Crosslinking of Fluoroelastomers by "Click" Azide–Nitrile Cycloaddition

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Fluoroelastomers exhibit excellent resistance to heat, weather, oil, solvents, and other chemicals.¹ Commercially available materials are either fluorosilicones or fluorophosphazenes, as well as fluorocarbon copolymers based on vinylidene fluoride (VDF), hexafluoropropylene, tetrafluoroethylene (TFE), and chlorotrifluoroethylene.² Other common fluoroelastomers include the copolymers of TFE with one or more hydrocarbon olefins such as propylene (P), and also the copolymers of TFE (and VDF) with a perfluoro(alkyl vinyl ether) such as perfluoro(methyl vinyl ether) (PMVE).

Many fluoroelastomers require the incorporation of a cure site monomer into their polymeric chains to enable an efficient crosslinking. Fluoroelastomers are usually cured by nucleophiles such as diamines, bisphenols, or with peroxides.³ Nevertheless, some curatives are toxic, whereas others containing reactive bromine or iodine atoms can release harmful byproducts during the curing reaction. Other cure site monomers (e.g., those containing double bonds at both ends of the molecule) may be so reactive that they disrupt polymerization of the fluoroelastomer by altering the polymerization rate, by terminating polymerization, or by causing undesirable chain branching. Lastly, the incorporation of a cure site monomer into a fluoroelastomer chain may induce a negative impact on the physical properties and the chemical resistance, once crosslinked.² New curing systems for fluoroelastomers that avoid the aforementioned limitations are thus in demand and this is the objective of this article.

Actually, Huisgen was the first to understand the breadth of the 1,3-dipolar cycloaddition between an azide and a terminal or an internal alkyne to give a 1,2,3-triazole.⁴ Such a reaction was described as "the cream of the crop of click chemistry" by Sharpless and coworkers.⁵ Nowadays, the metal catalyzed azide/alkyne "click" reaction (a variation of the Huisgen 1,3-dipolar cycloaddition reaction between ter-

minal acetylenes and azides) has vastly increased in broadness and application in the field of polymer science.⁶ However, those type of 1,3-dipolar cycloaddition are still scarcely employed in the fluoropolymers area.⁷

We describe here an appealing crosslinking method for fluoroelastomers via the formation of tetrazoles by using Huisgen cycloaddition between an azide and a nitrile.⁸ The chosen polymer was $DuPont^{TM}$ Kalrez[®] perfluoroelastomer (Fig. 1).⁹

DuPontTM Kalrez[®] perfluoroelastomer is a terpolymer based on TFE, PMVE, and perfluoro(8-cyano-5-methyl-3,6-dioxaoct-1-ene) (8-CNVE), that contain weight proportions ranging from 65 to 80%, 20 to 34%, and 1 to 3%, respectively.

This fluoroelastomer is used as high performance seal in areas ranging from aerospace, pharmaceuticals, and electronics.¹⁰ However, the conventional method used to carry out the crosslinking of DuPontTM Kalrez[®] perfluoroelastomer requires too much energy.¹¹ In fact, the crosslinking reaction via the cyclotrimerization of nitrile groups and the subsequent formation of triazines¹² interchain bridges (Supporting Information Fig. S1) is carried out at 300 °C for two days.¹³ To decrease the energetic cost, the Huisgen cycloaddition between the pendant cyano groups of 8-CNVE and a bisazido fluorinated telechelic was considered, with the expectation that it would decrease both the reaction temperature and the reaction time.

A model study has been first carried out to determine the feasibility of such a "click" reaction (Scheme 1).

In a first step, 1-iodoperfluorohexane ($C_6F_{13}I$) was ethylenated in *tert*-butanol using di-(4-*tert*-butylcyclohexyl) peroxydicarbonate as the radical initiator.¹⁴ The structure of compound **1** was confirmed by ¹H and ¹⁹F NMR

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spectroscopies. The ¹⁹F NMR spectrum of **1** (Supporting Information Fig. S2) displayed the characteristic peak at -122.6 ppm attributed to the CF₂CH₂ pattern while it did not exhibit any peak at -59 ppm (characteristic of a CF_2I end-group in $C_6F_{13}I$). In agreement with the literature,¹⁵ this step afforded 1 in about 80% yield. The second step is a nucleophilic substitution of the terminal iodine group by an azido group, vielding **2** in 94% vield (Scheme 1).¹⁶ Azido compound 2 was then characterized by Fourier transform infrared spectroscopy (FTIR) and ¹H NMR spectroscopy. The FTIR spectrum of 2 (Supporting Information Fig. S3) displaved the characteristic azide band at 2110 cm^{-1} . The ¹H NMR spectrum of 2 (Supporting Information Fig. S4) showed an expected downfield shift of the protons adjacent to the terminal azido group. The various tests (Supporting Information Table S1) of "click" reactions between 2 and 8-CNVE were carried out using a 1.1-fold excess of 2 with respect to 8-CNVE. The reactions were monitored by ¹⁹F NMR spectroscopy. The most appropriate reaction conditions afforded 3 in 90% yield in the absence of any catalyst at 150 °C for 24 h. The ¹⁹F NMR spectrum of **3** superimposed with that of 8-CNVE is presented in Supporting Information Figure S5. The fluorine atoms adjacent to the nitrile group (i.e. "g" signal at -109.4 ppm, Supporting Information Fig. S5 top spectrum) in 8-CNVE underwent an upfield shift after the reaction (i.e., "g" signal at -112.6 ppm, Supporting Information Fig. S5 bottom spectrum). The characteristic signals corresponding to the C_6F_{13} group were also identified.



SCHEME 1 "Click" azide–nitrile cycloaddition reaction between 8-CNVE and perfluoroazido compound **2**.



SCHEME 2 Crosslinking of DuPontTM Kalrez[®] perfluoroelastomer by "click" azide–nitrile cycloaddition.

The above method was then applied to crosslink DuPontTM Kalrez[®] perfluoroelastomer. Bis-azido fluorinated curing agent **5** was synthesized according to a similar procedure as that of perfluoroazido compound **2** (Scheme 2).^{7(a),17} DuPontTM Kalrez[®] perfluoroelastomer and **5** were solubilized in perfluoro(butyltetrahydrofuran) and the resulting solution was casted to obtain a film after evaporation. The evaporation step has to be slow to prevent any formation of bubbles within the film. Therefore, a pre-evaporation was carried out at 5 °C for 24 h in a cold room then at 35 °C for 24 h in an oven. Finally, the film was press cured at 150 °C for 24 h (Scheme 2).

The crosslinked film obtained from a **5**:perfluoroelastomer 0.5:5 weight ratio was analyzed by FTIR spectroscopy



FIGURE 2 TGA thermograms under air of uncured DuPontTM Kalrez[®] perfluoroelastomer and cured films, where Kalrez *x*:*y* represents the **5**:perfluoroelastomer weight ratio.

(Supporting Information Fig. S6). The corresponding FTIR spectrum displayed a small band at 1675 cm⁻¹ due to the presence of C=N stretching vibrations in tetrazole.¹⁸ As an evidence of efficient crosslinking, the film was totally insoluble in perfluoro(butyltetrahydrofuran).

Crosslinked films with various **5**:perfluoroelastomer weight ratios were analyzed by thermogravimetric analysis (TGA) under air to compare their degradation profile to that of a perfluoroelastomer film obtained from the same procedure but without any addition of crosslinking agent **5** (Fig. 2). Overall, the thermograms revealed an improvement by about 20 °C of the thermal stability under air for the press cured films with telechelic crosslinking agent **5**. In contrast to polymeric tetrazoles that decompose with evolution of significant amounts of gas at 120–250 °C,¹⁹ DuPontTM Kalrez[®] crosslinked perfluoroelastomers exhibit an improved thermal behavior, thanks to the perfluorinated backbone that acts as a protective shield for tetrazoles.

To summarize, on the basis of a model study, DuPontTM Kalrez[®] perfluoroelastomer that bears pendant nitrile groups was successfully crosslinked with a bis-azido fluorinated curing agent by "click" azide–nitrile cycloaddition. Thermogravimetric analyses of the resulting press cured films revealed an improvement by about 20 °C of the thermal degradation profile under air, compared to that of the corresponding uncured fluoroelastomer. This method is simple to implement and requires much less energy than that currently used in the fluoroelastomers industry.

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