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Publication Date
1978-01-27
Submitted to Science

CR-39: A NUCLEAR-TRACK-RECORDING POLYMER OF UNIQUE SENSITIVITY AND RESOLUTION

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Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48

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CR-39: A Nuclear-Track-Recording Polymer
of Unique Sensitivity and Resolution
Abstract. CR-39 is a commercially available, optically clear, amorphous, thermoset plastic in which nuclear particle tracks can be revealed by etching in a hot NaOH solution. Its uniformity of response (<1% variation), high sensitivity (e.g., it records 1 MeV protons, 6 MeV alphas, and minimum-ionizing Fe), and superb optical quality make it ideal for identification of mass and charge of nuclear particles and for other applications.
Nuclear-track-recording solids, in which tracks can be enlarged to visible size by chemical etching, have found wide application (1). For example, such a solid can be used to identify energetic nuclear particles, because the rate of growth of the conical etch pit that develops at the intersection of the particle's trajectory with the surface is an increasing function of the rate of energy loss of the particle. The track etch rate is, in principle, nearly immune to the energy-loss statistics that plague all other charged particle detectors, because it is controlled by the energy density deposited within a few tens of Angstroms of the center of the particle trajectory (2). An etched detector suffers only negligible fluctuations in response resulting from delta-ray generation (3) and ought to provide the greatest resolution of any charged particle detection system yet developed. In practice, non-uniformities and inhomogeneities in the track-recording solids used to date have prevented their theoretical resolution from being attained. For example, in Fig. 1(a) one can see for a Lexan detector the somewhat ragged mouth of an etched track and the rough and uneven surface around it--obvious evidence of locally non-uniform etching that limits detector resolution. The irregularities in commercially available Lexan are largely a consequence of the extrusion and quenching process by which it is made (4).

In this paper we report the discovery of the track-recording properties of a very homogeneous polymer called CR-39 with which we have achieved a resolution much higher than that for any other track-recording solid. In a systematic study of the properties required of a high-resolution polymer detector, one of us (BGC) concluded that such a
material should have (a) high homogeneity and isotropy, (b) high radiation sensitivity, and (c) high optical transparency and uniformity; and that (d) there must exist a stable, non-solvent chemical reagent that can accomplish interfacial polymer chain degradation of the material. A logical chain of reasoning (5) leads one to conclude that the ideal polymer detector should be an optically clear, amorphous, non-cross-linking, radiation-sensitive, thermoset material that is susceptible to interfacial degradation by a convenient etchant.

The first material we have found to satisfy these requirements is the polymer whose monomer is the oxydi-2,1-ethanediyl di-2-propenyl diester of carbonic acid. The monomer, commercially known as "CR-39" (6), presently finds application as the major component in copolymers used for eye-glass lenses. Flat plates of a convenient size, 0.2 cm x 5 cm x 10 cm, but of variable composition and quality, are sold at welding supply shops as cover plates for welding shields. Cast sheets 1.2 m x 1.8 m in area and of quite uniform properties are available from several suppliers (7).

We have exposed welding shield cover plates to $^{252}$Cf fission fragments and alpha particles (6.07 MeV), to protons of various energies (obtained at the 88-inch cyclotron at the Lawrence Berkeley Laboratory) and to 20 GeV argon ions (obtained at the Bevalac, also at Lawrence Berkeley Laboratory). Figure 1(b) is a photomicrograph showing the extraordinary optical quality of the material and of the mouth of a track after etching in NaOH solution. The contrast between the precision of the ellipse in the case of CR-39 and in the case of Lexan speaks for itself. The clarity with which 6.07 MeV alpha particles
(and also protons of ~1 MeV) are revealed is striking, and the signal to noise ratio is unprecedented.

For one set of etching conditions (6 hours in 6.25 N NaOH at 75° C), Fig. 2 shows the response of the welding shield cover plates to protons, alpha particles, and argon ions as a function of range. Assuming that ionization is proportional to $Z^2/\beta^2$, the response to argon ($Z = 18$) is approximately $V_T/V_B = 1 + (Z/Z_0)^3$, where $V_T$ is the track etch rate, $V_B$ is the bulk etch rate, $\beta$ is the speed of the particle in units of the speed of light, and $Z_0$ is a constant for a given sample. Typically $Z_0 \approx 23$, but it can be as low as ~20, which means this material ought to detect vertically incident, fully relativistic ions as light as calcium. This sensitivity is higher than that of any track-recording material reported to date.

With these samples, in contrast to Lexan (1), there is no enhancement of the ratio $V_T/V_B$ after exposure to ultraviolet radiation. $V_T/V_B$ is unaffected after annealing for one-hour periods at temperatures up to ~100° C. $V_B$ is characterized by an activation energy of $0.85 \pm 0.05$ eV for NaOH etchants. For normalities between 3N and 10N, $V_B$ is approximately linear in the normality of the NaOH solution. Whereas $V_T/V_B$ for Lexan increases rapidly during the first day or so after irradiation (1), we detect no difference of $V_T/V_B$ in samples etched minutes after irradiation and in those etched after seven days.

Figure 3 shows some of the results of our first study of the resolution of a CR-39 detector. From a single 0.5 m² sheet of CR-39 obtained from Polytech, Inc. (7), we cut many 3 cm x 3 cm x 0.2 cm squares, randomly assembled them into two stacks, irradiated both
stacks with a beam of 33 GeV Fe ions at the Bevalac, and etched one stack for 144 hours at 40° C in 6.25 N NaOH and the other stack for 21 hours at 70° C. As Fig. 3 shows, the response curves change markedly with etch temperature. At all etch temperatures studied (28° C to 95° C), CR-39 is much more sensitive than Lexan. The sensitivity increases with etch temperature, but the resolution, which is related to the rate of change of \( \frac{V_T}{V_B} \) with range, is best at a low etch temperature and an intermediate range. For a sample of 100 Fe nuclei for which \( \frac{V_T}{V_B} \) was measured at residual ranges between 0.1 and 0.2 cm in the stack etched at 40° C, the 100 measurements fit a smooth curve with a standard deviation of 1.34%. This is equivalent to a charge resolution of \( \sim 0.09 \) charge at Fe (assuming ionization \( \propto Z^2/\beta^2 \)) and a mass resolution of 0.6 amu at Fe. For the 40° C etch the track etch pits were only \( \sim 0.1 \) to 0.2 mm in length, leading to measurement errors (always \( \sim 1 \) to 2 μm) that could account for most of the spread. The actual variability in response is thus smaller than 1.34%. No variability from top surface to bottom or from one square to another was detected.

In another test using 20 GeV argon ions we etched for a longer time to produce larger pits and were unable to detect a variation of as much as 0.5% from one region of the sample to another. These results represent an impressive improvement over the ~3 to ~8% variability typical of Lexan (8). The goal of resolving isotopes of charged particles with mass differences of only 1 or 2% may be attainable by etching until the pit lengths are >2 mm, so that measuring errors of \( \sim 2 \) μm are unimportant, and by carefully controlling the process of cell
casting by which CR-39 is made.

In conclusion, the sensitivity, resolution, and optical properties of CR-39 are unrivalled among track-recording solids. Even after removal of 500 microns by etching, the surface remains glassy smooth, in fact, difficult to detect in the microscope in the absence of tracks or scratches. There are grounds to hope that with careful manufacture, this material may be unique among all detectors in resolving power.

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References and Notes


2. Ibid., pp. 10-15.

3. As a concrete example, the spread in signal of an Fe nucleus with velocity 0.8 c in a 1 mm thick detector is ~4% for a plastic scintillator, which responds only to close collisions, is ~2% for a semiconductor detector, which responds to total dE/dx, and is less than ~0.15% for an etched track detector, which responds only to distant collisions (S.P. Ahlen, private communication).


5. The chain of reasoning used is as follows:

   The requirement of homogeneity and isotropy can be satisfied only by totally amorphous polymers. Polymers exhibiting crystalline tendencies are inherently heterogeneous, being composed of a mixture of amorphous zones and crystalline regions of quite different density and chemical reactivity. The tendency to crystallize may be inhibited by rapid quenching from the liquid state, but this process is violent, freezing in stresses that are themselves a source of inhomogeneity. Lexan is eliminated from consideration by this requirement.

   The requirement of high radiation sensitivity divides polymers into two classes: those that form cross-links upon irradiation and those that undergo molecular weight degradation under irradiation (some materials simultaneously exhibit both responses). Since cross-linking polymers are made stronger by irradiation, they are poor candidates for further consideration. One therefore is looking for
a chain-breaking material characterized by a very small average energy deposited per chain rupture. Cellulose nitrate is an example.

A suitable etchant—but not a solvent—must be found for materials that survive these first two tests. A solvent removes molecules unbroken into solution, a process often associated with swelling in polymers. An etchant, on the other hand, chemically degrades molecules (i.e., breaks bonds) solely at the liquid-solid interface. A chemically attractive etchant must be rejected if it is also a solvent. "Thermosetting" polymers, which form random three-dimensional cross-linked structures, are favored, since by definiting, no solvent exists for a thermosetting material. (A sample of a thermosetting material can be considered to be a single molecule, in that covalent bonds link every portion of the material with every other.)

6. CR-39 in the liquid monomer form is available from Pittsburgh Plate Glass Industries, Pittsburgh, PA.

7. Available in large sheets from the Homalite Corporation, Wilmington, DEL., and from Polytech, Inc., Owensville, MO.


9. We thank C.T. O'Konski and S.P. Ahlen for discussions. P.B.P. thanks the John Simon Guggenheim Foundation for a fellowship. Research supported by USERDA.
Figure Captions

Figure 1. Comparison of surfaces of (a) Lexan and (b) CR-39 etched in NaOH solution. The thickness of material removed by etching was 25 μm for Lexan and 45 μm for CR-39. The elliptical holes are the mouths of track etch pits that intersected the surface at an angle. For CR-39 the particle that produced the track was $^{40}$Ar; for Lexan it was an ultraheavy cosmic ray with $Z > 75$. The minor axis of the ellipse for CR-39 is 80 μm. The greater homogeneity of CR-39 than of Lexan results in a far smoother etched surface, far more uniform etched track lengths and diameters, and less variability of response to particles of a given ionization rate.

Figure 2. Data for track etch rate as a function of range for protons, alpha particles and $^{40}$Ar ions of various energies in a sample of welding shield cover plate made of 80% CR-39 and 20% an unknown copolymer. Some samples of pure CR-39 are considerably more sensitive. For example, the reduced etch rate, $V_T/V_B - 1$, for an alpha particle of 40 μm range can be as high as 1.5.

Figure 3. Response of two stacks of Polytech CR-39 to $^{56}$Fe ions from the Lawrence Berkeley Laboratory Bevalac, compared with the response of Lexan. The experimental points were obtained for Fe tracks in the stack etched 144 hours in 6.25 N NaOH at 40°C. The fractional standard deviation of the large sample of data at ranges between 0.1 and 0.2 cm about a
smooth curve is 1.3%. Most of the deviation may be due to errors resulting from the limited resolution of an optical microscope and could be decreased by etching the tracks to a larger size.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.