorless mass. It is washed and dried.

26. Methyl Tiglate Polymer

5 g. methyl tiglate and 0.5 g. benzoyl peroxide are heated at 60° without polymerization, after 44 hours.

27. Ethyl Tiglate Polymer

5 g. ethyl tiglate and 0.5 g. benzoyl peroxide are heated 44 hours without polymerizing.

28. Ethyl Tiglate Polymer

5 g. of ethyl tiglate, and 0.5 g. of benzoyl peroxide are heated for 24 hours at 100°. Then the mixture is heated at 150° for 24 hours. After the first heating, the polymer is soft, but on further heating it becomes hard, brittle, and full of cracks.

TABLE I

Acetone cyanohydrin	70°/12mm.	Methyl ethyl ketone cyano- hydrin	81°/12mm.
Hydroxyiso- butyric acid	M.P. 79°		
Methyl hydroxy- isobutyrate	137°; H ₂ O sol.		
Ethyl hydroxy- isobutyrate	150°		
Α-chlor-iso- butyric acid	87-93°/13mm.		
Methyl α-chlor- isobutyrate	133-5°		
Ethyl α-chlor- isobutyrate	149°		
Methacrylic acid amide	M.P. 105°		
Methacrylic acid	62°/12mm.	Tiglic acid M.P.	63°
Methyl methacrylate	100°	Methyl tiglate	131°
Ethyl methacrylate	116°	Ethyl tiglate	141°
N-propyl methacrylate	141°	N-propyl tiglate	66°/14mm.
Iso-propyl methacrylate	125°	Iso-propyl tiglate	63°/22mm.
Methacrylic acid chloride	90°	Tiglic acid chloride	41°/13mm.
Sodium methacrylate	White solid		
Potassium methacrylate	White solid		

TABLE II

Rate of Polymerization With Benzoyl Peroxide as Catalyst

Temperature 60°		Hours	Appearance
Methyl methacrylate		21	Clear, colorless
Ethyl	"	21	Clear, colorless
N-propyl	"	27	Clear, colorless
Iso-propyl	"	46	Clear, slightly tinted
Temperature 75°			
Methyl methacrylate		2	Cracks, colorless
Ethyl	"	2	Cracks, colorless
N-propyl	"	4	Partly clear, colorless
Temperature 60°; Dyestuffs			
Methyl methacrylate		41	Transparent, orange, clear
Ethyl	"	27	Transparent, red, clear
N-propyl	"	65	Transparent, red, clear
Iso-propyl	"	24	Opaque, brown, clear
Temperature 60°; mixed polymers			
Methyl and ethyl methacrylates		27	Clear, colorless
Methyl	" n-propyl "	45	Clear, colorless
Methyl	" iso-propyl "	45	Clear, colorless
Ethyl	" n-propyl "	18	Clear, colorless
Ethyl	" iso-propyl "	21	Clear, colorless
N-propyl	" iso-propyl "	18	Clear, slightly tinted

CONCLUSION

In making a survey of methyl methacrylate and similar compounds, various processes have been tried, and the best chosen for the preparation. The preparation of α -hydroxyisobutyric compounds, and their conversion by dehydration to the methacrylic series, and the preparation of the α -chlor-isobutyric series and conversion to the unsaturated series by dehydrohalogenation have been found to be unsatisfactory. The method which gave the best results in the laboratory is the direct conversion of the cyanohydrin by means of one hundred per cent. sulfuric acid at temperatures not over 80° , with subsequent addition of water and alcohol to form the amide, acid, esters, and salts, of the methacrylic acid series. The corresponding tiglic series was also prepared in this manner.

The second part of the work is a survey of the polymerization of the methacrylic and tiglic compounds. The general processes of polymerization, casting, solution of monomer, dispersion of monomer, have been carried out with catalysts to determine the effect of such factors as catalyst, temperature, and time for polymerization, and to determine the best process. Each of the methods is useful, castings for making products directly, solutions and dispersions for molding powders. The best catalyst is found to be benzoyl peroxide, the best temperature between 60° and 100° . The time is proportional to the catalyst and temperature. The methacrylate series gives the best polymers.

CURRICULUM VITAE

I was born in Providence, Rhode Island, U.S.A., August 16th, 1914. I lived in Providence until 1932 where I attended Moses Brown School until June 1932. I then lived in Thompson, Conn., U.S.A., my present home. I attended Williams College in Williamstown, Massachusetts, U.S.A., from 1932 until 1936, and there received my B.A. degree. From 1936 until 1939 I lived in Zurich, and studied in the Chemistry Department of the E.T.H. under Professor Fierz for the Dr. sc. techn. degree in chemistry. The laboratory work was finished in January 1939.

Zurich, December 1939

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