Characterization and Developments of Polymers of Intrinsic Microporosity (PIM)

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DESCRIPTION

PIMs have shown efficacy for producing membranes and sensors because they combine solution process ability, microporosity, and structural diversity. There are certain key techniques for determining intrinsic microporosity like gas absorption, along with the relationship between structure and property. A continuous network of interconnected intermolecular gaps, known as intrinsic microporosity, is a property of polymers that results directly from the rigidity and shape of the constituent macromolecules. In general, polymers enclose the space to minimize blank space and enhance favourable interactions between the constituent macromolecules (from a molecule's perspective, "empty space is wasted space"). The majority of polymers have enough conformational flexibility to change their shape in order to increase cohesive connections between molecules and effectively use packing space. Polymers were designed with extremely stiff and distorted molecular structures to produce "awkward" macromolecular forms that cannot pack space effectively as our method for enhancing inherent microporosity. In particular, due to their fused ring structures, PIMs do not possess rotational freedom along the polymer backbone, which ensures that the macromolecular components cannot rearrange their conformation so that their highly contorted shape is fixed during synthesis.

The author's research on phthalocyanine materials served as the inspiration for PIMs. Metal-containing phthalocyanines can exhibit important catalytic activity, particularly for oxidation reactions. Phthalocyanines are large aromatic macrocycles related to naturally occurring porphyrins. The face-to-face aggregation of the macrocycles, however, impairs the phthalocyanines ability to catalyse reactions in the solid state. Following a number of exploratory synthetic studies to develop a suitable polymerization reaction that created the necessary spirocyclic framework, including the idea of using spiroketal polymerizations, it was discovered that the phthalocyanine-forming reaction of a spirocyclic bisphthalonitrile was the most straightforward way to achieve the formation of a spirocyclic phthalocyanine network polymer. Because the efficiency of network creation during the synthesis of the microporous networks was impossible to determine directly due to their insolubility, the parallel production of non-network PIMs unexpectedly resulted from some straightforward control studies.

As a result, alternative methods have to be used to examine the effectiveness of the dibenzodioxin-forming polymerization procedure used to create the network.

Synthesis

To create the dibenzodioxin linkage, PIMs are created using a polymerization reaction based on a double-aromatic nucleophilic substitution mechanism. One of the rare reactions that can create two covalent connections simultaneously and with enough efficiency to produce a connecting group made up of fused rings, allowing it to produce ladder polymers with high average molecular masses. In general, it is known that aromatic nucleophilic replacements go forward quickly, especially if an electron-withdrawing substituent activates the halide-containing monomer. This procedure has been used in the past to create extended planar molecules and oligomers for discotic liquid crystals as well as phthalocyanine oligomers.

Structural characterization

PIMs can be structurally studied using solution 1H and 13C Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC) in the same way as other soluble polymers. The polydispersity (M_w/M_n) can be determined using the number average (M_n) and weight average (M_w) of molecular mass estimation is provided by GPC. The GPC figures should be used with some caution because they were generated using calibrations against reference polymers with known molecular masses (such as polystyrene), which have different structural properties. Nonetheless, any difference should be minimal because PIMs and polystyrene are both random coil polymers. By

using matrix-assisted laser desorption ionization mass spectrometry, it is possible to identify the type of end-groups and determine whether cyclic oligomers are present.

Characterization of microporosity

Information on the microporous structure derived from the packing of the PIM macromolecules in the solid state can be obtained using a variety of techniques. However, it should be stressed that all techniques depend on the form (such as powder, thin film, etc.) and historical history of the solid due to the ensuing amorphous structure and lack of a covalent network (solvent of solid fabrication, exposure to vacuum, exposure to heat, ageing, etc.). Even during examination, micropore structure could alter. For instance, the adsorption of gas molecules that causes the material to inflate. Gas Sorption Analysis, Positron Annihilation Lifetime Spectroscopy (PALS), and computer simulation are all used in the characterization of microporosity. Solubility, mechanical, chemical, and thermal properties, and microporosity are the defining characteristics of PIM. PIMs are the only materials that combine the solution process ability of a polymer with some of the benefits of a microporous material, such as the ability to take in and transport specific molecular species.

As a result, they have potential for use in sensors, gas separation membranes, Organic Solvent Nanofiltration (OSN) membranes, and membranes for membrane pervaporation.