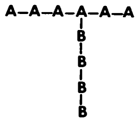
Reports

Detection of Charged Particles by Polymer Grafting

Abstract. *Tracks of fission fragments from a californium-252 source have been revealed by graft copolymerization. A 15 percent solution of propenoic (acrylic) acid monomer was reacted with irradiated cellulose triacetate for 24 hours at 55°C. Copolymer forms preferentially at the track sites and it can be dyed with rhodamine B because of its acid and hydrophylic properties. After the dyeing, the tracks were seen by using fluorescence microscopy.*

A new way to detect the tracks of ionizing particles and visualize their trajectories has been discovered (*1*). The technique is entirely different from conventional chemical etching methods. The principal idea behind the new method is the formation of a graft copolymer along a particle's path.

The principle of graft copolymerization has already been explained in detail (*2*). Briefly, if a polymer chain A_n is represented by a row of monomer elements A, such as A–A–A–A–A, then a graft copolymer made with another monomer B can be represented as A–A–A–A–B–B–B–B, or



$$\begin{array}{ccccccccccc} A & - & A & - & A & - & A & - & A & - & A \\ & & & & & & | & & & & \\ & & & & & & B & & & & \\ & & & & & & | & & & & \\ & & & & & & B & & & & \\ & & & & & & | & & & & \\ & & & & & & B & & & & \\ & & & & & & | & & & & \\ & & & & & & B & & & & \end{array}$$

Ionizing radiation induces the formation of copolymer by creating chemically active sites, such as trapped radicals or peroxidized elements, on the original polymer chain A_n. Radiation doses of the order of 10 krad are sufficient in some cases to induce the grafting of measurable amounts of monomer.

An energetic, charged particle creates large doses of ionizing radiation around its path. Theoretical calculations show that a dose of the order of 10 krad or more is deposited within a unit volume at a radial distance of 30 nm from the core of alpha particles in plastics (*3*). The dose per unit volume increases with a decrease of the radial distance. The chemical change induced by ionizing radiation has been successfully utilized to detect particles by the method of track etching (*4*). This creation of chemically active sites along the particle's path should be sufficiently large to induce the formation of graft copolymer, since previous experiments (*2, 5*) have shown that doses of the order of 10 krad were large enough to induce bulk grafting.

The formation of an appropriate copolymer along a particle trail can be used to make the particle path visible. Specifically, we have chosen a monomer called propenoic (acrylic) acid, which is hydrophylic as well. The copolymer formed with it retains these properties and, consequently, is easily colored with a basic dye.

We grafted acrylic acid along the paths of fission fragments in cellulose triacetate (Bayer Triafol TN). Using a ^{252}Cf source, we irradiated samples of cellulose triacetate (CTA) with a fission fragment density of about 10^5 particles per square centimeter. The sample was immersed into acrylic acid solutions at room temperature, and the reaction vessel was covered with aluminum foil to protect the solution from light (light can initiate homopolymerization). The grafting solution was prepared with acrylic acid twice distilled under vacuum and deionized distilled water. The acid was found to be more than 99.9 percent pure by gas chromatography.

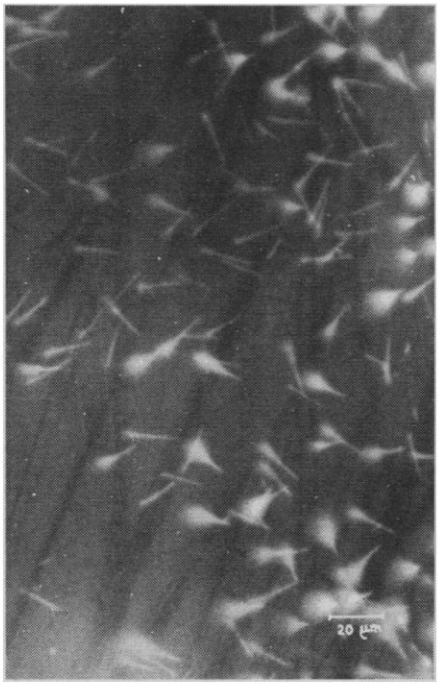


Fig. 1. Tracks of ^{252}Cf fission fragments obtained by grafting propenoic acid onto cellulose triacetate (for details see text).

We performed some preliminary experiments to determine the change in grafting with variations of concentration and temperature. Concentrations of 15 percent and 20 percent acrylic acid successfully form tracks. Grafting is more rapid in the 20 percent solution, but since the degree of swelling of CTA samples increases and they become fragile, we generally used a 15 percent solution. We obtained well-grafted tracks after 24 hours at 55°C and after 6 hours at 70°C. Qualitatively, the grafting rate varied with temperature with a dependence similar to that found by Davenas (*6*) for copolymer formation.

After the grafting reaction, we extracted the excess monomer and any homopolymer formed in deionized water at 50°C for 2 hours. We then dyed the sample in a boiling, 3 percent solution of rhodamine B for 2 hours. We removed the unfixed dye in a 2.5 percent acid soap solution for 1 hour, or until no further color was removed.

We viewed the sample with a Leitz Ortholux microscope equipped with an ultraviolet lamp. With blue filters to give peak illumination at 400 nm, the rhodamine B fluoresces with an orange color. The excess blue light was eliminated with a 530-nm cutoff filter, so that the tracks appeared as bright lines on a dark field (Fig. 1). It was necessary to employ fluorescence microscopy when the tracks were not intense or the background was high. The background is due to a slight surface absorption of rhodamine B by the plastic sheet. This commercially available plastic has a bright smooth surface and an irregular fluffy one; the dye is absorbed especially on the fluffy surface and gives the perturbing background. In our best samples, however, we could see the tracks with visible light.

We are sure that the lines correspond to fission fragments. Since the monomer diffuses well through the plastic, it should polymerize all along the particle range. The measured length of the tracks was 20 ± 1.5 μm, which corresponds to the average expected range of fission fragments. Furthermore, the density of the tracks varied directly with the irradiation time. However, at the present state of development, we have a recording efficiency of about 50 percent for etched tracks in CTA. (Track efficiency is the percentage of tracks relative to the total number of bombarding particles.) Since oxygen inhibits polymerization, we performed an experiment in an oxygen-free environment. The results indicate that it should be possible to detect fission fragments with 100 percent efficiency.

The tracks are not etched by acrylic acid, nor does the dye fix onto them in ungrafted samples. Before being dyed, irradiated samples treated with acrylic acid do not show any tracks when the grafted samples are viewed under the microscope. Therefore, it is concluded that acrylic acid does not etch. Furthermore, irradiated samples were processed in 15 percent acrylic acid solution at 55°C for 24, 48, 72, and 96 hours, and then dyed. In the last sample, the background was too intense for any tracks to be seen, but in the other samples the diameter (1.5 to 2 μm) and the length of the tracks remained approximately the same. If the tracks were due to acrylic acid etching we would expect them to increase in diameter. We tried to obtain tracks by processing ungrafted samples for more than 6 hours in the boiling dye solution and then for 48 hours in the same solution at room temperature, which increased the opportunity for the dye to fix if this could possibly happen: no tracks were formed. Therefore, we conclude that the tracks observed after the whole graft-and-dye process are not due to preferential fixation of the dye along the particle's path.

The question can be raised whether we have really formed graft copolymer. Although the low density of fission fragments precludes the measurement of any increase in weight, we demonstrated in several ways that acrylic acid was grafted along the tracks. One indication of grafting is that the dye was preferentially fixed on the tracks. Tracks were still visible in a sample extracted for 48 hours at room temperature and then for 16 hours in a Soxhlet apparatus before dyeing. This apparatus keeps fresh pure solvent (water) around the sample, and increases the efficiency of the extraction process. Since we extracted much longer than the time necessary to remove the water-soluble monomer, the dye must have been fixed onto copolymer. A compelling indication of the formation of copolymer is that the efficiency of track recording decreased when polymerization inhibitors were added to the acrylic solution. When the grafting solution was made with 0.004 percent *p*-ethoxyphenol added as an inhibitor, the track recording efficiency decreased to about 5 percent. If a small amount of copper ions was also added, we rarely found a track.

We believe that polymer grafting can be developed into a valuable method for detecting ionizing particles. Our progress in grafting acrylic acid onto CTA indicates that we will be able to obtain tracks as distinct as those obtained by etching. An advantage of polymer grafting over particle track etching is that it does not remove the track core. Also, plastics that are difficult or impossible to etch, such as Teflon and the polyolefins, have been graft copolymerized in bulk (*2*, *7*). The development of tracks by graft polymerization in these materials would be especially interesting.

This new technique may find useful applications in many problems. The track etching technique implies a continuous trail of damage, the intersection of this trail with the surface detector, and a detection threshold. In principle, these three limitations should be suppressed in the graft polymerization technique of particle detection. This means that it might be possible to record tracks of relativistic heavy ions or particles with low linear energy transfer. It would also be possible to visualize an event originating in the detecting medium, such as fission induced by neutrons or pions. In addition, if we can fix a heavy element compound instead of rhodamine and use the electron microprobe associated with a Stereoscan electron microscope, we should be able to record and count the tracks automatically. The graft polymerization technique is not restricted to acrylic acid copolymerization but can be extended to several other convenient monomers. It would be possible to choose the monomer according to the detection sensitivity needed without degrading the detectors, which occurs with the track etching technique. But much more has to be done before this new detection technique for ionizing particles is developed into a valuable method.

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Late Glacial and Postglacial Productivity Changes in a New England Pond

Abstract. *During the late glacial and postglacial the productivity of Berry Pond in Berkshire County, Massachusetts, underwent a number of significant oscillations. This is suggested by data on sedimentary chlorophyll degradation products, diatoms, and Cladocera. The productivity changes were apparently controlled by changes in weathering, terrestrial vegetation in the watershed, litter production, and runoff. There are associated changes in cladoceran community structure.*

Berry Pond is a small glacial lake (surface area, 3.9 ha; water depth, 2.8 m) located on a ridge crest (elevation, 600 m) in the Pittsfield State Forest, Berkshire County, Massachusetts. The pond has one outlet, a small stream which flows over a rocky ledge on the western shore, and is surrounded by a forested watershed of about 28 ha. The forests are northern hardwoods.