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SYNTHESIS OF COPOLYMERS CONTAINING POLYFUNCTIONAL GROUPS BASED ON ACRYLONITRILE

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Abstract
Acrylonitrile (AN) is a versatile monomer extensively utilized in the synthesis of copolymers with polyfunctional groups, imparting enhanced properties suitable for various applications. This article reviews the synthesis methods, reaction mechanisms, and applications of such copolymers, focusing on their structural characteristics and functional capabilities.

Keywords: Acrylonitrile, copolymerization, polyfunctional groups, synthesis methods, reaction mechanisms, applications.

Introduction

Acrylonitrile (AN) is a key monomer in polymer chemistry, known for its ability to copolymerize with various monomers to introduce diverse functional groups into the polymer backbone. These copolymers exhibit enhanced properties, including improved reactivity, solubility, and functionality, making them valuable in fields such as membrane technology, drug delivery, and environmental remediation.

Synthesis Methods. Free Radical Copolymerization. Free radical copolymerization is a widely used method for synthesizing AN-based copolymers. This process involves the reaction of AN with monomers containing reactive groups, leading to the incorporation of these groups into the polymer chain. For instance, copolymerization of AN with maleic anhydride has been conducted using a water-phase precipitation copolymerization process (WPPCP) with $K_2S_2O_8$–Na_2SO_3 as the initiator system, resulting in copolymers suitable for ultrafiltration membranes.

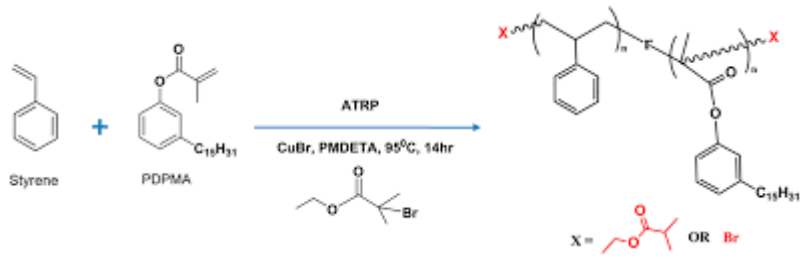
Aqueous Precipitation Copolymerization. This method involves the copolymerization of AN with other monomers in an aqueous medium, leading to the precipitation of the copolymer. For example, polyacrylonitrile copolymers containing amine groups were synthesized by aqueous precipitation copolymerization of AN, vinyl acetate, and methacrylic acid 2-dimethylaminoethyl ester (DEMA) using a $Na_2S_2O_5$–$NaClO_3$ redox initiating system.

Reversible Addition–Fragmentation Chain Transfer (RAFT) Polymerization. RAFT polymerization allows for the controlled synthesis of copolymers with specific functional groups. The influence of introducing acrylic acid into the reaction mixture with AN during RAFT polymerization has been analyzed, affecting the rheological properties of their solutions and the capability to spin fibers by the mechanotropic method.

The copolymerization of AN with monomers containing functional groups typically involves free radical mechanisms, where the initiator generates radicals that react with the monomers, leading to the formation of copolymer chains. The reactivity ratios of the monomers influence the copolymer composition and molecular weight distribution.

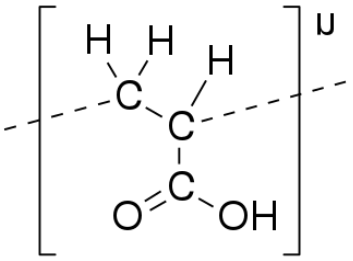
Copolymerization with Styrene

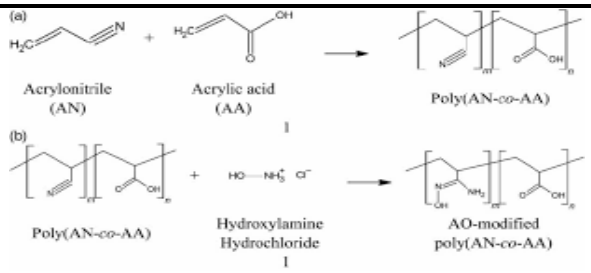
The copolymerization of AN with styrene (S) yields styrene-acrylonitrile (SAN) copolymers, which are known for their high strength and thermal stability. This reaction typically proceeds via free radical mechanisms, initiated by radical initiators such as potassium persulfate (KPS) or hydrogen peroxide/ascorbic acid systems. The reaction conditions, including temperature and monomer feed ratios, significantly influence the copolymer composition and molecular weight distribution. Studies have shown that the thermal stability and runaway behavior of SAN copolymerization can be evaluated using thermal analysis techniques, providing insights into the reaction kinetics and safety considerations.



2. Copolymerization with Acrylic Acid

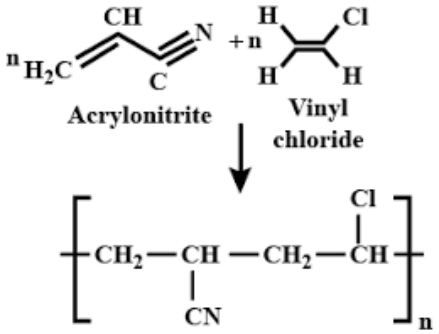
Introducing acrylic acid (AA) into the copolymerization mixture with AN result in copolymers with enhanced hydrophilicity and reactivity. The synthesis of AN-AA copolymers can be achieved through free radical polymerization, with the influence of AA concentration and reaction conditions on the copolymer properties being significant. The rheological properties of their solutions and the capability to spin fibers by the mechanotropic method have been analyzed, indicating that the synthetic procedure affects the polymer's performance.

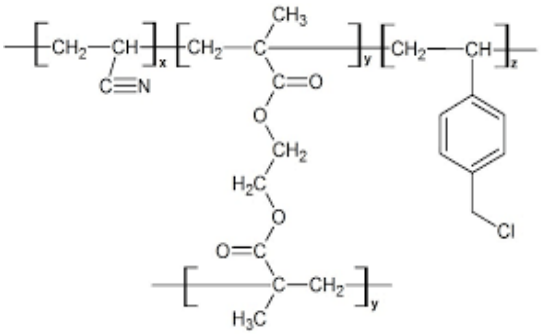




3. Copolymerization with Vinyl Chloride

The copolymerization of AN with vinyl chloride (VC) can be catalyzed by transition metal complexes, such as $EtAlCl_2$. This reaction typically requires specific conditions to proceed effectively, and the presence of the catalyst influences the polymerization rate and copolymer composition. Studies have investigated the reaction conditions and the role of the catalyst in the copolymerization process, providing insights into the mechanism and potential applications of the resulting copolymers.





4. Copolymerization with Methyl Acrylate

The copolymerization of AN with methyl acrylate (MA) has been studied in various polymerization media, including emulsion polymerization. The reaction conditions, such as solvent choice and temperature, significantly affect the copolymerization kinetics and the properties of the resulting copolymers. Research has shown that the reaction medium influences the polymerization rate and the molecular weight distribution of the copolymers.

5. Copolymerization with Nitrogen-Containing Esters

The copolymerization of AN with nitrogen-containing esters, such as 1-chloro-3-piperidino-2-propylacrylate, has been investigated to synthesize copolymers with enhanced functionality. The reaction is typically carried out in organic solvents at elevated temperatures in the presence of radical initiators. Studies have shown that the copolymerization rate increases with temperature, and the structure of the synthesized compounds can be confirmed by spectral analyses.

In summary, the copolymerization of acrylonitrile with various monomers allows for the design of polymers with tailored properties suitable for diverse applications. The choice of monomer,

reaction conditions, and polymerization method significantly influence the copolymer composition, molecular weight distribution, and overall performance of the resulting materials.

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