

Modification of acrylic acid and Acryloyl chloride polymers

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Summary

In this work many amide polymers were prepared according to the modification reaction of polyacryloyl chloride or polyacrylic acid with different primary amines to corresponding N – substituted acrylamide polymers. These polymers were identified and characterized by IR, UV.

Spectroscopy, elemental analysis and their physical properties were determined by measuring of softening points. The intrinsic viscosity was measured by using Ostwald – Fenske viscometer. The thermal analysis (DTA and TG) were studied for several polyamides and we concluded from all results of two different ways that the modification of polyacryloyl chloride to N – substituted acrylamide polymers gave best results and the probability of their uses due to the functional groups were substituted on nitrogen atom, such as aromatic or heterocyclic or aliphatic groups, the results appeared good thermal properties and chemical resistance and high yield.

Introduction

In the last years, the industrial use of acrylamide polymers has grown commercial advances have included development of catalytic processes for the preparation of monomer, introduction of easily handled emulsion polymers, and identification of larger potential uses in enhanced oil recovery.

Many other uses for polyacrylamides have been explored but the principal outlets continue to be in water treatment, mining, and paper manufacture. Production of copolymers has setted on a few cationic and anionic comonomers and on polymer

modification through controlled hydrolysis, (1 – 5). A large number of N – substituted acrylamides are known (4, 5, 6). Three main routes have been used to prepare these compounds:

1. Acrylonitrile – Ritter reactions (7, 8).
2. Acryloyl halide – amine condensations (9).
3. Acrylamide – formaldehyde reactions (10).

The amide group is readily hydrolyzed by acid or base to yield acrylic acid(11, 12, 13).

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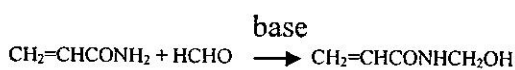
Hydrolysis of N – alkyl derivatives proceeds at slower rates. The presence of an electron – withdrawing group on nitrogen not only facilitates hydrolysis, but also affects the polymerization behaviour of these derivatives (14, 15).

Acrylamide reacts with concentrated sulfuric acid to form acrylamide sulfate. The intermediate of the old sulfuric acid process for producing acrylamide. Acrylamide sulfate can be converted to acrylic esters by reaction with alcohols (11). Many acrylamide transition metal complexes have been reported (16 – 19).

In dimethyl sulfoxide solution acrylamide forms complexes with nucleosides (20) and with several inorganic salt (21 – 23).

Dehydration of acrylamide by treatment with fused manganese dioxide (24) at 500°C or phosphorus pentoxide (25) yields acrylonitrile.

Several important acrylamide derivatives are obtained from the reaction of acrylamide with aldehydes. Under basic conditions, formaldehyde and acrylamide readily form an adduct – N – methylol acrylamide (26 – 27).



Two equivalents of acrylamide react with formaldehyde to form N,N'-methylene bis acrylamide under acid catalysis (28 – 29).

Experimental

A. Free radical

Polymerization of Acrylic acid or Acryloyl chloride

5 gm of the pure monomer was dissolved into 30 ml of freshly distilled dry THF in a screw – capped polymerization bottle. An amount equal to 0.02% of the monomer's weight of azobisisobutyronitrile was added. The bottle was flashed with argon for few minutes inside a glove bag. At firmly stopped. The clear solution was maintained at 60°C in a constant temperature oil bath for 1 h. the solution was then poured into about 50 ml of ethanol to obtain a milky precipitate. The suspension was warmed to coagulate the colloidal product before filtration. The colorless precipitate was washed with ether for several times, dried in a vacuum over night and characterized. The softening point of the poly acrylic acid was 75°C and for poly acryloylchloride was 60°C.

The IR spectrum gave absorption at 3500 cm^{-1} for –OH carboxylic acid and at 1720 cm^{-1} for C = O group for poly acrylic acid. See Fig. 1.

Acryloyl chloride gave absorption at 1660 cm^{-1} for – C = O group and disappearing absorption at 650 cm^{-1} for C – Cl, see Fig. 2.

B. Preparation of poly [N – substituted acrylamide/

In a round – bottom flask provided with condenser were placed 2 gm of a – poly acrylic acid or b – polyacryloyl chloride dissolved in 10 ml of distilled dry THF, then added 1 mole of different amines, the contents were stirred with magnetic bar, heated by using water bath about 2 hrs. Cooled and poured into 25 ml ethanol, white