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Polyelectrolytes With High Charge Density

Polyelectrolytes with high charge densities and molecular weights have a number of applications. For example, these polymers can be used as flocculants to clarify residential and industrial water supplies and as bactericidal and fungicidal agents. They can be used also in the preparation of electroconductive photocopy papers, to improve living cell adhesion to glass or plastic, and as anticancer agents.

Polyelectrolytes are produced by the copolymerization of dihalides and tertiary amines. However, many of these turn out to be cyclic polymers which have lower charge densities and lower molecular weights than linear polymers.

By using a tertiary amine monomer with the appropriate (CH₂) chain length, long-chain linear polymers with molecular weights of 60,000 g/mole or higher may be formed. These can be further converted into branched or star-shaped polymers by attachment to a polymeric substrate or by reaction with other monomers.

Cationic polyelectrolytes with molecular weights exceeding 60,000 are formed, in the absence of oxygen, by the polymerization of a monomer having the following formula:

$$\begin{array}{c|c} CH_3 & \\ \hline \\ CH_3 & \\ \end{array} N \longrightarrow (CH_2)_{\chi} \longrightarrow Z \tag{1}$$

Where x is either 3 or 7 through 10 and Z is I, Cl, or Br. The homopolymer formed from this monomer has the following structure:

$$\begin{array}{c|c} CH_3 & \hline \\ CH_2 & \hline \\ CH_3 & \hline \\ CH_2 & \hline \\ CH_3 & \hline \\ CH$$

where n is an integer. The key feature of the reaction is the $(CH_2)_X$ chain length, as other chain lengths result in cyclic compounds. This homopolymer can be used to form branch and star polyelectrolytes which have even higher molecular weights by using the end group of (2).

The branch polymers have a comblike structure formed by attaching units of the developed homopolymer to a polymeric substrate. The substrate should contain functional groups reactive with the homopolymer and should have a repeating structure of one of the following forms.

where R¹ is the residue of the polymerization reaction forming the backbone of the polymer and may be an aliphatic or aromatic hydrocarbon or a heterocarbon, containing from 2 to 30 carbon atoms depending on the spacing desired for the branches.

R² can be hydrogen or low molecular-weight alkyl or aryl groups such as phenyl. R³ is a short-chain linking group such as low molecular-weight alkylenes, phenylenes, and alkyl esters. D is a functional group reactive with either the amine or the halide in the monomer.

Star polyelectrolytes are formed by attaching radial sections of the developed homopolymer to a central monomer as follows:

(continued overleaf)

where Y is a polyvalent, comparatively low molecularweight organic group having a valence from 3 to 6 and R³ and D are as defined above. Y can be an aromatic compound such as benzene or alkylated benzene. Suitable central monomeric compounds are 2,4,6-tri-(chloromethyl)-mesitylene, 1,2,4-tri(chloromethyl)-benzene, and 1,2,4,5-tetra(chloromethyl)-benzene.

In both cases, the polymerization involves a head-to-tail quarternization reaction of the monomer (1) to form linear chains. The reaction is conducted in the absence of oxygen to prevent the formation of water-insoluble products. A relatively high monomer concentration is used in the reaction mixture, and the reaction temperature is maintained at from 90° to 110° C approximately. Polymerization is completed when the monomer is consumed in the reaction mixture.

Note:

Requests for further information may be directed to: Technology Utilization Officer NASA Pasadena Office 4800 Oak Grove Drive

Pasadena, California 91103 Reference: TSP74-10159

Patent status:

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457(f)], to the California Institute of Technology, Pasadena, California 91109.

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