

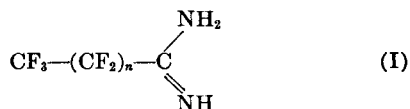
## Some Mechanical and Optical Properties of CFN Polymers\*

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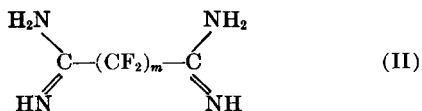
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### INTRODUCTION

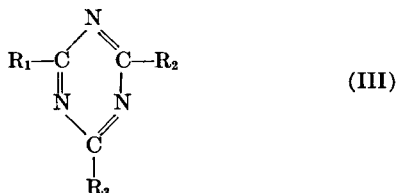
Thermally stable elastomers prepared by condensation polymerization of perfluoroalkyl amidines have been reported by Brown of the University of Florida.<sup>1</sup> These are copolymers of monomers of the types



and



These gave polymers which presumably incorporate triazine-type rings



The R groups are short CF<sub>2</sub> chains which may terminate in a CF<sub>3</sub> group or in another triazine ring. Depending on the type of termination, a given triazine ring may be a low molecular weight entity or exist as a mono-, di-, or trifunctional group in the polymer chain.

In this paper the mechanical and optical properties of films prepared from polymers of this type are reported.

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### EXPERIMENTAL

#### Preparation of Test Specimen

About 1 g. of SC-CFN-GBV polymer, which was heat-treated in oxygen for 1 hr. and was a light-brown, tacky powder, was hot-pressed between aluminum foil (Reynolds Aluminum Frozen Food Wrap, 1.7 mils thickness) and cellophane (du Pont No. 3100 clear, nonmoistureproof cellophane, 1.1 mils thickness) by using a Carver Laboratory Press of ten-ton capacity equipped with 6 × 6 in. electric hot plates. (The polymer was prepared by the Stauffer Chemical Co., Richmond, California, from singly sublimed *R*<sub>1</sub> butyroamidine and *R*<sub>2</sub> glutaroimidine obtained from doubly distilled *R*<sub>1</sub> glutaronitrile. The starting molar ratio was 1.3/1 butyroamidine/glutaroimidine. The polymer was heated in oxygen for 1 hr. and was believed to be still somewhat unstable in moist air.)

The electric hot plates were switched off when an inserted thermometer in the plate reached a temperature of 172°C. and were then allowed to cool gradually to room temperature. The hydraulic pressure of the press was kept at 2200 psi at the beginning of casting at 172°C.

The favorable casting condition was critical. For example, when the electric plate was switched off at 185°C., the polymer flowed out, and, at 165°C., the polymer did not yield a clear film.

Under the optimal casting condition mentioned above, however, a continuous and translucent circular film of polymer laminated between aluminum foil and cellophane was obtained. The diameter of the film was about 5 cm. and the thickness was about 0.02 cm.

The circular laminate was cut with a sharp knife into several specimens of dimension of 1 cm. width and 4 cm. length. The cellophane was easily removed when the laminate was kept in ice water, and the aluminum foil was dissolved away in about 4*M* hydrochloric acid.

The polymer specimen thus obtained was rinsed

in cold distilled water for about 2 hr. and was hung in the air to dry. Before measurement, every polymer specimen was annealed at 115°C. for 10 min. while hanging freely in an oven and then cooled slowly down to room temperature in order to avoid effects of contained moisture and of thermal stress due to hot-press casting.

### Apparatus Used

An Instron tensile tester, Model TM (Table Model Instron, Model TM, Instron Engineering Corp., 2500 Washington St., Canton, Mass.) was modified to be able to measure simultaneously the mechanical and optical properties of the polymer film at various temperatures. Temperature control was achieved by setting a forced hot air current bath of constant temperature between the upper and lower jaws. An optical system which crosses the polymer film at various angles of 90° to 45° usually used at 90°, (i.e., perpendicular to the plane of the film) was used, consisting of a light source (General Electric H100-A4 mercury lamp, low pressure type), condenser lens, polarizer and analyzer (Polaroid, laboratory J filters, No. 310, Central Sci. Corp., Cambridge, Mass.), green 5460 Å. interference filter (Farrand Optical Co., Inc., New York, N. Y.), and Babinet compensator (Gaertner Scientific Corp., Chicago, Ill.).

The temperature deviation along the test specimen of about 3 cm. length was found to be fairly small,  $\pm 0.5^\circ\text{C}$ . at 70°C.,  $\pm 1^\circ\text{C}$ . at 140°C., and  $\pm 2.5^\circ\text{C}$ . at 200°C.

### Procedure

One series of experiments was carried out by measuring tensile stress relaxation and birefringence change with lapse of time up to 1 hr. at various constant strains up to 25% at a constant temperature of 35°C.

Another series involved measuring changes of equilibrium stress and birefringence under constant strain of 10.2% as temperature varied according to the following schedule: from 85 to 33°C., from 33 to 115°C., from 115 to 33°C., and from 33 to 170°C. The change of strain in the specimen due to thermal expansion of sample clamps and specimen itself during temperature cycle cannot be neglected. According to a preliminary experiment, the apparent linear thermal expansion of the whole system, including clamps and 1-in. length specimen itself (the length of specimen under test was always kept at 1 in.), was found to be  $7.8 \times 10^{-4}$  in./°C.

for the temperature interval of 30–200°C. Therefore, the initial constant strain of 10.2% was always corrected manually by using this value of the thermal expansion during the temperature cycles.

## RESULTS

### 1. Tensile Stress Relaxation and Birefringence Change under Constant Strain and Constant Temperature

Figures 1 and 2 show typical results of stress relaxation and birefringence changes under various strains up to 24% at a constant temperature of 33°C. The stress relaxation is rather small and reaches equilibrium after about 10 min. The equilibrium stress is proportional to applied strain at least within 20% strain. This means that the material has linear mechanical properties at least in equilibrium elastic behavior.

Figure 3 is a check of ideal rubber elasticity behavior by using the well-known equation between stress and strain for ideal rubber.<sup>3</sup> This equation is

$$\sigma = N_c k T [\alpha^2 - (1/\alpha)] \quad (1)$$

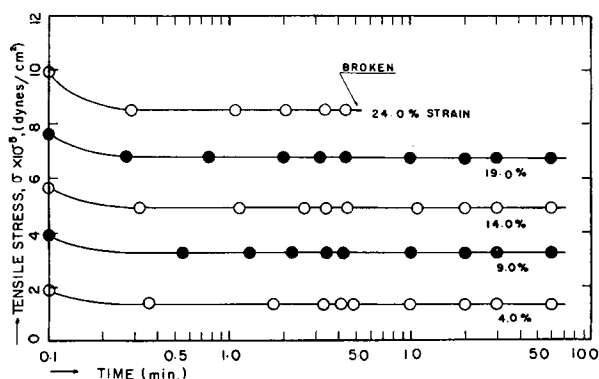


Fig. 1. Stress relaxation at several strains at 33°C.

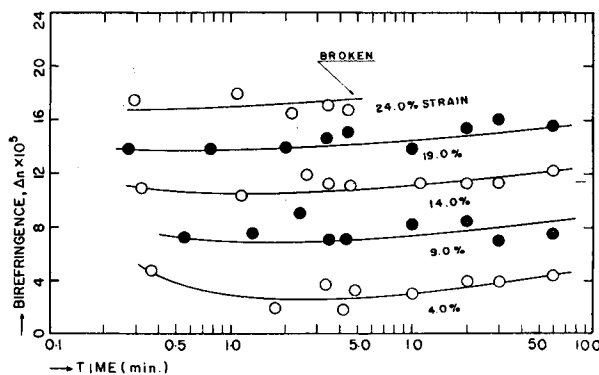


Fig. 2. Birefringence relaxation at several strains at 33°C.

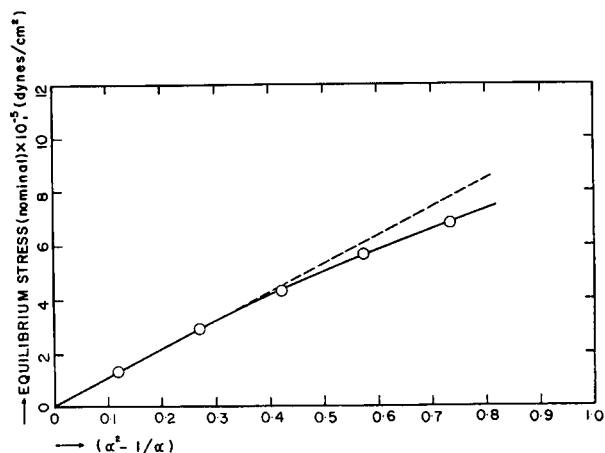


Fig. 3. Stress at 1 hr. vs.  $[\alpha^2 - (1/\alpha)]$  at 33°C.

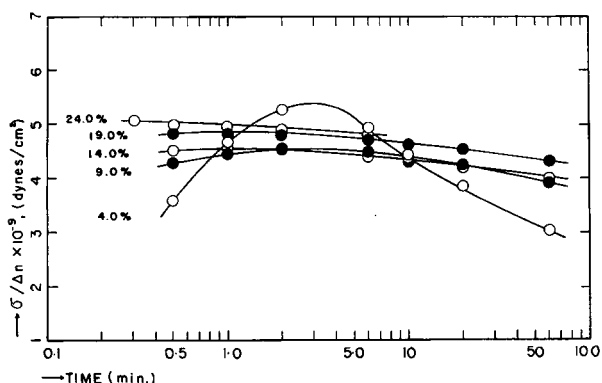


Fig. 4. Strain and time dependency of stress-birefringence ratio at 33°C.

where  $\sigma$  is tensile nominal stress (stress manifested by original cross sectional area),  $N_c$  is the number of crosslinks per cubic centimeter,  $k$  is the Boltzmann constant,  $T$  the absolute temperature, and  $\alpha$  the ratio of the elongated length to the original length of the specimen.

The equilibrium stress-strain relation does not obey the theory beyond a strain of about 10%, as shown in Figure 3. The value of  $N_c$  calculated from the slope of the linear portion (within a strain of 9%) is found to be  $2.58 \times 10^{19}/\text{cm}^3$ . This value is consistent with that which might be expected from network theory for the monomer ratio used.

The birefringence change  $\Delta n$  is, however, somewhat strange. It seems to decrease in an earlier stage and increase in a later one. The increase seems to appear earlier when the strain becomes greater. This suggests a possibility of the superposition of quite different birefringence behaviors. One decreases with lapse of time in the usual man-

ner as shown in rubbery materials,<sup>4</sup> while the other increases with a rate which is affected by the magnitude of the strain itself.

Figure 4 shows the strain and time dependencies of the stress-birefringence ratio. The ratio has a maximum occurring at a time which becomes earlier as the applied strain becomes greater. Except for anomalous behavior at 4.0% strain, the ratio becomes greater as the applied strain increases.

According to the stress-birefringence theory of ideal rubber,<sup>5</sup> the ratio should be independent of the magnitude of the applied strain when the strain is kept relatively small. The discrepancy between the results and the theory might be due to the fact that the material differs from an ideal rubber, as shown not only by the mechanical properties (Fig. 3) but also in the anomaly of increasing birefringence at later stages of straining. However, the strain dependence of stress-birefringence behavior is not so serious, in that the value of  $\sigma / (T\Delta n)$  remained between  $1.3 \times 10^7$  and  $1.6 \times 10^7$  dynes/cm.<sup>2</sup> °K.

#### The Change of Equilibrium Stress and Birefringence under Constant Strain during Temperature Cycles

In order to investigate further the conformance of this sample to rubber elasticity theory, the changes in stress and birefringence with temperature at constant length were observed. Before the temperature cycle, the specimen was held at a constant strain of 10.2% and temperature of 86.5°C. for 1 hr. until equilibrium was reached. Then the temperature was decreased to room temperature, increased to 150°C., decreased to room temperature, and increased again to 200°C., where almost every sample broke. The rate of change of temperature was kept about 0.5°C./min., and the

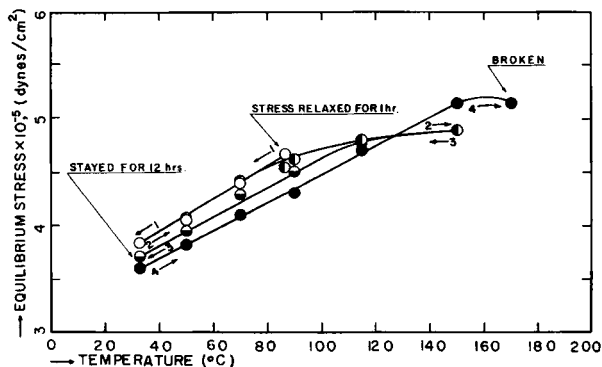


Fig. 5. Stress vs. temperature at 10.2% strain for heating-cooling cycles.

strain correction for thermal expansion of the specimen itself and the clamp was done as described in the procedure.

Figure 5 shows the change of tensile stress during the temperature cycles. During every temperature cycle, the stress versus temperature relation was fairly linear within the temperature range of the cycle. The maximum temperature of this was always lower than the highest temperature at which the specimen had been kept during the former temperature cycle.

An ideal rubber would have a stress proportional to the absolute temperature [eq. (1)]. The above data vary linearly with absolute temperature in the manner

$$\sigma = A + BT \quad (2)$$

Consequently,

$$\begin{aligned} (\partial E/\partial l)_{v,T} &= \sigma - T(\partial\sigma/\partial T)_{v,l} \\ &\cong \sigma - T(\partial\sigma/\partial T)_{P,l} \\ &= A \end{aligned}$$

The value of  $A$  obtained in this way is about  $-0.6 \times 10^6$  dynes/cm.<sup>2</sup>. The negative value indicates that internal energy decreases with elongation. This is characteristic of samples exhibiting a tendency toward crystallization on stretching, the crystals being a lower energy phase.

The possibility of crystalline order is also indicated in the birefringence-time curves of Figure 2. The increase in birefringence could indicate slow crystallization of crystals having positive birefringence in the stretched samples.

The birefringence-temperature behavior shown in Figure 6 is also consistent with this explanation. Below about 70°C. the birefringence does not vary much with changing temperature; however, on

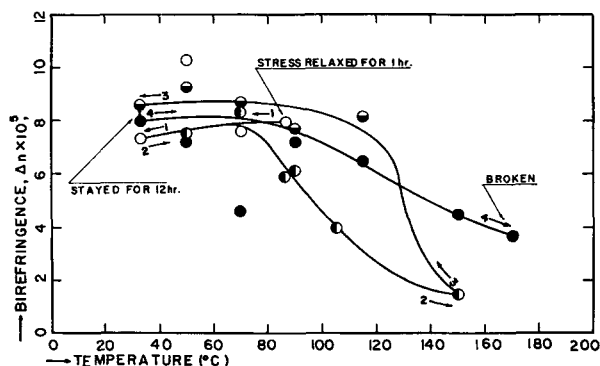


Fig. 6. Birefringence vs. temperature at 10.2% strain for heating-cooling cycles.

exceeding 70°C., there is a steep decrease in birefringence which continues until at least 160°C. On recooling, the birefringence again increases and appears even to exceed the original value. This would be consistent with the melting of crystals at about 70°C. and their re-forming on cooling in a more perfect or more highly oriented state.

The suggestion of crystallization was tested by taking x-ray diffraction photographs of the stretched film at room temperature. The photographs are diffuse and show no indication of crystallites of appreciable size or order, showing two diffuse rings with spacings of 4.98 Å. (strong) and 2.65 Å. (very weak). Perhaps highly disordered or small crystals are detected by the stress and birefringence studies but are too imperfect to give sharp x-ray diffraction. The situation is somewhat similar to that encountered with *N*-substituted polyamides<sup>6</sup> and polyvinyl chloride.<sup>7</sup> The above phenomena could also be explained in terms of rotational isomerism, where the more extended (and more birefringent) conformer of the amorphous chain was of lower energy and hence more favored at low temperature.

## DISCUSSION

The data presented are not of high precision because of the difficulty in preparing a homogeneous film. This is probably a result of the highly crosslinked gel nature of the polymer.<sup>8</sup> In the region of reversible elasticity, the materials behave approximately as rubbers with low tensile strength and low elongation at break. The tensile breaking behavior is affected not only by stress and temperature but also by time. For example, most samples broke in 3 hr. at 15% strain at room temperature but in 1 hr. at 86.5°C. This breaking strain of 15% is quite small as compared with the 50 to 100% obtained in the usual load elongation test under a strain rate of 100%/min.

There appears to be no preliminary indication of impending failure in either the stress or the birefringence relaxation curves. This indicates that failure is not a result of uniform degradation or chain breaking but is a process which is localized at "weak points." These weak points are likely to be the points of fusion of gel particles which are probably physically intermeshed but not chemically bonded during the sintering process used in film preparation.

There appears to be a tendency toward ordering or forming of "pseudo-crystals" on stretching.

Because of the random structure of the polymer, it does not seem likely that true crystals can form. However, there is probably some specific interaction between chains giving rise to a departure from randomness in the chain arrangement.

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### Synopsis

Mechanical and optical studies have been carried out on high temperature fluorinated triazine-derived elastomers. These behave as crosslinked rubbers, having low ultimate elongations and tensile strengths and showing a tendency toward development of a crystallike order.

### Résumé

On a étudié les propriétés mécaniques et optiques à haute température d'élastomères dérivés de triazines fluorées. Ceux-ci se comportent comme des caoutchoucs pontés ayant des elongations extrêmes et des résistances à la traction faibles et montrant une tendance à se développer suivant un phénomène semblable à la cristallisation.

### Zusammenfassung

Mechanische und optische Untersuchungen wurden an hochtemperaturfluorierten Elastomeren auf Triazinbasis ausgeführt. Diese verhalten sich wie vernetzter Kautschuk, besitzen niedrige Reissdehnung und Zugfestigkeit und zeigen eine Tendenz zur Ausbildung eines kristallinen Ordnungszustands.

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