Chemical and Engineering News 41, 46-47 (1963) # 38, September 23

yet whether this result is in agreement with x-ray data, Mr. Lentz says.

While the other polysilicate minerals gave significant amounts of lower silicate species (because of acid cleavage of the siloxane bond), only trace quantities of a lower silicate were produced with laumontite. Therefore, Mr. Lentz believes that the silicate ring structure containing four silicon atoms is probably less vulnerable to acid attack than are linear silicate structures.

Sodium Silicate. Studies on aqueous solutions of sodium silicate show that sodium orthosilicate solutions contain a variety of silicate structures. In fact, only 43.5% of the silicate was recovered as the orthosilicate derivative in a 1M sodium orthosilicate solution. This fact, together with other experimental observations, indicates that some of the silicate solution is polymeric.

Sodium silicate solutions having sodium-to-silicon ratios ranging from 4:1 to 0.6:1 were studied. They were found to contain SiO_4, Si_2O_7, Si_3O_{10}, $(SiO_3)_4$, and polysilicate structures. Other specific species have also been indicated by gas-liquid chromatographic analysis, but have not yet been isolated and identified.

The monomer is always found in greater quantity than the dimer, which is always found in greater quantity than the trimer. The relative amounts of all of these species generally decrease as the sodium-to-silicon ratio decreases. An exception to the other species, the cyclic tetramer's yield is nearly as great at a sodium-to-silicon ratio of 1:1 as it is at a sodium-to-silicon ratio of 4:1.

A solution of sodium metasilicate contained 25.7% monomer, 12.0% dimer, 6.9% trimer, 10.0% cyclic tetramer, and 23.3% of a polysilicate structure. Thus a sodium metasilicate solution also contains a variety of silicate structures, even though its sodium salt is a crystalline compound.

Portland Cement. Silicate structure changes occurring in a hydrated portland cement paste were also studied. Rapid formation of a pyrosilicate together with a slow rate of polysilicate formation were observed during the early stages of hydration. Structure analyses on concrete samples up to 15 years old indicate that the pyrosilicate is an intermediate product. Thus the polysilicate could be the end product of the hydration reaction, Mr. Lentz says.

Fluorothiocarbonyl Polymer Prepared

Mechanism proposed by Du Pont team points to ionic intermediate, fluoride ions as chain initiators

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Thiocarbonyl fluoride polymerizes readily at low temperatures to form a resilient, high-molecular-weight product, according to workers at Du Pont's Central Research Laboratory, Wilmington, Del. Details of the polymer's mechanical properties and a proposed mechanism for its polymerization have been put forth by Dr. W. H. Sharkey, who carried out the research along with Dr. W. J. Middleton, Dr. H. W. Jacobson, D. S. Acker, and Dr. H. C. Walter. The work is part of Du Pont's exploratory fluorine chemistry program.

Thiocarbonyl fluoride itself has previously been synthesized [*J. Gen. Chem. U.S.S.R. (Eng. Transl.)*, 29, 3754 (1959)]; [*J. Chem. Soc.*, 3516 (1960)]. For the present study, Dr. Sharkey and his co-workers used the method previously developed at Du Pont by Dr. W. J. Middleton, Dr. E. G. Howard, and Dr. W. H. Sharkey [*JACS*, 83, 2589 (1961)].

Dithietane, obtained by ultraviolet irradiation of thiophosgene, is reacted with antimony trifluoride to produce tetrafluorodithietane. This compound breaks down into thiocarbonyl fluoride when pyrolyzed at 500° C.

Polymerization. Some early samples of thiocarbonyl fluoride prepared by Dr. Sharkey's group polymerized spontaneously when stored in sealed glass tubes or stainless steel cylinders. The resulting polymers were greases and waxes with molecular weights ranging from about 2000 to 5000, Dr. Sharkey says.

Further study of the polymerizability of this fluorothioacid fluoride revealed that when the reaction is carried out at temperatures about −80° C., a white, spongy polymer

RESILIENT. Dr. William J. Middleton, Dr. Robert E. Putnam, Dr. William H. Sharkey, Dr. H. W. Jacobson, and Dr. Henry C. Walter (left to right) of Du Pont demonstrates the resiliency of the fluorothiocarbonyl polymer. Ionic polymerization of thiocarbonyl fluoride gives the high molecular weight polythiocarbonyl fluoride

Proposed Mechanism Leads to Polythiocarbonyl Fluoride

In one series of reactions, dimethylformamide (DMF) reacts with monomer or traces of impurities to form a base initiator:

$$\mathrm{DMF} + \text{monomer or impurities} \rightarrow \mathrm{B}^-$$

$$\mathrm{B}^- + \mathrm{CF_2{=}S} \rightarrow \mathrm{BCF_2S}^-$$

$$\mathrm{BCF_2S}^- + n\mathrm{CF_2{=}S} \rightarrow \mathrm{BCF_2S{-}({-}CF_2S)_{n-1}CF_2S}^-$$

The chain is stabilized by loss of fluoride ion:

$$\mathrm{BCF_2S(CF_2S{-})_{n-1}{-}CF_2S}^- \rightarrow$$
$$\mathrm{BCF_2S{-}({-}CF_2{-}S{-})_{n-1}{-}CF{=}S} + \mathrm{F}^-$$

In another series of reactions, fluoride ions react with thiocarbonyl *fluoride, utimately forming polythiocarbonyl fluoride:*

$$\mathrm{F}^- + \mathrm{CF_2{=}S} \rightarrow \mathrm{CF_3S}^-$$

$$\mathrm{CF_3S}^- + n\mathrm{CF_2{=}S} \rightarrow \mathrm{CF_3S{-}({-}CF_2S{-})_{n-1}{-}CF_2S}^-$$

$$\mathrm{CF_3S{-}({-}CF_2S{-})_{n-1}{-}CF_2S}^- \rightarrow$$
$$\mathrm{CF_3S{-}({-}CF_2S{-})_{n-1}{-}CF{=}S} + \mathrm{F}^-$$

B is presumably removed by hydrolysis during workup leading to —SCFO end groups and fluoride ions

results. Its molecular weight is estimated from osmotic pressure measurements at more than 500,000. Dimethylformamide (DMF) was the most effective initiator found, though such compounds as triethylamine, diisopropylamine, triisopropoxyaluminum, and tetraethylammonium chloride also act as polymerization catalysts.

DMF does not seem to be a primary initiator, according to Dr. Sharkey, since it isn't bound in the polymer. The Du Pont workers propose a mechanism involving two series of reactions. In the first series, DMF reacts with monomer or traces of impurities to form the real initiator. Polymer from this initiator forms stable end groups by losing fluoride ions, which initiate additional chains, ultimately yielding polythiocarbonyl fluoride and more fluoride ions.

In a typical polymerization, a flask containing four drops of DMF in 50 ml. of dry ether is cooled in a solid carbon dioxide-acetone bath. Then 17 ml. of thiocarbonyl fluoride is distilled into the flask and the contents stirred. Over about two hours, polymer forms and separates from the ether in a spongy mass. Nitric acid (50%) is added to destroy the DMF, and the flask is returned to room temperature. The polymer is boiled in water, rinsed in acetone, and dried. About 22 grams of polymer is obtained.

Resilient. Amorphous polythiocarbonyl fluoride has a Yerzley resilience of 95%—a value equaled among elastomers only by the best grades of gum rubber, Dr. Sharkey says. The polymer has a crystalline melting point of 35° C. At room temperature, it crystallizes slowly, developing the appearance and feel of Teflon. As it is cooled further, it becomes stiff but is not embrittled until the temperature drops below −100° C. Its glass transition temperature is −118° C.

Like other fluorocarbon polymers, polythiocarbonyl fluoride resists chemical attack. Samples boiled in fuming nitric acid and in aqueous alkali show no detectable damage, Dr. Sharkey says. It is rapidly degraded by amines, however. Chloroform and some other chlorinated solvents dissolve the polymer, as does tetrahydrofuran.

Curing. The chemical inertness of polythiocarbonyl fluoride has prevented its being cured by cross-linking of the polymeric chains. The Du Pont group succeeded, however, in polymerizing divinylbenzene and trivinylbenzene in and around the polymeric chains, using α,α'-azodiisobutyronitrile as an initiator. A stiff matrix is formed around the polythiocarbonyl fluoride chains, with some attachment of the divinylbenzene polymer to the fluoride polymer, Dr. Sharkey says. He attributes the attachment to a reaction of divinylbenzene with the $-\mathrm{SCF{=}S}$ end group of the fluoride polymer.

This treatment effectively cures polythiocarbonyl fluoride. At 100° C., the tensile strength of the product is rated about 1000 p.s.i. at 500 to 600% elongation at break. The uncured polymer has no strength above 35° C. Chlorinated solvents won't dissolve the cured polymer, although they produce a swelling effect.

The cured polymer is somewhat less resilient than untreated polymer, having a Yerzley resilience of 80 to 84%. Its tear resistance, in Du Pont tests, was as high as 91 pounds per inch, compared to a typical value of 62 pounds per inch for natural rubber, Dr. Sharkey points out.

Copolymers. A number of fluorothioacid fluorides were found to copolymerize with thiocarbonyl fluoride. Chlorofluorothioacetyl fluoride, for example, copolymerizes in the low-temperature DMF system, forming about 3% of the product. This small amount of comonomer reduces the melting point of the copolymer to about 15° C. Dr. Sharkey suggests that the polymer may contain blocks of comonomer, or that the comonomer forms sites for development of giant chain branches.

Copolymers with difluorothioacetyl fluoride, some containing considerable amounts of comonomer, were also made, Dr. Sharkey adds. These products were of relatively low molecular weight and were weaker than the homopolymer.

Chemical and Engineering News 41, 42-44, 46-47 (1963) # 50, December 16

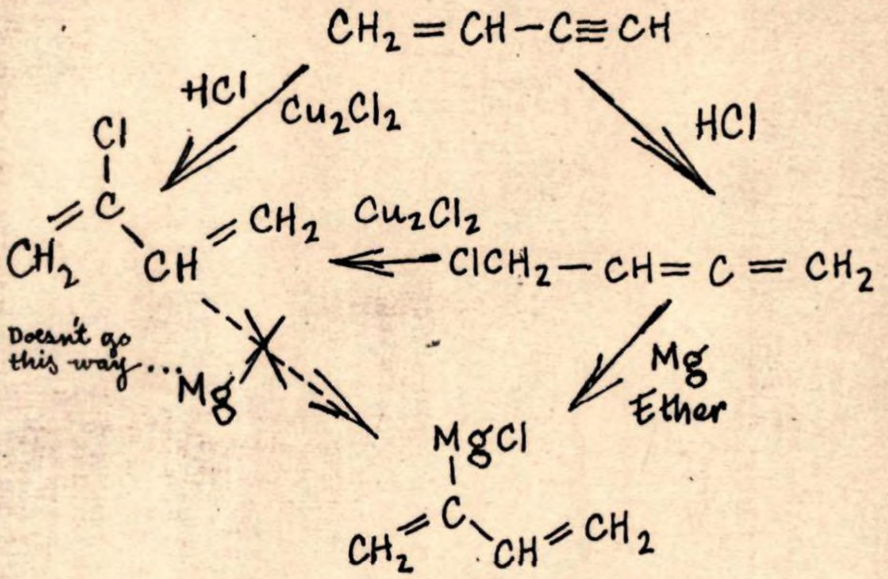
RESEARCH

Approaches to Three New Polymers Worked Out

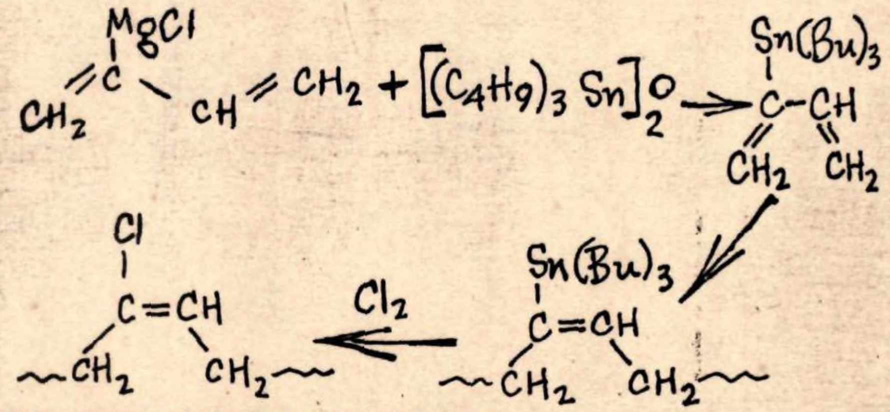
- *A stereospecific synthesis of cis-1,4-chloroprene.*
- *An approach to a fused cyclohexane ladder polymer.*
- *A free radical process for making thiocarbonylfluoride polymer.*

These were the three developments made public (C&EN, Dec. 2, page 37) by Du Pont chemists at a symposium honoring the late Dr. Wallace H. Carothers, Du Pont's pioneer polymer chemist. Dr. Carothers becomes the tenth member of the International Rubber Science Hall of Fame. The symposium was sponsored by the Institute of Rubber Research, University of Akron, and held at the university.

Grignard Reagent Used to Synthesize Linear Polymer



Monomer has metal bonded to olefinic carbon



Polymerization in bulk with an azo catalyst gives soluble, linear polymer with cis-1,4 structure

cis-1,4-Polychloroprene is a stereospecific elastomer made by an indirect approach from butadiene

A new stereospecific elastomer, *cis*-1,4-polychloroprene, has been synthesized by Dr. Carl Aufdermarsh and Dr. Raymond C. Ferguson of Du Pont's elastomers department. They believe the synthesis, although impractical for commercial use, is a useful, even necessary, step toward making *cis*-1,4-polychloroprene by direct polymerization of chloroprene (2-chloro-1,3-butadiene).

The Du Pont workers obtain *cis*-1,4-polychloroprene as a soft, amorphous, soluble gum. Molecular weights of fractions range up to 150,000. The *cis*-1,4-polychloroprene has a greater density and a lower degree of crystallinity than does the ordinary polychloroprene in which the trans-1,4 structure predominates. The cis isomer's glass transition temperature, −20° C., is higher than that of the trans, −45° C. The *cis*-1,4-polychloroprene can be milled and vulcanized by standard procedures, according to Dr. Aufdermarsh.

The few grams of *cis*-1,4-polychloroprene laboriously synthesized to date won't have an immediate impact on elastomer markets. Direct polymerization of chloroprene into *cis*-1,4-polychloroprene might, however. The first polymer made from chloroprene was a milestone in polymer chemistry. It became the basis for neoprene, the first commercial synthetic elastomer. In 1962, U.S. production of polychloroprene totaled about 283 million pounds.

In neoprene, trans-1,4 units make up 70 to 95% of the polymer; the remainder is mostly cis-1,4 units. Temperature of the free radical polymerization has a limited effect on the structure of the polymer, according to earlier work by Du Pont's Dr. J. T. Maynard and Dr. W. E. Mockel [*J. Polymer Sci.*, 13, 251 (1954)]. Content of cis-1,4 units is less than 30% at the highest operable temperatures. There are only traces of 1,2 and 3,4 units.

Success of *cis*-polybutadiene and *cis*-polyisoprene preparations made the preparation of *cis*-1,4-polychloroprene an interesting challenge, Dr. Aufdermarsh says. However, the organometallic catalysts, so successful in making other cis polymers, yield polychloroprenes which are indistinguishable from high-trans polymers available through free radical polymerization.

Thus, the Du Pont workers decided on an indirect approach. They prepared a butadiene monomer with a large, bulky group at C-2 which interacts with the hydrogen on C-4. Although butadienes normally exist in the planar S-trans (transoid) conformation, the interaction forces the butadiene to assume the planar S-cis conformation, according to Dr. D. Craig, Dr. J. J. Shipman, and Dr. R. B. Fowler at B. F. Goodrich Research Center, Brecksville, Ohio [*JACS*, **83**, 2885 (1961)]. In the S-cis conformation (single bond between C-2 and C-3), there is less steric interaction with the bulky group, Dr. Aufdermarsh says.

Polymerization of the S-cis monomer yields a cis polymer. Replacement of the bulky group with chlorine converts the polymer to *cis*-1,4-polychloroprene.

Dr. Aufdermarsh had to synthesize a butadiene monomer suitably substituted at C-2. The substituent has to be one that is readily replaceable by chlorine, does not inhibit polymerization, and is bulky enough to favor the S-cis configuration. The Du Pont group chose an organometallic group in which the metal is bonded directly to the olefinic carbon.

First Steps. They first made the Grignard reagent of chloroprene, a 2-butadienylmagnesium chloride. To get it, they allow isochloroprene (4-chloro-1,2-butadiene) to react with magnesium in ether. With proper initiation, the desired Grignard reagent of chloroprene is produced in high yields. The isochloroprene comes from addition of hydrochloric acid to monovinylacetylene in the absence of copper salts, the Du Pont workers explain.

The Grignard reagent synthesized by Dr. Aufdermarsh and Dr. Ferguson reacts with bis(tri-*n*-butyltin)-1,3-butadiene. This is the butadiene monomer that exists in the S-cis form. The Du Pont workers polymerize it in bulk with an azo catalyst to yield a soluble, linear polymer of cis-1,4 structure. It is a clear, colorless sirup or gum, with inherent viscosities (obtained by fractionation) as high as 0.7.

Chlorinolysis under mild conditions (dilute solution of chlorine in carbon tetrachloride added to a dilute solution of polymer at 0° C.) removes the tributyltin side chains. Chlorine replaces tin groups with high selectivity and retention of configuration, Dr. Aufdermarsh says. He then obtains a soluble, nearly colorless amorphous gum in quantitative yield. That this gum is essentially *cis*-1,4-polychloroprene is shown by its elemental analysis and cleavage with ozone, together with infrared and nuclear magnetic resonance spectra, the Du Pont workers say.

Elemental analyses for carbon, hydrogen, and chlorine show that the polymer can contain as much as 97% polychloroprene. The remainder is residual tributyltin units and trichlorobutane units resulting from addition of chlorine to the double bond, according to the Du Pont chemists.

Cleavage with ozone yields 62% succinic acid, as opposed to 90% succinic acid for *trans*-polychloroprene. Each mole % of residual tributyltin units, trichlorobutane units, or 1,2 or 3,4 units reduces the yield of succinic acid by 2 mole %. Because extraneous units have this twofold effect on the yield of acid, the ozonolysis results indicate that a minimum of 81% of the product is 1,4-polychloroprene, Dr. Aufdermarsh says. Spectroscopic data were used to establish the cis configuration of the product, he notes.

Spectral Data. Spectra of Dr. Aufdermarsh's product differ in the expected way from those of *trans*-polychloroprene. The C=C stretching frequency near 1650 cm.$^{-1}$ was analyzed by high resolution IR. The cis polymer shows a peak at 1652 cm.$^{-1}$ Ordinary high-trans polymer shows a peak at 1660 cm.$^{-1}$ The 8-cm.$^{-1}$ shift is the same size and in the same direction as observed in the model compounds *cis*- and *trans*-2-chloro-2-butene and *cis*- and *trans*-4-chloro-4-octene.

Differences between the *cis*-1,4-polychloroprenes are seen in their NMR spectra at 100 megacycles. Resonances of the olefinic protons at infinite dilution are located at 535 cps. and 551 cps. downfield (lower frequency) from tetramethylsilane. The relative positions are in excellent agreement with the infinite dilution values (542 and 552 cps.) of *trans*- and *cis*-2-chlorobutene, Dr. Ferguson says.

Polymer contains double-chain or ladder segments; cyclization of poly-3,4-isoprene is approach used

Cyclization of poly-3,4-isoprene is an approach that can lead to a high polymer consisting of a linearly-fused polycyclic structure, Dr. R. J. Angelo of Du Pont's film department told the symposium. The cationic cyclization uses boron trifluoride or phosphorus oxychloride, and leads to a polyhydrocarbon that contains double-chain or ladder segments.

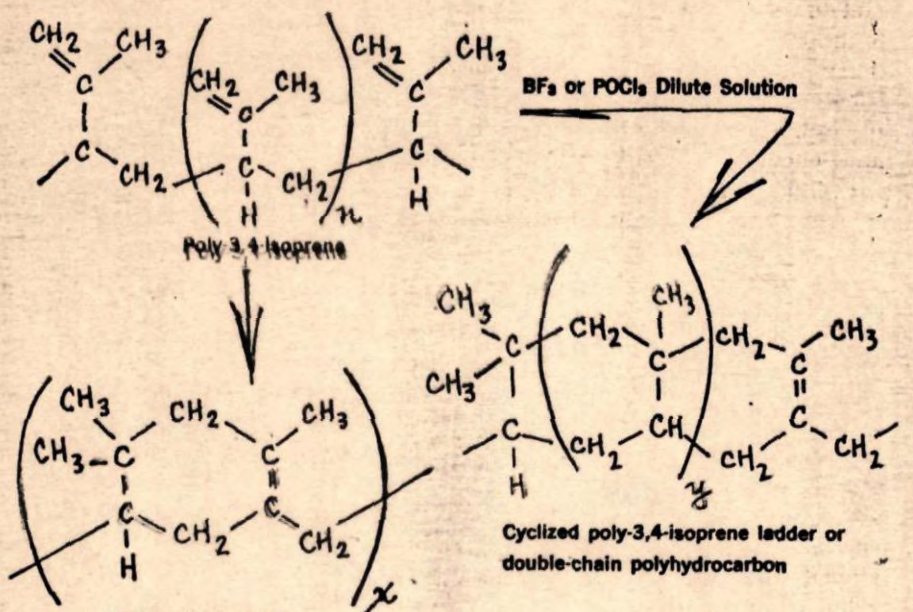
Ring closure through pendant nonconjugated 1,6 unsaturation yields enough of a fused structure to provide a polymer with properties significantly different from those of the elastomeric poly-3,4-isoprene precursor, Dr. Angelo says. The cyclized polymer forms clear and reasonably flexible films by melt-pressing at 150° C., or by solvent-casting. Thin films exhibit initial modulus of elasticity of about 300,000 p.s.i., tensile strength of about 3000 p.s.i., and elongation of about 2%. Rubbery uncured films of poly-3,4-isoprene show an initial modulus and tensile strength of about 500 p.s.i. and elongation of about 500%.

The powdery, fusible polymer is off-white. It is soluble in a variety of solvents, including hydrocarbons, tetrahydrofuran, and carbon disulfide. Number average molecular weight is about 40,000, and inherent viscosity is about 0.5. Density is 0.96 to 0.97 gram per cubic centimeter; the x-ray pattern is amorphous. Softening point is 140° C. By contrast, poly-3,4-isoprene is soft at 25° C. and has a density of 0.91 gram per cubic centimeter.

Ladder polymers are of interest because of their potential stability and rigidity at high temperatures. A notable success in synthesis of ladder materials is the double-chain polyphenylsilsesquioxane reported by Dr. John F. Brown and co-workers of General Electric in 1960.

Dr. Angelo's approach toward synthesis of a polyhydrocarbon with linearly fused structure is to form condensed, six-membered rings from

Polycyclization Gives Ladder Polymer



pendant nonconjugated 1,6 unsaturation along the chain of a macromolecule. Pendant isopropenyl unsaturation of poly-3,4 isoprene was expected to be readily susceptible to cationic ring closure, and Dr. Angelo believes he has achieved polycyclic segments of from three to seven fused rings. If the cationic ring closure involving successive cyclizations should occur along the whole length of the precursor chain, the desired polycyclic structure would result.

Ladder Polymer. Cyclization of poly-3,4-isoprene under proper conditions yielded enough cyclized polymer for evaluation of its physical properties. Dr. Angelo carries out the cyclization of 10 grams of poly-3,4-isoprene with 5 ml. of benzene for 20 hours at 80° C. Addition of 5 to 10 liters of ethanol gives recoveries of 70 to 90%. The dilute solution (0.25%) limits recovery but is essential to avoid cross-linking. Cross-linking, or intermolecular reaction, becomes competitive at concentrations of 1 to 5%.

Problems abound in achieving a complete ladder polyhydrocarbon by this approach. But the segments of fused structure in the Du Pont material give hope that such polymers may eventually be synthesized. Structural imperfections can result from isolated unreacted groups (18.4%, as predicted by theory), from alternative cyclizations or isomerizations, and from cross-linking and chain scission reactions, Dr. Angelo suggests.

Cross-linking can be avoided by high dilution, but chain scission seems to take place in all cases. A poly-3,4-isoprene that starts at a number average molecular weight of 163,000 yields a cyclized polymer with a molecular weight of 39,600.

Dr. Angelo suspects small amounts of 1,4 structural units in the polyisoprene may be responsible for chain scission. The poly-3,4-isoprene he used contains up to 10% of the 1,4 structure. It was prepared with a triethylaluminum/titanium tetraisopropoxide catalyst system in heptane, as worked out by Nobel Laureate Dr. Giulio Natta and his co-workers (French Patent 1,154,938).

Junctions between 3,4 and 1,4 units are perhaps the chain links most susceptible to scission during cationic treatment, Dr. Angelo says. Cyclization of polyisoprenes of different isomeric composition reveals that when either 1,4 or 3,4 content in polyisoprene is low, molecular weight is reduced during the cyclization reaction to from one third to one sixth of the original value. But for an approximately equimolar composition (poly-3,4/1,4-isoprene, prepared via Ziegler-Natta catalysis), the molecular weight is reduced to 1/128th of the original value.

The cyclization leaves about 15% of the original poly-3,4-isoprene unsaturation ($R_2C{=}CH_2$ measured at 888 cm.$^{-1}$) after one hour at 80° C., and reaches a 5% level after 20 hours at 25° C. (about 150 hours are required to reach the residual 5% level). These results suggest that the isolated unreacted isopropenyl groups may take part in further cyclization with adjacent chain segments containing a double bond from terminal deprotonation. A similar interpretation for the cyclization of natural rubber has been made by Dr. W. F. Watson and Dr. J. Scanlan of the Rubber and Plastics Research Association of Great Britain, and D. F. Lee of the National Rubber Producers Research Association in England (C&EN, June 17, page 44).

Dr. Angelo uses infrared spectra, nuclear magnetic resonance spectra, and dehydrogenation to provide structural evidence that the cyclized polymer is polycyclic rather than monocyclic. IR and NMR spectra of the poly-3,4-isoprene starting material show that about 10% of the starting material has the 1,4 configuration. IR data on the cyclized poly-3,4-isoprene show that some cyclization has occurred (but not what kind) by loss of original unsaturation.

Dr. Angelo does not consider the NMR spectrum of the cyclized polymer to be in accord with a monocyclic repeating unit. The original olefinic proton peak disappears and two broad peaks centered at 0.9 and 1.6 ppm. appear. There is no sharp and distinct peak at 2.0 ppm. From estimates of the area (8 to 18% of the total) due to allylic methylene proton at about 2.0 ppm., he calculates that, on the average, from three to seven fused rings exist per polycyclic segment.

Chromatographic fractions obtained from dehydrogenated cyclized poly-3,-4-isoprene have fluorescent emission spectra of anthracene and naphthacene. Partial aromatization of cyclized poly-3,4-isoprene was carried out with rhodium-on-alumina at 300° to 340° C. The reaction gave a 20% yield of fluorescent liquid (boiling at 52° to 185° C. at 0.7 mm.) from the dehydrogenation residue. No fraction boiling at less than 52° C., corresponding to monocyclic fragments, was isolated.

The distillate, a mixture of degraded chain fragments of varying degrees of aromatization, has ultraviolet maxima in the same region as naphthalene, anthracene, and naphthacene. The detection of linearly fused aromatic compounds supports the view of the cyclized polymer as consisting of segments of fused polycyclic structures, Dr. Angelo says.

Free radicals used to polymerize CF_2S; alkyl radicals made in trialkylborane/oxygen initiator at −80° C.

Thiocarbonylfluoride (CF_2S) can be polymerized in free radical systems to high-molecular-weight elastomers. These elastomers resemble the earlier thiocarbonylfluoride polymers made at Du Pont by anionic polymerization (C&EN, Sept. 24, page 46). In the more recent work, homo- and copolymers of CF_2S have been made by a free radical polymerization in which the radicals are generated in a reaction between trialkylboranes with oxygen, according to Dr. William H. Sharkey and his co-workers at Du Pont's central research laboratory.

The basic discovery involved here, Dr. Sharkey explains, is the generation of free radicals using a trialkylborane/oxygen (R_3B/O_2) initiator at low temperature (as low as $-100°$ C.). The Du Pont workers generally use a dry-ice-in-acetone bath at $-80°$ C. The Du Pont group includes Dr. Sharkey, Dr. W. J. Middleton, Dr. H. W. Jacobson, Dr. D. S. Acker, Dr. H. C. Walter, Dr. R. E. Putnam, Dr. A. L. Barney, Dr. J. M. Bruce, Dr. J. N. Coker, and Dr. D. G. Pye.

In the free radical polymerization, CF_2S is polymerized by the R_3B/O_2 initiator in dichlorodifluoromethane at $-80°$ C. The first step in this reaction is the formation of a peroxide from the trialkylborane and oxygen. But this peroxide isn't the catalyst; it reacts with more trialkylborane to produce alkyl radicals. These radicals, in turn, initiate the polymerization. Triethylborane and tri(*n*-butyl)borane are the boranes usually used by the Du Pont chemists. Long-chain alkyls (for instance, tridodecylborane) won't work in this system.

However, the peroxide made by reacting tridodecylborane with oxygen will generate free radicals if it's allowed to react with another borane such as triethylborane. What probably happens during the free radical formation stage is generation of the radical from the trialkyl borane rather than from the peroxide. The reaction is:

$$R_3B + O_2 \longrightarrow R_2BOOR$$

$$R_2BOOR + 2R'_3B \longrightarrow 2R'\cdot + R_2BOBR'_2 + R'_2BOR$$

Dry. In an actual polymerization, great care is taken to keep the system dry. Anhydrous materials are used, and the polymerization carried out in a dry helium atmosphere.

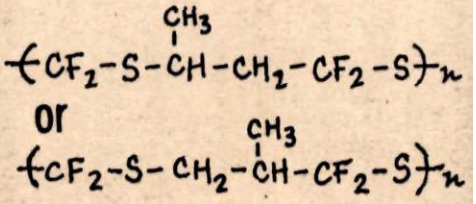
Polythiocarbonylfluoride itself has a relatively high crystallization point, about 35° C. The homopolymer crystallizes to a nonrubbery plastic over several days at room temperature. Its glass transition temperature of $-118°$ C. is low enough, though, to keep it from becoming brittle.

But crystallization is, as a rule, undesirable in an elastomer, Dr. Sharkey notes. So the Du Pont chemists have also made copolymers via the free radical system. Copolymers have lower melting points than do homopolymers because the chain regularity is interrupted. Moreover, copolymers lend themselves more readily to cross-linking, since they may contain cross-linking sites.

The same R_3B/O_2 initiator serves in copolymerization of CF_2S with a variety of compounds:

- Thioacid fluorides such as $CF_3CF{=}S$, $HCFClCF{=}S$, and $CF_2ClCF{=}S$.
- Ethylene, propylene, and higher terminally unsaturated olefins.
- Vinyl compounds such as vinyl acetate and vinyl chloride.
- Allylic compounds, including allyl chloride, acetate, and chloroformate.
- Acrylic esters.

Special. The propylene copolymer rates special mention, Dr. Sharkey says. Propylene copolymerizes to give products that contain as little as two CF_2S molecules for every propylene molecule. Nuclear magnetic resonance studies show the copolymer to be:



$$\left(CF_2-S-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2-CF_2-S\right)_n$$

or

$$\left(CF_2-S-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CF_2-S\right)_n$$

The copolymer has good flexibility at below −50° C., as shown by the Clash-Berg test (which is used to show low-temperature serviceability of elastomers.

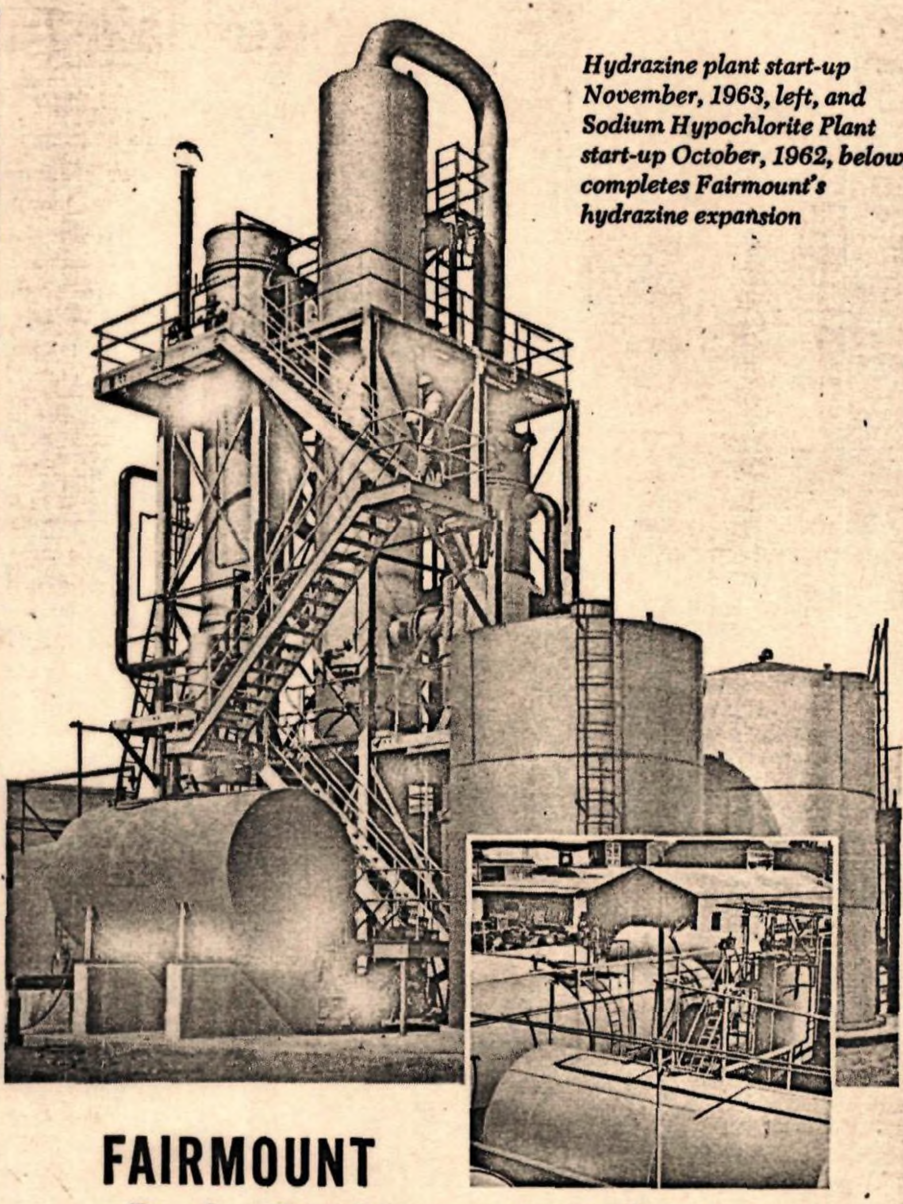
Of the copolymers made so far, the product from CF_2S and allyl chloroformate is the easiest to cure, Dr. Sharkey and his co-workers find. The two materials copolymerize rapidly, and the products can be made to contain as much as 25 mole % allyl chloroformate. But most of the studies involved copolymers containing from 1 to 5 mole % allyl chloroformate. These copolymers melt as low as −15° C. They have molecular weights ranging from 300,000 to 500,000 (by osmotic pressure), and are highly resilient, the Du Pont chemist adds.

The allyl chloroformate copolymer cures readily with zinc oxide. Mechanical properties of the cured copolymer come close to those of the homopolymer made in the earlier anionic polymerizations. Products containing 1.5 to 3.5 mole % allyl chloroformate (molecular weight of about 400,000) and cured with 4 to 5% zinc oxide have tensile strengths of 2000 p.s.i. or higher at elongations of at least 500%. Resilience values of the cured copolymer also approach those of the homopolymer, with Yerzley values up to 88%. The curing of the allyl chloroformate copolymer with zinc oxide seems to involve the active halogen, although the curing mechanism isn't known.

Incorporating zinc oxide into the copolymer posed some problems at first. The thiocarbonyl fluoride polymers do not mill well, Dr. Sharkey says. So a mixing method differing from that used with diene elastomers had to be devised.

The first—and fairly good—method used was mixing finely ground copolymer with zinc oxide in a Wiley mill. But homogeneity wasn't easy to obtain. Uniform distribution was then obtained by dissolving the copolymer in chloroform, adding zinc oxide, then reprecipitating the polymer with petroleum ether.

Probably the most effective mixing method is to add zinc oxide to the polymerization mixture; zinc oxide doesn't interfere with the reaction, the Du Pont workers find. When isolated, the copolymer has zinc oxide uniformly mixed in it. Curing is done in a positive pressure mold at 135° C. and 3000 p.s.i. for several hours.



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CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION

July 27, 1964

Dr. K. T. Jacob, Director
The Rubber Research Institute
of India
Rubber Board P O, Kottayam
Kerala, India

Dear Dr. Jacob:

Your request for copies of reports on polythiocarbonyl fluoride has been referred to me. The articles in which this polymer was discussed appeared in Chemical and Engineering News. I am sure these articles are the source for the information given in Rubber World, 149, 96 (1963).

I am enclosing reprints of the original Chemical and Engineering News articles.

Sincerely yours,

W. H. Sharkey /mac

W. H. Sharkey

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Enclosures

BETTER THINGS FOR BETTER LIVING . . . *THROUGH CHEMISTRY*