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PERFLUOROETHER TRIAZINE ELASTOMERS

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INTRODUCTION

The weakest link in high performance equipment is often an elastomeric component. Seals, gaskets, diaphragms and couplings are inherently less stable than structural metals and composites. This is true of such diverse applications as fuel tank sealants in high speed aircraft, couplings for drill bits used in geothermal formations, deep wells and wells exposed to sour gas, electrical connectors, firewall seals, and tough-service parts in automobile engines, pumps, compressors, pipelines and scientific equipment. All of these applications require elastomeric materials with outstanding thermal and environmental stability.

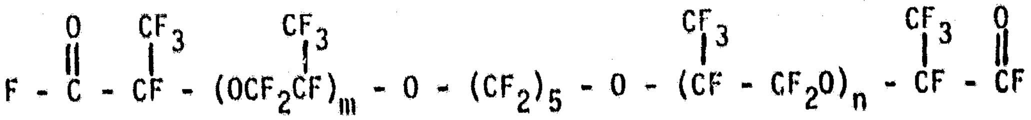
Development of high performance, thermally stable elastomers has concentrated on the fluorocarbons and fluorosilicones. Fluorocarbons are generally superior to fluorosilicones in thermal stability and fluid resistance. However, most fluorocarbons are not useful as elastomers at low temperatures (less that -40°C) because of their high glass transition temperatures. In particular, perfluoroalkylene-triazine elastomers have promised a clear superiority over other known elastomers in thermal and oxidative stabiltiy. Their reduction to practice has been frustrated by the complex nature of the chemical system used for polymerization and the non-availability of desirable synthetic intermediates (Young, 1972).

In order to obtain high performance elastomers with the high thermal stability and chemical inertness of perfluoroalkylene triazine and a low glass transition temperature, perfluoroether triazine elastomers were proposed as potentially superior high performance elastomers (Rosser et. al., 1975). However, perfluoroether synthesis was limited to low molecular weight polymers. Elastomers with high tensile strength and with a low glass transition temperature were not produced at this time. Before an improved high performance elastomer could be produced, high molecular weight linear perfluoroether traizine polymers were required that could be crosslinked by a stable linkage with the average chain length between crosslinks controlled in order to achieve desired mechanical properties.

Measurement of molecular weight distributions of fluorinated polymers is difficult because of their insolubility in organic solvents. So fluorinated solvents must be used. To determine the molecular weight distribution of perfluoroether polymers, size exclusion chromatography with small particle silica column packing was used (Korus and Rosser, 1978). This rigid packing is compatible with fluorinated solvents whereas the polystyrene gel packings shrink in the presence of fluorinated solvents. Thermally stable perfluoroalkylether oxidiazole elastomers have been crosslinked by tri-functional triazine and characterized by size exclusion chromatography (Rosser et. al., 1979). This stable triazine crosslink can also be used in the synthesis of perfluoroether triazine elastomers.

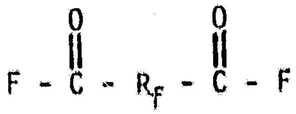
Elastomer Synthesis

The starting material for the synthesis of perfluoroalkylether triazine elastomers is a high molecular weight ether diacid fluoride. Perfluoroalkylether diacid fluorides and trifluoroacetic anhydride were obtained from PCR, Inc. These diacid fluorides are prepared by the step-wise addition of hexafluoropropylene oxide to hexafluoroglutaryl fluoride (Rosser et. al., 1975). The resulting oligomer has the following structure with the number of hexafluoropropylene oxide units added equal to m + n + 2:



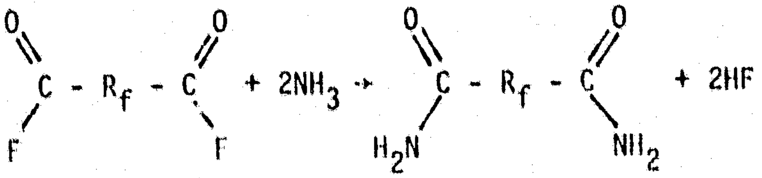
$$F - \overset{O}{\overset{\|}{C}} - \overset{CF_3}{\overset{|}{CF}} - (OCF_2\overset{CF_3}{\overset{|}{C}F})_m - O - (CF_2)_5 - O - (\overset{CF_3}{\overset{|}{CF}} - CF_2O)_n - \overset{CF_3}{\overset{|}{CF}} - \overset{O}{\overset{\|}{C}}F$$

or



$$F - \overset{O}{\overset{\|}{C}} - R_f - \overset{O}{\overset{\|}{C}} - F$$

Perfluoroalkylether diacid fluorides were converted to diamides by the addition of ammonia

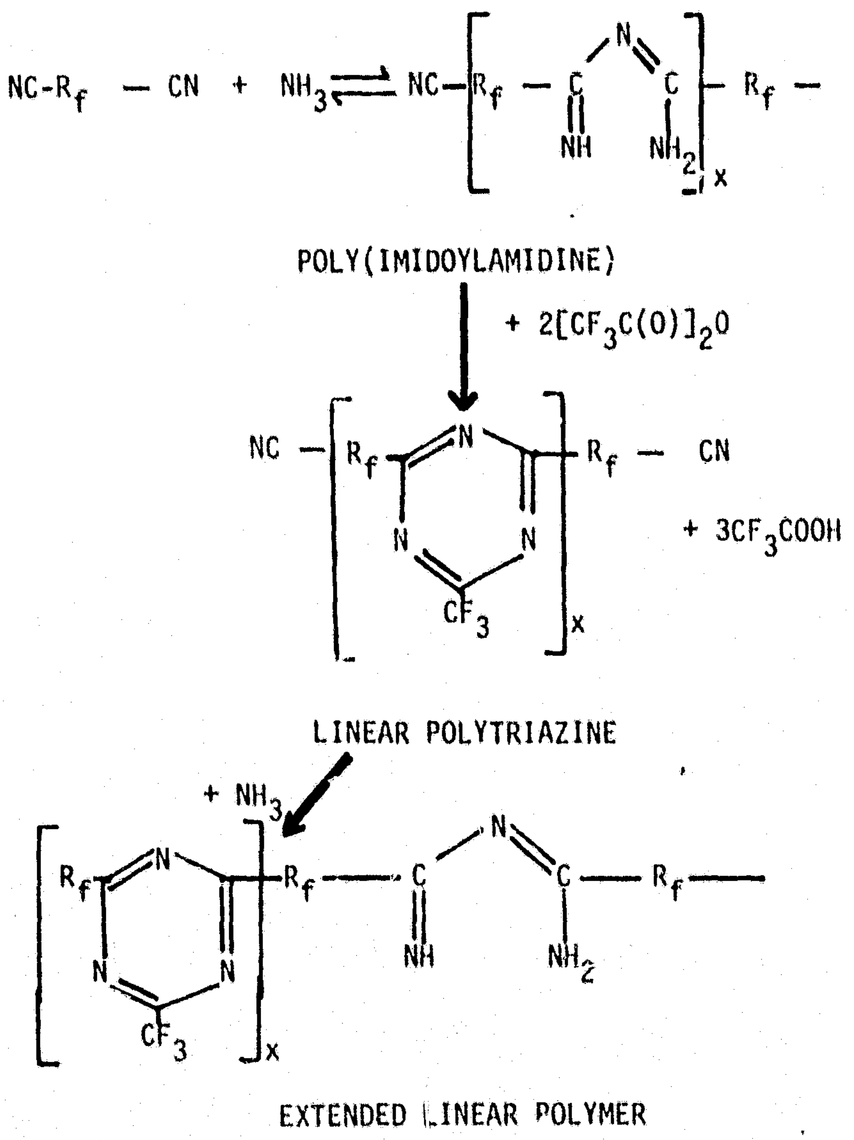


(1)

Ammonia was bubbled through a solution of the diacid fluoride in 1, 1, 2-trichloro-1, 2, 2, - trifluoroethane (Freon 113). The reaction flash was connected to a reflux condenser loaded with dry ice so that ammonia was refluxed. Reaction completion required 30-60 minutes and could be detected by a cooling of the reaction flask as the exothermic reaction reached completion. There was a phase separation in the reaction product as the diamide has a very low solubility in Freon 113. Methanol was added to dissolve the diamide, and the solution was filtered under vacuum through a course filter paper to remove the ammonium fluoride by-product. Then Freon 113 and methanol were removed by distillation, and the diamide dried in a vacuum oven. Diamide is recovered with a yield of 80 to 90%.

Perfluoroalkylether dinitrile was prepared by dehydration of the diamide in the presence of P_2O_5. The P_2O_5 slurry was heated at 150 to 160°C for approximately five days and then vacuum distilled to remove the dinitrile. Dinitrile is produced from diamide at a yield of 60 to 80%. Infrared spectroscopy was used to monitor the above reactions since the acid fluoride, amide, and nitrile infrared bands have higher frequencies than the ether, carbon-fluorine, and carbon-carbon infrared bands (Figure 1).

Crosslinked perfluoroalkylether triazine elastomers were prepared from perfluoroalkylether dinitriles by the following four step reaction sequence:



(2)

(3)

(4)

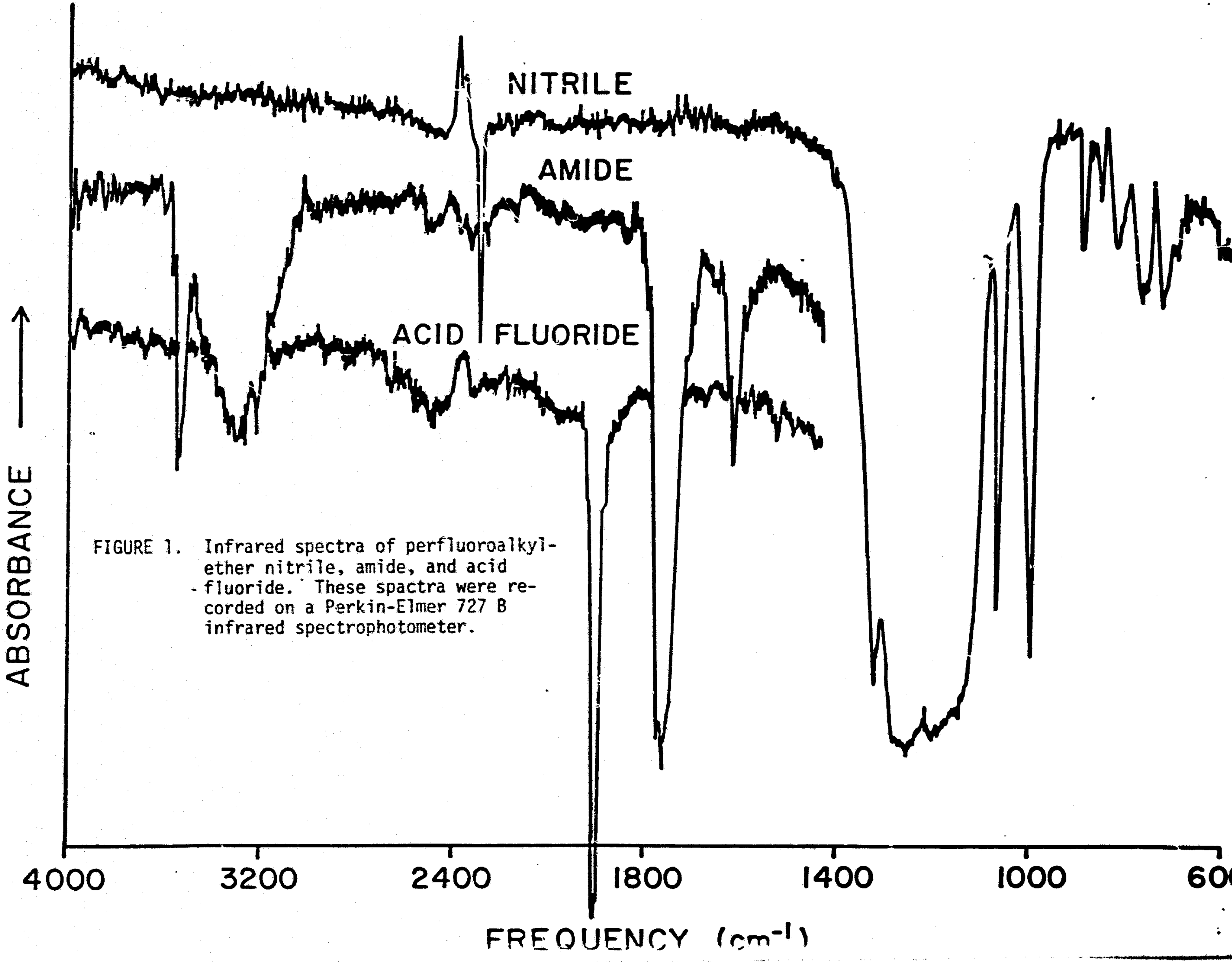
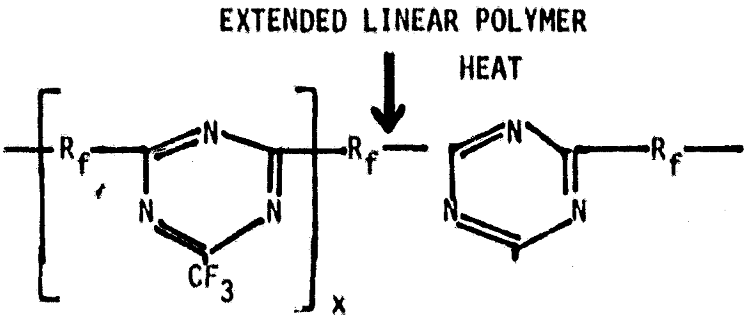


FIGURE 1. Infrared spectra of perfluoroalkylether nitrile, amide, and acid fluoride. These spectra were recorded on a Perkin-Elmer 727 B infrared spectrophotometer.



(5)

This reaction sequence involves:

(1) A step-growth polymerization which occurs with ammonia addition to the dinitrile forming poly(imidoylamidine) (See reaction 2). It is important to exclude water vapor during this reaction to prevent amide formation. Before ammonia addition, the reaction flask was purged with nitrogen. Nitrogen and ammonia were purified by passage through drying tubes packed with calcium oxide. The extent of reaction was followed by IR spectroscopy and viscometry (Rosser and Korus, 1980). The extent of this first polymerization reaction determines the eventual molecular weights between crosslinks. The terminal nitrile groups of the poly (imidoylamidine) are the active sites for crosslink formation, and all subsequent reactions were carried out to completion.

(2) Linear polytriazines were formed with the addition of trifluoroacetic anhydride (See reaction 3). The polymer solution was added dropwise to trifluoroacetic anhydride in an amber bottle with the weight of trifluoroacetic anhydride at least 0.3 times the weight of the polymer. An amber bottle is necessary to prevent photoinitiated decomposition of the anhydride. Slow addition of poly (imidoyl amidine) to the trifluoroacetic anhydride solution is required in order to maintain a high concentration of the anhydride during ring closure. The anhydride acts as a dehydrating agent, and prevents hydrolysis products, especially amides, from forming. Amides act as a polymer chain terminator and are formed if water is not excluded from this reaction. The resultant solution was allowed to stand overnight. Freon 113 was then removed by distillation. After solvent removal a two phase, poly (perfluoroalkyether triazine) and trifluoroacetic acid, system resulted. The poly (perfluoroalkylether tria-

zine) layer was removed and placed under vacuum for complete trifluoroacetic acid removal.

(3) Ammonia was introduced to reflux as in reaction 2 until completion of poly (imidoylamidine) formation.

(4) The resultant polymer was heated for approximately one day periods at 100°C, 130°C and 150°C to form the crosslinked elastomer. Heating of imidoyl amidine gives a mixture of imidoyl amidine, nitrile, ammonia, and triazine. Amidines and imidoyl amidines condense to form triazine with ammonia being liberated as cyclization occurs (Young, 1972).

RESULTS AND DISCUSSION

Using synthetic methods similar to those described here, Dorfman et al. (1966) have synthesized high molecular weight perfluoroalkyl triazine polymers. These linear polymers were crosslinked to form tough, rubbery elastomers with glass transition temperatures from -17 to -5°C. Young (1972) stated that the materials made by Dorfman, et al. represent the closest approaches to practicable perfluoroalkylene-triazine elastomers. However, only perfluoroalkyl monomers were used by Dorfman et al. whereas perfluoroalkylether monomers have been used for perfluoroalkylether triazine synthesis. Using perfluoroalkylether groups produces improved low temperature properties. Perfluoroalkylether triazine elastomers have glass transition temperatures of approximately -45°C or about 35 degrees less than the corresponding perfluoroalkyl triazine elastomers. Also, the method of perfluoroalkylether triazine crosslinking (reactions 4 and 5) is novel. Dorfman et al. do not even discuss crosslinking methods. Young discusses possible ways for incorporating sites for crosslinking in a linear triazine polymer. The methods that he discusses are considerably more complex, requiring higher curing temperatures, and are not as specific as the crosslink reactions 4 and 5.

Perfluoroalkylether synthesis has previously been limited to low molecular weight polymers, and elastomer synthesis was severely restricted. However, linear polymers with weight average molecular weights from 20,000 to 28,000 can be prepared following reactions 2 and 3 (Korus and Rosser, 1978; Rosser and Korus, 1980). Size-exclusion chromatography, viscometry, and infrared spectroscopy have been used to monitor reactions 2 and 3. Previous polymerization reactions of imidoylamidine and triazine derivatives gave products with molecular weights too low for good physical properties. These products were also sensitive to the reaction conditions and therefore were not easily reproduced (Young, 1972).

The properties of the cured perfluoroalkylether triazine elastomers are affected by the length of the alkylether region of the polymer, m + n value, and by the degree of polymerization between crosslinks, x. Increasing the alkylether portion of the elastomer gives more chain flexibility and a lower glass transition temperature (Table I). Increasing the degree of polymerization between crosslinks reduced the elastomer modulue (Table II).

TABLE I: Glass Transition Temperatures

m + n	Tg (°C)
2	-36
4	-41
6	-45

TABLE II: Elastomer Moduli for m + n = 6

x	Modulus (Nm^{-2})
4	10^7
6	10^6
8	10^5
10 - 20	10^4

Perfluoroalkylether triazine elastomers show lower isothermal weight losses than poly (trifluoropropylmethane siloxane), a thermally stable polyester sealant, and perfluoroalkylether oxadiazole elastomers (Rosser and Korus, 1980a). The high temperature oxidative stability of the perfluoroether triazine elastomers show a very marked improvement over state-of-the-art thermally stable elastomers. Initial weight losses of perfluoroalkylether triazine elastomers in air at 300°C are only about 2% of the weight losses experienced by poly (trifluoropropyl methyl siloxane). After 6-12 hours in air at 300°C the triazine elastomers show little change in physical properties while the siloxane elastomers are reduced to a char.

Triazine polymer synthesis is not limited to the perfluoroalkylether triazine polymers described. Similar synthesis procedures have been used for several perfluorodinitrile monomers and ring-closing reagents other than trifluoroacetic anhydride (Rosser and Korus, 1980 b).

CONCLUSION

The difficulties experienced in fluoroalkyltriazine elastomer synthesis can be overcome by a four-step reaction process involving chain extension, triazine ring closure, crosslinking, and elastomer curing. Molecular weight can be controlled in the initial polymer formation so that elastomer modulus can be determined. The final product elastomers exhibit a useful elastomeric range of approximately -45°C to 325°C with an oxidative stability superior to other broad range elastomers.

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