

Synthesis and Polymerization of Several Unsaturated Amides

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Abstract:

New unsaturated amides such as N-substituted acrylamides, crotonamides and cinamamide were synthesized from reaction of unsaturated carboxylic acid such as acrylic acid, crotonic acid and cinamic acid with different primary amines. All new prepared acrylamide monomers were polymerized easily free radically by using Azobisisobutyronitrile.

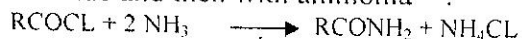
N-Substituted crotonamide and N-substituted cinamamide monomers couldn't polymerized free radically as homopolymerization this is due to steric effect factor of the substituted groups, on the vinylic amide and the allylic acid hydrogen.

All prepared monomers were studied by IR, UV spectroscopy and element analysis. Also the physical properties of the types acrylamide polymers, were studied and the intrinsic viscosity, was measured indicated the high molecular weight. The shear studying with various solution of polymers were measured.

Introduction:

Polyamide (PA), known by the trade name nylon consist of highly ordered molecules with give polyamides high tensile strength, some polyamides are made by reacting dicarboxylic acid with diamines (carbon molecules with the ion – NH₂ each end), as in nylon-6,6 and nylon-6,10 (the two number in each type of nylon represent the number of carbon atoms respectively ^(1,2), other types of nylon are synthesized by condensation of amino acid.

Acids may be converted to amides by treatment with thionyl chloride and then with ammonia ⁽³⁾:

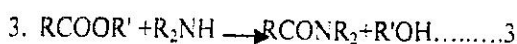


Analides, toluides and P-bromo analides may made either from the free acid ⁽⁴⁾ or from its salt. Acrylamide H₂C=CHCONH₂, 2-propenamamide exhibits, good thermal stability and long shelf life in the absence of light ⁽⁵⁾. The

acrylamide solution is stabilized by oxygen and small amounts (25–30) ppm based or acrylamide of cupric ion, several other types of stabilizers, such as ferric ion ^(6,7) and ethylenediamine tetraacetic acid (EDTA) ^(8,9,10). For many years, acrylamide was made by reaction of acrylonitrile with H₂SO₄, H₂O followed by separation of acrylamide from its sulfate salt by use of a base or an ion-exchange column ⁽²⁾.

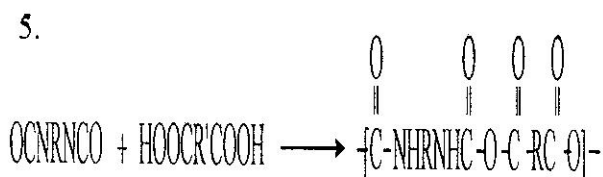
N-Substituted acrylamides known ⁽¹¹⁾. Many main routes have been used to prepare these compounds ^(12,13,14):

1. Acryloyl halide – amine condensatrou ⁽¹²⁾:



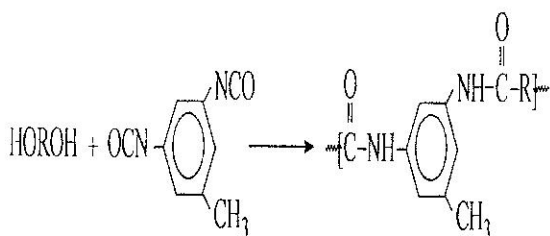
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4. From diisocyanate with dicarboxylic acid



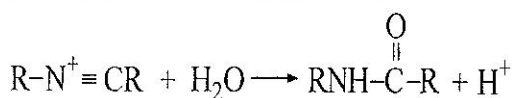
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5. Ritter reaction:



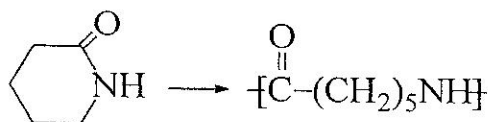
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6. Addition alcohol to nitrile by using acid catalyst ^(15,16):



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7. Polymerization of lactams ⁽¹⁶⁾:



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Experimental:

❖ **Materials:**

All unsaturated acids and amines and AIBN initiator were used in this work supplied by BDH-limited, poole England.

❖ **Preparation of N-substituted unsaturated amides (1-12):**

Several primary amines were gradually added stoichiometric amounts to a cold solution of unsaturated acids in dry ether with stirring, the precipitated of unsaturated amide was filtered and washed with cold ether and recrystallized from THF, then dried under vacuum.

The melting point and element analysis and IR-spectroscopy of the prepared amides are listed in table 2.

❖ **Free radical Polymerization of monomers (13-18):**

To a screw-capped polymerization bottle containing 2 gm of prepared monomers were added 0.05 gm (0.025 % by weight of the monomers concentration) of AIBN and 25 ml of freshly distilled THF. The clear solution was flushed, the bottle was then closed and incubated in a water bath at 65 °C for 1 hr. The mixture was cooled and the contents poured into a beaker of methanol. A viscous precipitate was formed which coagulated when warmed, then separated and dried in vacuum overnight. The yield of polymer was 1.8 gm. All physical properties are listed in table 3. The IR absorptions for prepared polymers are listed in table 4.

❖ **Viscosity measurements:**

Ubbelohde, capillary viscometer was used to determined viscosities of the prepared polymers at 30 °C. The intrinsic viscosity of three types of polyamide polymers were obtained from the intercept of graph by plotting (η_{sp} Vs. C%) ⁽⁴⁾.

Result and discussion:

Although there are several procedures for the preparation of N-substituted amides ^(12,13,14) one of them was found suitable for the preparation of N-substituted acrylamide, crotonamide