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MASTER

SYNTHESIS OF NEW FUNCTIONALIZED FLUOROCARBON POLYMERS

FOR USE AS BATTERY SEPARATORS AND MEMBRANES

Contract #EG-77-S-05-5462

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Synthesis of New Functionalized Fluorocarbon Polymers

For Use as Battery Separators and Membranes

Two years ago, a grant from the Department of Energy (then ERDA) provided funds so that we could engage in a speculative program designed to prepare functionalized fluorocarbon polymers employing three main synthetic routes. Initially, we chose to study the oxyfluorination of branched polymers such as poly-4 methylpentene and the synthesis of functionalized polymers via hydrolysis of perfluorinated pendant polyesters and perfluoro-anhydride polymers obtained by direct fluorination of polyester and anhydride hydrocarbon starting materials. All three routes have been highly successful and applications oriented funding will be sought for further development of the promising materials.

A. "Oxyfluorination" Program

Much effort has been devoted to the synthesis of new polymeric materials employing the oxyfluorination reaction. Almost any polymer containing pendant methyl, ethyl or other alkyl groups may be treated with a mixture of oxygen and fluorine to produce a functionalized fluorocarbon material as in examples 1 a and b.

This process is very efficient in the case of finely powdered or 5 mil thick polypropylene. Up to 65% of the methyl groups may be successfully converted to acid fluoride functionality. As was previously discussed, the degree of functionality may also be controlled by the reaction conditions and particularly by the oxygen-fluorine ratio. Of primary importance here is the crystal structure or amorphous character of the starting material. A number of investigations will be made with polymers crosslinked by chemical or by radiation processes. From our experiments we have found that this has a very important effect on the properties of the resulting fluorocarbon. Some specific examples of polymers of prime interest include a functionalized fluorocarbon material from low density polyethylene.

Low density polyethylene, of course, contains a high degree of methyl and ethyl pendant groups.

B. Preservation of Functional Groups of Polymers

In this program the goal was to maintain functional groups during direct fluorination and use these as sites in the membranes or to preserve groups and then hydrolyze or alter chemically the group to become a site in the membrane. Capabilities developed in the fluorination of small molecules prove very important here.

1. Perfluorester groups (Pendant Polyesters)

One of the more important and promising groups are the polyesters which can be fluorinated as in example (a) and preserve up to 80% of the ester linkages.

Of ester linkages which do decompose, most end up acid fluorides directly. The perfluoroesters are extremely hydrolytically unstable and are easily hydrolyzed to give the perfluoro acids. Specific examples of interest include methyl methacrylate.

b.

Alternatively since both sides of a perfluoroester upon hydrolysis are converted to perfluoroacids, polymers such as polyallylic acetate may be converted to functional fluorocarbon polymers:

The physical properties of the new materials prepared under DOE contract EG-77-S-05-5462 have been evaluated and studied by Dr. Dean Sheibley and Dr. Li Hsu of the Electrochemistry Branch, Power Generation and Storage Division of the National Aeronautics and Space Administration's Lewis Research Center in Cleveland. Drs. Sheibley and Hsu have studied new materials from the oxy-fluorination process, new materials from the pendant polyester approach and new materials from the polymeric anhydride approach, and all are thought to be promising new functionalized fluorocarbon polymers. In each case, a conducting material was obtained and a development program involving these materials is now planned.

Recent Advances in Membrane Synthesis and Characterization

In addition to developing new methods for preparing new structures having perfluorocarboxylic acid functionality, we have designed film-forming polymer mixtures which permit independent control of the cross-link density and the concentration of ionizable groups. This achievement is particularly important because a single polymer combining all three characteristics would be difficult to synthesize. For example, polyacrylic acid contains too many carboxyl groups and is a poor film-former, while copolymers of polyethylene and acrylic acid or its esters commonly contain too few carboxyl groups, but are good film formers. In the case of maleic anhydride, alternating copolymers

are available (where R = H, or C₂ to C₁₆ alkyl chains). However, these resins are not good film-formers, and the concentration of carboxyl groups is too high.

Our discovery that the film-forming and carboxyl content can be separately balanced has allowed us to prepare fluorinated films with resistance less than 10 ohm-cm², and stable enough to withstand boiling aqueous acid for many hours. The water uptake is a measure of cross-linking in the films and can be controlled. We are already in the desired range of 5-20% weight increase.

Our Differential Scanning Calorimeter has been extensively employed to study the crystallinity and glass transitions of the polymer blends, and the effects of fluorination on these crucial properties. For several systems we have observed that fluorination under mild conditions leaves crystalline material unaffected: that is, the melting temperature is unchanged. Quantitative studies are underway to determine the fraction of crystalline material remaining under various conditions, using the heat of fusion of the sample as a monitoring tool.

We are investigating methods of making the crystalline fraction of the films accessible to fluorine under the mild conditions necessary to preserve physical strength and functionality in the films. It is not clear that partially fluorinated structures will be unsatisfactory, but the rate of diffusion of oxygen in crystalline polyethylene (10^{-16} cm²/sec. compared to 10^{-8} cm²/sec. amorphous polyethylene) suggests that oxidation will occur eventually.

The compatibility and film-forming characteristics of polymer pairs structurally related to the carboxylic acid materials described above are being explored, and additional methods of characterizing the microstructure of these new membranes are under study.

Cross-linking and Microstructure

Cross-linking has been carried out in the absence of air at room temperature and the results as determined by swelling and conductivity are acceptable. However, the detailed behavior of the membrane may be affected by the distribution of cross-links, as for example between amorphous and crystalline domains in the membrane. We plan to study the effect of cross-linking conditions on membrane performance for selected systems.

Patents and Publications Resulting From Contract EG-77-S-05-5462

To date, one manuscript has been submitted from this research program:

Synthesis of Functionalized Fluorocarbon Polymers by Direct Fluorination of Pendant Polyesters, Chem. Comm., in press, R.E. Aikman and R.J. Lagow.

The other manuscripts are being prepared and have been withheld in consideration of patent priority. These manuscripts will involve:

1. A study of the oxyfluorination reaction of poly-4 methylpentene
2. The synthesis of functionalized polymers from maleic anhydride copolymers
3. The synthesis of functionalized fluorocarbon membranes from the polyacrylic acid-ethylene copolymer

We are in the process of writing a patent disclosure entitled "New Functional Fluorocarbon Membranes" and the University of Texas is in the process of requesting patent waiver on this invention from the Department of Energy.