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Courtland L. Agre  
*St. Olaf College*

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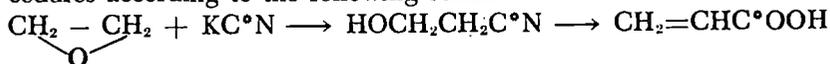
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## Vinyl Polymers Containing Acrylic Acid-1-C<sup>14</sup>

Data were recently reported, (Agre, 1956,) on the interpolymerizations of acrylic and methacrylic acids, respectively, with a number of acrylate and methacrylate esters, styrene, acrylonitrile, vinyl esters, and similar monomers. In that study the greatest difficulty encountered was due to the limited solubility of some of the polymers, a factor which made analysis of the acid content both difficult and somewhat inaccurate. Furthermore, polymers containing two different acids could not be titrated to determine directly the amounts of the respective acids present.

It is evident, therefore, that the use of C<sup>14</sup> tagged acid, acrylic acid in this study, has certain inherent advantages. It would not be necessary to have a soluble polymer. If two different acids were perhaps present, radioactive count would allow determination of the acrylic acid-1-C<sup>14</sup> while titration would determine the total acid content. Furthermore, polymers containing two acrylate esters, for example, could be analyzed readily by having one of them contain the isotopic carbon.

Acrylic acid-1-C<sup>14</sup> was made by a combination of known procedures according to the following series.



The tagged acrylic acid was obtained in about 50 percent yield and by titration appeared to be 98 percent pure. Glacial acrylic acid was used as a diluent to allow convenience in the preparation and to give counts in the desired range. The diluted acrylic acid-1-C<sup>14</sup> had a

specific activity of 17,200 counts per minute for a barium carbonate plate.

Polymerization was effected by adding to the carefully weighed monomers a drop of diacetyl catalyst and then exposing the mixture to intensive ultraviolet light. Moderate viscosity rapidly developed and then the "instantaneous" polymer was isolated by pouring the material into heptane. The polymer was purified and dried.

The polymers were analyzed both by direct titration and by radioactive counting. In the first instance, a weighed specimen was dissolved in acetone or other appropriate solvent. Titration was made with aqueous base to a phenolphthalein endpoint. Radioactive counting was made according to the procedures of Calvin. The specimen was burned and an infinitely thick plate of barium carbonate was prepared. The plate then was placed in an Atomlab, Model 21 Pre-flush Counter with Q-gas atmosphere and counting was made by a Nuclear Model 165 Scaling Unit equipped with an automatic timer.

Calculation of the acrylic acid content in the polymer was made on the following two bases. Combustion and count for a particular system, n-butyl methacrylate containing 10.36 percent acrylic acid in this instance, were made on both the monomer and the instantaneous polymer. Variation on the count beyond experimental error would thus show deviation of polymer composition from the monomer charge. The monomer and polymer, respectively, gave 1330 and 683 counts per minute, corrected for background, coincidence, and adjusted to a standard. These results show that the polymer is much lower in acrylic acid content than the monomer. Aside from a small correction, the acid content in this polymer is approximately  $683/1330 \times 10.36$  or 5.3 percent.

A simpler method is to compare the radioactive count of the polymer with the calculated value based on the specific activity of the acrylic acid. The specific activity of an infinitely thick plate of barium carbonate from the diluted acrylic acid-1-C<sup>14</sup> was determined to be 17,200 cpm. Based on the difference in comparison of the acrylic acid and the butyl methacrylate, it can be calculated that a monomer mixture of 10.36 percent acrylic acid will give a barium carbonate plate in which 7.87 percent of the carbonate comes from the acrylic

acid. The calculated count for the monomer is  $0.0787 \times 17,200$ , or 1,350 cpm. The actual count for the polymer was 683, so the acid content of the polymer is  $683/1350 \times 10.36$ , or 5.24 percent.

The data obtained for a number of interpolymerization are given in Table I. The data also are recorded from the curves of the earlier publication. While the discrepancy between the comparable data is sometimes appreciable, it is evident that qualitatively the methods give reasonable comparison.

TABLE I

Monomer	Polymer by titration	Polymer by count	Polymer by S.A.	Previous paper	
Methyl acrylate-Acrylic acid	10.46	11.5	10.3	10.1	13
Butyl acrylate-Acrylic acid	10.46	11.9	10.3	10.3	12
Methyl methacrylate-Acrylic acid	10.66	5.3	4.8	4.9	7
Butyl methacrylate-Acrylic acid	10.36	5.8	5.3	5.2	6

#### EXPERIMENTAL DETAILS

*Preparation of Acrylic Acid-1-C<sup>14</sup>*—The reaction of KC<sup>14</sup>N with ethylene oxide is a modification of the procedure of Ryan and O'Connor (1952). A solution of 80 g. of magnesium sulfate heptahydrate in 125 ml. of water was placed in a 1-liter round-bottom flask. To this was added with shaking an aqueous solution (50 ml.) of 31 g. of sodium cyanide containing KC<sup>14</sup>N of 1 millicurie activity. The cold solution was further cooled in a salt-ice bath and 100 g. of cold ethylene oxide was added rapidly. The flask was capped and kept in the ice bath, with occasional shaking, for four hours. The cap on the flask was equipped with a stopcock which was opened periodically to prevent the pressure from becoming excessive. The flask was allowed to stand overnight at room temperature with the stopcock open. The solution was neutralized with 35 percent sulfuric acid and then was extracted seven times with 125 ml. portions of ethyl acetate. The solvent was removed during two hours to leave about 38 g. (theory is 45 g.) of crude, tagged ethylene cyanohydrin. This was used in the next step of the synthesis without purification.

A solution was made of ferrous sulfate (1 g.) and sulfuric acid (94 g.) in water (12 g.) containing a trace of suspended copper oxide. The temperature was raised to 120°C. and the crude ethylene cyanohydrin was added portionwise during one hour at that temperature.

The temperature was maintained an additional two hours. The volatile material was removed by vacuum distillation. The distillation progressed from an initial value of 52°/55 mm. with a pot temperature of 125° to final conditions of 82°/12 mm. with a pot temperature of 190°. The product (34 g.) was diluted with 21.4 g. of glacial acrylic acid. This mixed product was poured into 100 ml. of ethylene chloride to give an upper, aqueous layer which then was extracted once with 20 ml. of ethylene chloride. A trace of hydroquinone was added to the combined organic layers and the mixture was dried over magnesium sulfate. The solvent was removed under reflux through a 10" Raschig ring filled column under partial vacuum and a maximum temperature of 85°. The residue was distilled directly from the flask (no column) at 43°/10 mm. and gave 40 g. of acrylic acid containing acrylic acid-1-C<sup>14</sup>. This amounts to about 50 percent yield of acid which titrated 98 percent pure. This monomer gradually polymerized even when kept under refrigeration. This diluted acrylic acid-1-C<sup>14</sup> had a specific activity at infinite thickness of plate of 17,200 cpm.

#### SUMMARY

Acrylic acid-1-C<sup>14</sup> has been prepared in acceptable yield. Interpolymers have been made with selected acrylate and methacrylate esters. Analyses of these polymers by radioactive count gave values for the acid content of the respective polymers qualitatively equal to that obtained by direct titration.

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