be produced either by a primary soft particle or by the cascade process for the following reasons:

(1) Any highly energetic soft particle capable of producing so many (more than 200) particles would have surely multiplied long before in the thickness of lead of 13 cm that it had to cross before it reached the third lead plate inside the chamber.

(2) This high multiplication in such a short range (less than two radiation units) is almost impossible by the cascade process.

(3) A cone of a shower produced in a direction opposite to the direction of the incident particle is not possible in a cascade process.

The shower is therefore due to some explosive process which has taken place just inside the upper surface of the third lead plate. The production of particles in almost all directions and particularly a copious number in the upward direction indicates a time lag between the incidence of the initiating particle and the occurrence of the explosion.

The nature of the particles constituting the shower is difficult to determine. The occurrence of one or two heavy nuclei inside the downward cone cannot be detected. It is, however, clear that most of the particles emitted in the upward direction are soft and of low energies as they could not penetrate the second lead plate (thickness 2 cm). Among the particles emanated in the downward direction, there are some very straight and thin tracks which appear to be highly energetic and penetrating.

We believe this picture to be unmistakable evidence of the production of soft and penetrating particles in one act by the nuclear interaction of an incident particle with a lead nucleon. There are three particles entering the chamber from above; but none of these seem to be the originator of the shower and nothing can be said with certainty about the initiating particle except that it is definitely not electronic in nature.

The author is indebted to Dr. D. M. Bose for very helpful discussions on this photograph.

[1] B. Rossi, Rev. Mod. Phys. **21**, 104 (1949).
[2] M. S. Sinha, Phys. Rev. **64**, 248 (1943).

Study of High Polymers by Nuclear Magnetism*
I. Line Widths at Room Temperature

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QUALITATIVE observations on nuclear magnetism in rubber-like high polymers have been reported by Alpert.[1] Recently, we have obtained quantitative data on the magnetic resonance line widths of various polymers. We have also followed the line width as a function of temperature through the transition range which separates the soft, rubbery state from the hard, glassy state. (See following Letter to the Editor.)

The line widths, in gauss, at room temperature, obtained in a field of approximately 7000 gauss at about 30 Mc, are shown in Table I.

The width of 0.19 gauss represents the line width due to magnetic field inhomogeneity, determined by obtaining the line width for a water sample. Both unvulcanized natural rubber and GR-S

TABLE I. Line widths.

Sample	Unvulcanized	Vulcanized	Carbon black loaded 30%	Carbon black loaded 50%
Natural rubber	≤0.19	≤0.19	≤0.19	
GR-S	≤0.19	0.27	0.57	0.67
Hycar OS-10	0.38	0.51	0.57	
Butyl rubber	0.38	0.42	0.91	
Polyethylene	0.57			
Plexiglas (at 103°C)	1.2			
S-polymer 30	1.5			
S-polymer 50	1.9			
S-polymer 75	5.8			

may have, therefore, a width narrower than 0.19 gauss. The GR-S signal is perhaps slightly broader than that for natural rubber.

GR-S and Hycar OS-10 are approximately 70/30 and 50/50 butadiene styrene co-polymers respectively. The S-polymers 30, 50, GR-S and Hycar OS-10 are approximately 70/30 and 50/50 butadiene styrene co-polymers respectively. The S-polymers 30, 50, and 75 are isobutylene-styrene co-polymers, the number giving the approximate styrene content. Plexiglas is polymethyl-metacrylate.

The narrowness of the line width for unvulcanized natural rubber and GR-S shows that the "free" rotation of molecules containing proton groups is about as fast in these rubbery materials as that of the protons in water. This "free" rotation must take place with a frequency much higher than that of the r-f field (30 Mc), so that the magnetic interaction of the "freely" rotating protons averages out. One expects that vulcanizing (cross linking of flexible long chains) and loading with carbon black will impede the "free" rotation, thus broadening the line as observed. One also expects increasing amounts of styrene to impede "free" rotation more and more, again broadening the line as observed in going from GR-S to Hycar OS-10 and from S-polymer 30 to 50 and 75. The large line widths for the S-polymers indicate that the "free" rotation is slowed down to a frequency comparable to that of the r-f field of 30 Mc. It seems that the method of nuclear magnetism is the first one to prove *directly* the existence of "free" rotation in polymers, a concept which was previously inferred *indirectly* from other phenomena and which forms the basis of the statistical network theory of rubber elasticity.

[1] N. L. Alpert, Phys. Rev. **75**, 398 (1949).

Study of High Polymers by Nuclear Magnetism*
II. Line Widths through Transition Temperatures

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July 10, 1950

THE polymers investigated (see preceding Letter to the Editor) exhibit in a certain temperature region a transition from the soft rubbery state to a hard, glassy state. The line width was found to increase with decreasing temperature through this transition region. For natural rubber this increase in line width was not large. However, the signal weakens so much as one approaches the transition region (−70°C) that accurate measurements of line width or shape are precluded. Since natural rubber is known to crystallize, it seems reasonable to attribute these results to crystallization or a related process which suppresses the rotation of molecular groups in a major fraction of the material. This would drastically broaden the contribution of these groups to the resonance line and correspondingly weaken it; the observed sharp resonance line would then be due to a relatively
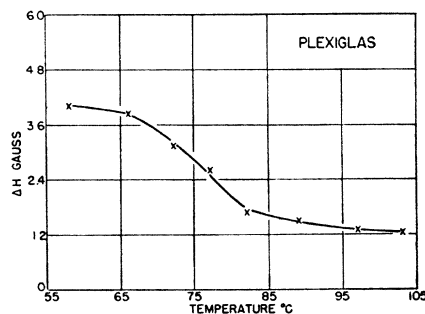

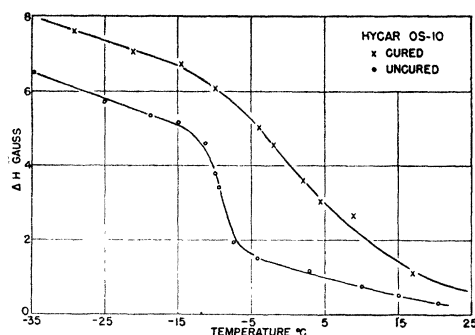FIG. 1. Line width as a function of temperature for polymethylmetacrylate.

FIG. 2. Line width as a function of temperature for cured and uncured Hycar OS-10.

few groups with rotation still unhindered, and would be superposed on a broad "background" due to the rest of the groups. This interpretation is being checked experimentally. For Hycar OS-10 and Plexiglas, known not to crystallize, it was possible to study the line width as a function of the temperature through the transition region. The results are presented in Figs. 1 and 2.

The curve of Fig. 1 for the unvulcanized Hycar OS-10 shows a change in line width that is surprisingly sharp for a material so inhomogeneous and irregular.[1] It seems plausible to consider the change as a three-step process. As one lowers the temperature, the first step is an initial increase of the line width; it may be associated with a gradual decrease of the free volume of the molecules, which interferes with the relative motion of adjacent chain segments. The second step is a sudden increase in line width which suggests an abrupt cessation of some type of motion, presumably the rotation of molecular groups. The third step, a further gradual increase of the line width, may be connected with a gradual stopping of the sliding of adjacent segments past each other. Conversely, starting at low temperatures, "holes" must first be created for motion of the segments, before free rotation in the segments can set in.

The whole three-step transition must be due to short-range forces involving near neighbors only. The suddenness of the second step suggests that it is due to a cooperative effect, such as the formation of domains in which molecular rotations are impeded, but which are too small for detection by x-ray spot diagrams. One must expect an abrupt change in the elastic properties of the material to result from such a suppression of rotations. One must also expect that curing will interfere with group rotation, but even more with the formation of cooperative domains, just as it interferes with the crystallization of natural rubber. Thus one can understand the larger initial line width and the absence of abrupt changes in ΔH observed in cured Hycar OS-10.

The line-width transition for Plexiglas, shown in Fig. 2, is more gradual. The initial line width is considerably higher here than for unvulcanized Hycar OS-10. One would expect this from the polar character of Plexiglas. The broadness of the transition resembles that of the vulcanized Hycar OS-10. Not only is the "second step" in the transition broad, but the initial and final steps are quite gradual. Comparison of unvulcanized Hycar OS-10 and Plexiglas shows clearly that the transition is qualitatively the same for all long-chain polymers. Quantitatively, however, wide differences can occur. The second step for Hycar OS-10 may be a cooperative phenomenon while that for Plexiglas may be compatible with a non-cooperative transition.—The above interpretation of Figs. 1 and 2 is very tentative, and awaits checking by further experimental and theoretical work.

We are indebted to Professor H. M. James (Purdue University) for stimulating discussions on the interpretation of our results.

* Supported in part by the ONR.
[1] For transitions in simpler compounds, see N. L. Alpert, Phys. Rev. 75, 398 (1949); H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 18, 162 (1950).

On the Nature of a Soldered Contact on a Semiconductor

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WHEN studying the rectifying properties of semiconductors, it is customary to neglect the behavior of the "non-rectifying contact" which consists of a large area soldered contact. Measurements[1] made on germanium crystals to which connections were made through two soldered contacts of considerably different area showed no rectification, thus clearly indicating that the lack of rectification is a property of the nature of the contact and not of its geometry.

The following experiment was performed to verify the assumption that the soldered contact is effectively a gradual transition from a metal to a semiconductor. Metal atoms diffuse into the semiconductor during soldering, their concentration being greatest near the surface through which they have diffused.

A small soldered region ($< 10^{-4}$ cm^2) on an N-type germanium crystal was etched repeatedly, removing electrolytically about 1000 atomic layers at a time. The purpose of this etch was to expose successively regions having a decreasing density of metallic impurities.

Forward and back currents were measured (at 1.5 volts) through a tungsten probe contacting each new surface at the same location and with an identical pressure. The ratio of forward to back currents was plotted on a logarithmic scale as a function of depth (Fig. 1). The resulting relation below a 100 to 1 rectification ratio agrees with the above assumption. Above 100, the experimental rectification ratio shows the fluctuation which is usually found when probing the surface of a germanium crystal.

The following interpretation attempts to explain a mechanism responsible for this result. When metallic atoms are introduced in a semiconductor, new energy levels, which were forbidden before the addition of metallic atoms, are made available locally. The number of new allowed energy states is proportional to the concentration of these metallic impurities. The presence of new allowed energy states effectively reduces locally the energy gap and brings the Fermi level closer to the filled band. Eventually, as the concentration of metallic atoms becomes large enough,
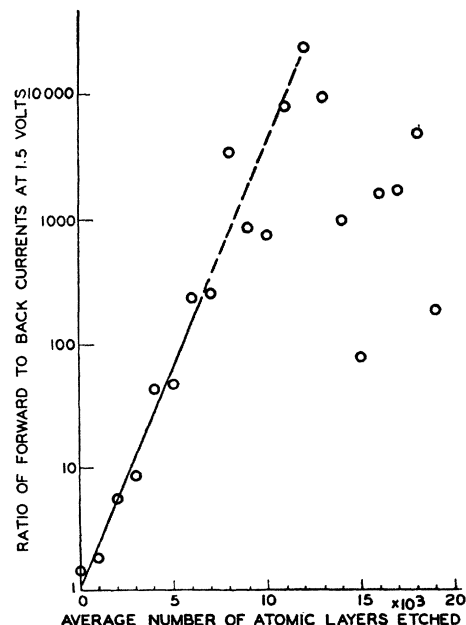

FIG. 1. Forward and back currents through a soldered region.