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A perfluoropolyether-based elastomers library with on-demand thermorheological features

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ABSTRACT

Perfluoropolyether (PFPE)-based materials were obtained through thermal 1,3-dipolar Huisgen reactions. The formulations consisted in a combination of PFPE-functionalized oligomers (PFPE-diyne A_2 and PFPE-diazide B_2) and a pentaerythritol triazide cross-linker C_3. Increasing the amount of C_3 induced an increase of the cross-link density. This approach gave rise to materials ranging from rubber-like to gels. The networks formation was found to be governed by a constant activation energy and it was assumed that the whole process is controlled by the fast reaction between A_2 and C_3. Two glass transition temperatures were evidenced, one ascribed to hydrogen bonds that gradually shifted to a lower temperature with decreasing C_3, while the other one was attributed to PFPE segments that constantly appeared at -−105 °C. Thermogravimetric analyses under air recorded at a low heating rate of 1 °C min^{-1} provided a valid estimate of the true temperature of degradation of the materials (*ca.* 200 °C).

1. Introduction

Fluoroelastomers are a class of synthetic rubber which provides outstanding levels of resistance and service life above 200 °C [1]. The exceptional heat stability of these materials is due to the strength of the carbon-fluorine bond (the bond dissociation energy of the C-F bond ranges from 450 to 530 kJ mol^{-1}) [2], the high ratio of fluorine to hydrogen, and the absence of unsaturation. The design and manufacture of various industrial components used in harsh environments have typically relied on fluoroelastomers [3]. Nevertheless, their performances at low temperature remain unsatisfactory [4], and especially for aeronautics and aerospace applications that required materials endowed with a certain degree of flexibility at very low temperature (*i.e.* −80 °C or below). In 1986, the Space Shuttle "Challenger" disintegration occurred due to an O-ring seal that was not designed to fly under unusually cold conditions at liftoff.

The incorporation of soft segments is a good alternative to lower the *Tg* while preserving the thermal stability thanks to the carbon-fluorine bonds [5]. Among the known classes of fluoroelastomers (*i.e.* Fluorocarbon-elastomers, F-Phosphazenes, F-Silicones) [4], Sifel® products marketed by the Shin-Etsu company offer to date a good compromise between low temperature flexibility and heat resistance in spite of their complex and non-versatile synthesis [6]. Sifel® products are based on a perfluoropolyether (PFPE) backbone combined with silicone crosslinking and also exhibit enhanced performances in fuels, solvents, acids, and alkalis compared to standard fluoroelastomers.

Originally developed in the early 1960's, PFPEs have been widely used as high-performance lubricants for aerospace and industrial applications because of their excellent tribological properties [7]. PFPE-based lubricants are thermally stable, non-

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flammable, chemically resistant, and non-volatile over a broad temperature range (from –75 to 350 °C). The polymer chains are linear or branched depending on the monomer(s) used for their preparation. Several types are commercially available: (i) Fomblin® Z prepared by the photo-oxidation of tetrafluoroethylene (Solvay Specialty Polymers), (ii) Fomblin® Y synthesized by the photo-oxidation of hexafluoropropylene (Solvay Specialty Polymers), (iii) Demnum® obtained by the ring-opening polymerization (ROP) of tetrafluorooxetane (Daikin Ind.), and (iv) Krytox® produced by the ROP of hexafluoropropylene oxide (Chemours).

Some PFPEs such as Fomblin® Z contain functional groups and can be used as reactive intermediates in the synthesis of a wide range of polymers [8–16]. Guan et al. [17] designed a new type of PFPE-based elastomer by click reactions between a telechelic PFPE-diyne (prepared from Fomblin® Z-DOL) and a triazide aromatic cross-linker. As known, the click chemistry concept has the double advantage of being fast without release of harmful by-products. The obtained PFPE-based material showed a good resistance to a variety of organic solvents, heat and even harsh pH conditions, thanks to the presence of PFPEs and robust 1,2,3-triazole cross-linking knots. However, the Tg of -10 °C seems to be overestimated for a PFPE-based network in spite of the presence of rigid aromatic structures. The DSC and DMA experiments, performed from -80 °C to 80 °C, preclude the possibility to observe the usual Tg at *ca.* -100 °C for PFPE-based networks [12]. Conversely, the 3M company claimed the synthesis of PFPE-based elastomers having low Tgs (*ca.* -115 °C) using a similar approach (*i.e.* alkyne-azide or nitrile-azide cycloadditions) [18]. For instance, binary formulations composed of PFPE-dipropargylamide or dicyano-PFPE in combination with trimethylolpropane/epichlorohydrine-azide or polyisocyanate-azide adducts were cured at 177 °C for *ca.* 45 min. This patent, however, lacks of detailed physico-chemical data.

In our preliminary work, semi-crystalline and amorphous thermoplastics endowed with high thermostability (*ca.* 300 °C under air at a heating rate of 10 °C min^{-1}) and low glass transition temperature (*ca.* -100 °C) were obtained *via* $A_2 + B_2$ step-growth polymerization between a telechelic PFPE-diyne and fluorinated diazides [19,20]. Polymerizations were copper-catalyzed but also thermally activated in some cases, thus avoiding the presence of copper residues in the final materials. As previously reported, thermal polyaddition in bulk can afford polytriazoles with higher molar masses and thermal properties as compared to those obtained by CuAAC in solution [21]. Extrapolating from these previous results, the present work deals with innovative PFPE-based networks prepared *via* thermally-activated $A_2 + B_2 + C_3$ alkyne-azide reactions. Using thermal analyses in combination with rheometry allowed us to establish structure-property relationships for the resulting broad range of materials.

2. Materials and methods

2.1. Materials

All organic solvents used for the syntheses were of analytical grade. Fluorolink® E10H (M_n 1800 g mol^{-1}) was purchased from Acota (UK). Propargyl bromide solution (80 wt% in toluene), sodium azide, sodium hydroxide, tosyl chloride, triethylamine, allyl bromide were purchased from Sigma-Aldrich. Pentaerythritol tribromide was purchased from abcr (Germany). 1,1,1,3,3-Pentafluorobutane (Solkane® 365-mfc) was kindly provided by Solvay. Deuterated solvents ($CHCl_3$-*d*, acetone-d_6, and methanol-d_4) for NMR characterizations were purchased from Euriso-Top (Grenoble, France) (purity > 99.8%).

2.2. Synthesis of oligomers A_2 and B_2, and crosslinkers C_3 and C'_3

2.2.1. Synthesis of PFPE-diyne A_2

Fluorolink® E10H (1800 g mol^{-1}, 100 g, 55.6 mmol, 1 eq.) was added to a mixture of CH_3CN (150 mL), THF (150 mL), and sodium hydroxide (16 g, 400 mmol, 7.2 eq). The suspension was heated to 55 °C and propargyl bromide (80 wt% in toluene, 50 mL, 449 mmol, 8.1 eq.) was added. The reaction mixture was stirred for 7 days at 55 °C then filtered. The solvent was evaporated and the crude product was dried under vacuum (20 10^{-3} mbar) at 100 °C then purified by filtration through a 0.45 µm PTFE filter to afford 86 g (~85% yield) of a light brown oil.

2.2.2. Synthesis of PFPE-diazide B_2

Step 1: Synthesis of PFPE-bistosylate. Fluorolink® E10H (1800 g mol^{-1}, 100 g, 55.6 mmol, 1 eq.) was dissolved in a mixture of 1,1,1,3,3-pentafluorobutane (300 mL) and triethylamine (27 g, 277 mmol, 5 eq.). Tosyl chloride (53 g, 278 mmol, 5 eq.) was added to the reaction mixture, which was stirred for 7 days at 30 °C. The fluorinated phase was washed with water (3 × 300 mL), dried over $MgSO_4$, filtered and evaporated. The crude product was dried under reduced pressure (20 10^{-3} mbar) at 100 °C to afford 70 g (~70% yield) of a light brown oil. *Step 2: Synthesis of PFPE-diazide B_2*. A mixture of PFPE-bistosylate (70 g, 38.9 mmol, 1 eq.) and sodium azide (27 g, 415 mmol, 10.7 eq.) in DMSO (300 mL) was stirred at 100 °C for 7 days. The reaction mixture was poured into water (300 mL) and then extracted with 1,1,1,3,3-pentafluorobutane (3 × 150 mL). The organic phases were combined, washed with water (3 × 150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was then dried under reduced pressure (20 10^{-3} mbar) at 100 °C to afford 42 g (~60% yield) of a light brown oil.

2.2.3. Synthesis of crosslinking agent C_3

A mixture of pentaerythritol tribromide (10 g, 31 mmol, 1 eq.), NaN_3 (12 g, 186 mmol, 6 eq.) in DMSO (100 mL) was stirred at 100 °C for 3 days. The reaction mixture was poured into water (200 mL) and then extracted with chloroform $CHCl_3$ (3 × 100 mL). The organic phases were combined and washed with water (3 × 100 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford 5.70 g (87% yield) of a pale yellow oil.