

# Approaches to highly polar polymers with low glass transition temperatures

## 2. Fluorinated polymers via ring-opening metathesis copolymerisation and hydrogenation<sup>☆</sup>

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### Abstract

The synthesis, via ring opening metathesis polymerisation, and hydrogenation, using diimide, of a series of copolymers of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene with cyclopentene is described. The products were characterised via a detailed analysis of their <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra, along with thermal and GPC analysis. Hydrogenation using diimide resulted in a significant lowering of the glass transition temperatures of the copolymers.

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### 1. Introduction

In the introduction to our first paper on this topic [1], we described the background science and motivation for the study of which this report forms a part. One of the objectives of our work in this area is to establish routes to polar polymers displaying low glass transition temperatures, such materials might be additions to the range of elastomers and/or suitable for exploitation as electrostrictive materials [1–3]. In our earlier paper [1], we described the ring-opening metathesis polymerisation (ROMP) of two partially fluorinated bicyclo[2.2.1]hept-2-ene monomers, using the “classical” ill-defined initiator systems WCl<sub>6</sub>/Ph<sub>4</sub>Sn and MoCl<sub>5</sub>/Ph<sub>4</sub>Sn, to give partially fluorinated poly(1,3-cyclopentylene vinylene)s, and established that diimide hydrogenation could be efficiently achieved and resulted in the lowering of  $T_g$ , determined by DSC, by about 36/37 °C. Here, we report a study of the syntheses and hydrogenation of poly(5-trifluoromethyl-1,3-cyclopentylenevinylene-copentylene)s. The ROMP of fluorinated monomers is a

well-established process [4–8] but neither the homopolymers nor their hydrogenation products display a low enough glass transition temperature for the purposes of the present project. Here, we report the combination of copolymerisation of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene with cyclopentene and hydrogenation of the resulting polymers as an alternative approach to a material with low enough  $T_g$  and as high as possible fluorine content for our purposes [1].

### 2. Experimental

#### 2.1. General considerations

Cyclopentadiene was freshly prepared by thermal cracking from dicyclopentadiene (Aldrich). 1,1,1-Trifluoropropene (Bristol Organics) was used without further purification. Tetraphenyltin (Aldrich) was purified by successive soxhlet extractions with toluene, dried under vacuum and stored in a Braun glove box operating under an atmosphere of nitrogen having <1 ppm water and <1 ppm oxygen. Tungsten hexachloride (Aldrich,  $\geq 99.9\%$ ) was used without further purification and stored in the glove box. Toluene was distilled from sodium and stored over molecular sieves. Stock solutions were freshly prepared prior to use. Trifluorotoluene

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was distilled prior to use and stored over molecular sieves. *p*-Toluenesulphonylhydrazide was dried under vacuum at room temperature overnight prior to use.

## 2.2. Monomers

(±)-5-Trifluoromethylbicyclo[2.2.1]hept-2-ene was prepared as an *exo:endo* mixture via the Diels Alder reaction of 1,1,1-trifluoropropene with cyclopenta-1,3-diene, recovered and purified following the procedures reported previously [1]. In this study, two batches having respectively 62:38 and 74:26 *exo:endo* ratios were used. Cyclopentene (Aldrich) was distilled from CaH<sub>2</sub> and stored over phosphorous pentoxide.

## 2.3. General procedure for ring-opening metathesis polymerisation

Ph<sub>4</sub>Sn (2 equiv.) was placed in a dry ampoule equipped with a magnetic stirrer and flushed with dry oxygen-free nitrogen. A solution of WCl<sub>6</sub> in dry toluene (0.01 M, 1 equiv.) was injected into the ampoule via a rubber seal. After the required activation time (10–15 min), the colour changed from blue-black to dark brown, the mixture of monomers (500 equiv.) was injected into the initiator solution which was stirred vigorously. The solutions became progressively more viscous until the stirrer stopped. After quenching the reaction by addition of a few drops of methanol, the contents of the ampoule were poured in acetone and dissolved. The acetone solutions were concentrated by rotary evaporation to give viscous solutions and the product polymers were precipitated by dropwise addition of the viscous solution into a five-fold excess of cold hexane, recovered by filtration and dried under vacuum.

## 2.4. General procedure for the hydrogenation of the polymers

The polymers were dissolved in trifluorotoluene (ca. 50 ml for 1 g of polymer) and the resulting solution was placed in

three-necked flask purged with dry oxygen-free nitrogen and equipped with a reflux condenser and a magnetic stirrer. *p*-Toluenesulphonylhydrazide (15–20 times the weight of the polymer) was added in small portions at intervals of about 30 min while the solution was stirred at reflux (102 °C). The mixture was cooled to room temperature and the contents of the flask were poured directly into a 10-fold excess of cold methanol and stirred for 30 min. The precipitated solid was recovered by filtration and dried in a vacuum oven at 50 °C overnight. The products were re-dissolved in the minimum amount of acetone or benzene and re-precipitated in a five-fold excess of cold methanol. The white solids obtained were recovered by filtration and dried in a vacuum oven at 50 °C overnight to give the saturated polymers.

## 3. Results and discussion

The synthetic route is shown in Fig. 1 and the copolymerisations carried out are summarised in Table 1. Two batches of, (±)-5-trifluoromethylbicyclo[2.2.1]hept-2-ene having different *exo:endo* ratios were used and, although the differences were relatively small 62:38 cf. 74:26, they have to be kept in mind when analysing the results since

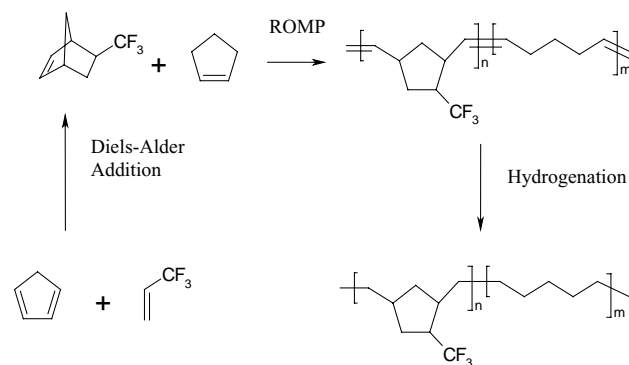


Fig. 1. Synthetic route to low  $T_g$  copolymers (5-trifluoromethylbicyclo[2.2.1]hept-2-ene was obtained as an *exo:endo* mixture).

Table 1  
Co-polymers synthesised and hydrogenated

Polymer	Monomers ratio <sup>a</sup>	Yield (%)	Fluorine content (%)	Fluorinated repeat unit incorporated (mol%)	$T_g$ (DSC) (°C)
I <sup>b</sup>	1:1	23	21.52	40	-7
II <sup>b</sup>	2:1	45	26.77	57	+8
III <sup>c</sup>	3:1	67	29.05	66	+42
IV <sup>c</sup>	4:1	72	31.45	78	+60
V <sup>d</sup>	3:1	-	28.06	64	+12
VI <sup>d</sup>	4:1	-	29.35	72	+36
VII <sup>b</sup>	2.5:1	57	28.29	63	+20
VIII <sup>d</sup>	2.5:1	-	26.99	60	-22

<sup>a</sup> Ratio of (±)-5-trifluoromethylbicyclo[2.2.1]hept-2-ene.

<sup>b</sup> From 62:38 *exo:endo* (±)-5-trifluoromethylbicyclo[2.2.1]hept-2-ene.

<sup>c</sup> From 74:26 *exo:endo* (±)-5-trifluoromethylbicyclo[2.2.1]hept-2-ene.

<sup>d</sup> Saturated polymers.

they may have consequences for the extent of fluorinated monomer incorporation and the glass transition temperatures of the product polymers. The feed stock composition was varied and the relative incorporation of monomers was calculated from the elemental analysis for fluorine using the method of potassium fusion in a closed vessel. This was the only reliable method accessible to us since there were no distinct resonances characteristic of each monomer residue in the  $^1\text{H}$  NMR spectra of the copolymers and calculation of the degree of incorporation from the carbon elemental analyses gave unreliable results. For example, from the percentage-carbon elemental analysis data obtained for samples of polymers (I), (II) and (III), approximately the same values for fluorinated monomer incorporations were computed, respectively 68, 72 and 70 mol%, which is intuitively unreasonable when the feed ratios were 1:1, 2:1 and 3:1, respectively and the product polymer  $T_g$ s varied from  $-7$  to  $+42^\circ\text{C}$ . Experience teaches that, depending on the nature of the system, combustion analysis for some fluorohydrocarbons can be unreliable, so this observation was not a total surprise. We therefore abandoned calculations based on carbon elemental analyses.

The first two polymerisations, carried out with feed ratios of 1:1 and 2:1 of fluorinated monomer: cyclopentene, using the batch of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene having a 62:38 *exo:endo* ratio, were carried out to determine how the inclusion of cyclopentene would affect the  $T_g$  of the new materials. Polymers (I) and (II) were obtained in disappointingly low recovered yields, 23 and 45%, respectively. The polymers were dissolved in acetone and precipitated in cold hexane to give, after drying, white rubbery materials. DSC analysis indicated  $T_g$ s of  $-7^\circ\text{C}$  for (I) with 40 and  $+8^\circ\text{C}$  for (II) with 57 mol% fluorinated monomer incorporation, which was encouraging. Subsequent copolymerisations and hydrogenations were carried out with a batch of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene starting material having a 74:26 *exo:endo* ratio.

The data recorded in Table 1 for the five unsaturated copolymers, I–IV and VII, indicate that in this system cyclopentene is marginally more reactive than the fluorinated monomer and it is also clear that incorporation of cyclopentene has a glass transition lowering effect; both these observations being consistent with reasonable expectation. At this stage, we attempted to maximise the fluorinated monomer content while producing a polymer that, after hydrogenation, would give a material with a  $T_g$  below room temperature.

When the feed compositions in Table 1 are compared to the polymer composition there is a qualitative correlation, in that the richer the monomer feed, the richer the polymer in fluorinated units; however, the correlation is not linear and, for reasons discussed above, the analysis cannot be assumed to be better than qualitative.

The double bonds in the polymers (III) and (IV) were hydrogenated and the analysis of the  $^1\text{H}$  NMR spectra of the resulting polymers (V) and (VI) showed the complete disappearance of the vinyl signals. Fluorine elemental analysis

indicated a small reduction in the proportions of the incorporated fluorinated repeat unit during the transformation of (III) and (IV) to (V) and (VI), respectively, this may indicate that a part of the fluorinated polymer backbone, possibly a small proportion of homofluoropolymer or material very rich in fluoromonomer residues, was lost during the recovery of the material. If this were true it would also explain the observed loss in weight of approximately 2–5% for the recovered hydrogenated materials; however, this may be pushing the analysis beyond what the quality of the data can support.

DSC analysis gave a  $T_g$  of  $12^\circ\text{C}$  for the saturated polymer (V) and  $36^\circ\text{C}$  for (VI). So, as in earlier work, hydrogenation results in a significant drop in  $T_g$  of 30 and  $24^\circ\text{C}$ , respectively and, unsurprisingly, within a particular class of polymer (unsaturated or saturated) as the incorporation of fluorinated units increases so does the  $T_g$ . With the data described above in mind, we prepared the polymer (VII), using a 2.5:1 monomer feed ratio, which had a fluorinated repeat unit incorporation of 63 mol% and a  $T_g$  of  $20^\circ\text{C}$ . Complete hydrogenation, monitored by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, gave (VIII) as a white rubbery material with a  $T_g$  of  $-22^\circ\text{C}$ . The fluorine elemental analysis for polymer (VIII) indicated a 60 mol% of the fluorinated repeat units in the polymer backbone, again showing the consistent small loss of fluorine during hydrogenation discussed above.

### 3.1. Structural characterisation of the copolymers

#### 3.1.1. NMR spectroscopy

The copolymer structure and the numbering system adopted is shown in Fig. 2. A few, of the many, spectra accumulated during the analysis of the copolymers and their hydrogenation products are discussed here by way of illustration of the methodology on which our conclusions are based.

Spectroscopic assignments were made with reference to those for the homopolymer of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene [1]. The expanded vinylic and saturated regions of the  $^{13}\text{C}$  NMR spectrum of the unsaturated polymer (III) are shown in Figs. 3 and 4, respectively with partial assignments of the signals. The vinylic region of the  $^{13}\text{C}$  NMR spectrum, Fig. 3, was more complicated than that for the homopolymer of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene with an increase in signal broadening and in the number of signals. The quartet for the carbon of the trifluoromethyl group is only partially resolved, two signals of the expected four can be seen and each occurs as two lines in the *exo:endo* ratio found in the monomer feed. This observation was confirmed in the analysis of the  $^{19}\text{F}$  NMR spectrum, see below. The saturated carbon region of the

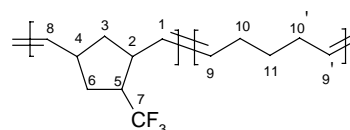


Fig. 2. Numbering of the carbon environments for the copolymers reported.

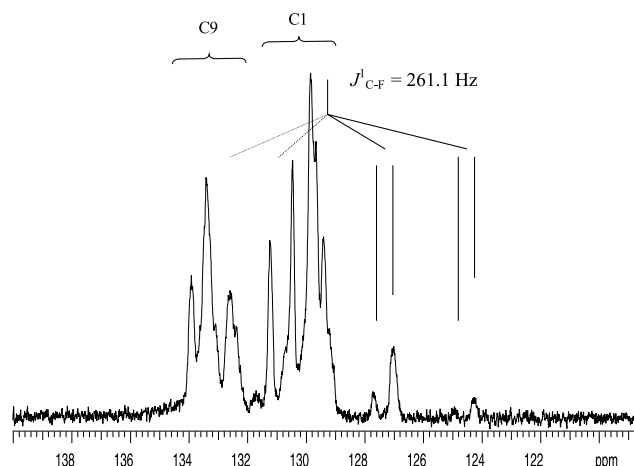


Fig. 3. Expanded vinylic region of the  $^{13}\text{C}$  NMR spectrum of polymer (III).

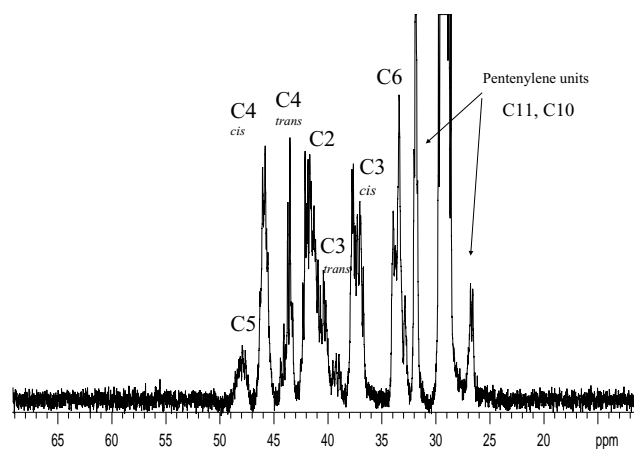


Fig. 4. Expanded saturated region of the  $^{13}\text{C}$  NMR spectrum of polymer (III).

spectrum, Fig. 4, was similar to that of the homopolymer of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene with the addition of signals associated with pentylenylene units.

The  $^{13}\text{C}$  NMR spectrum for the saturated copolymer (V), Fig. 5 shows a flat base line in the vinyl region confirming the complete hydrogenation of (III), the  $\text{CF}_3$  carbon signal is visible but partially obscured by the solvent signal, see the expanded spectrum in Fig. 6. The methylene region, shown in expansion in Fig. 5 displays an increased number of signals as compared to the hydrogenated fluorinated homopolymer [1], but the spectrum is very complicated, with many overlapping peaks and detailed interpretation in terms of monomer distribution was not possible. This evidence confirms the formation of the copolymer and implies a random rather than a blocky distribution of repeat units, since the latter might be expected to give a simpler spectrum.

The relative intensities of the signals in the  $^{19}\text{F}$  NMR spectra differed with the *exo:endo* ratios in the fluorinated monomer used as feed stock. Thus, the  $^{19}\text{F}$  NMR spectra for the unsaturated polymers (I) and (II), synthesised from 1:1 and 2:1 mixture of the 62:38 *exo/endo* mixture of ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene and cyclopentene, respectively display identical shifts and integration gave relative intensities of 61:39, which indicates that the propagation proceeded without discrimination between monomer *endo* and *exo* isomers. The same conclusions were drawn from the data for polymers (III) and (IV). The  $^{19}\text{F}$  NMR spectra of the hydrogenated polymers displayed chemical signal shifts and integrated intensities identical with those of their unsaturated analogues.

The  $^1\text{H}$  NMR spectra of polymer (III) recorded in  $d_6$ -acetone and its saturated analogue (V) recorded in  $d_6$ -benzene are compared in Fig. 7, it is clear that the hydrogenation is complete within the detection sensitivity of high-resolution  $^1\text{H}$  NMR.

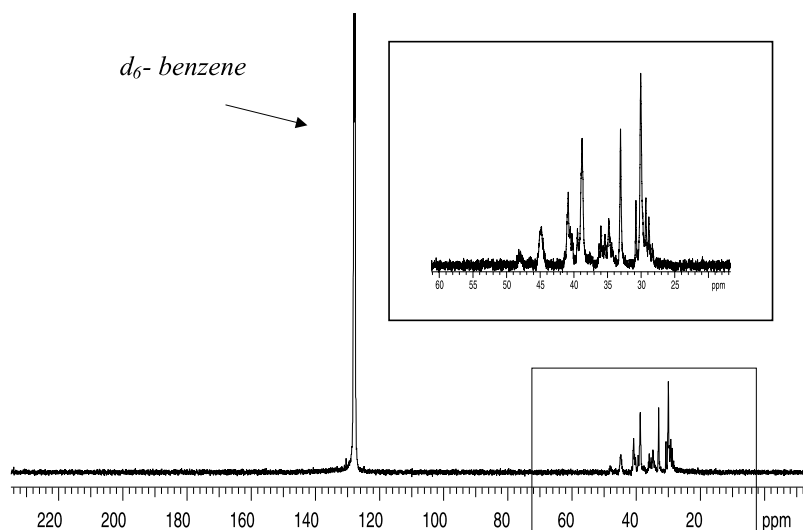


Fig. 5. The  $^{13}\text{C}$  NMR spectrum of polymer (V).

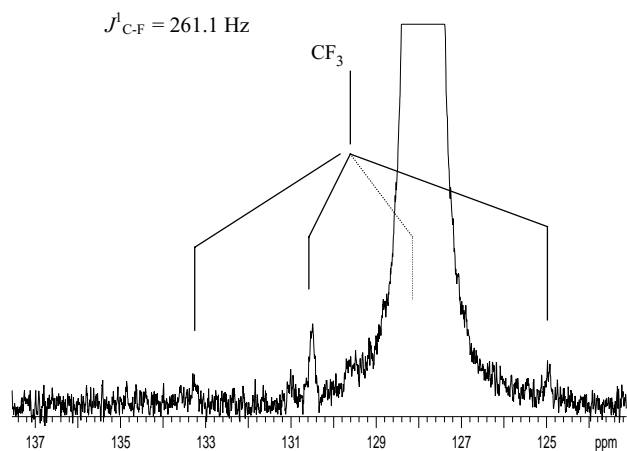


Fig. 6. The  $^{13}\text{C}$  NMR expanded vinyl region, showing the  $\text{CF}_3$  carbon quartet.

### 3.2. Physical characterisation of the copolymers

The results obtained from the DSC, GPC and TGA analysis for the copolymers synthesised are shown in Table 2.

Table 2  
Physical data for the copolymers reported

Polymer	$T_g$ ( $^{\circ}\text{C}$ ) (DSC)	GPC			TGA % wt.-loss at $300^{\circ}\text{C}$
		$M_n$	$M_w$	PDI	
I	-7	-	-	-	0.5
II	+8	-	-	-	1.3
III	+42	138,000	152,000	1.1	<0.5
IV	+60	116,000	189,000	1.6	0.5
V	+12	65,000	125,000	1.9	<1
VI	+36	102,000	123,000	1.2	<5
VII	+20	67,000	106,000	1.6	<0.5
VIII	-22	-	-	-	<1

From the obtained GPC data for polymers (III) to (VI), we can see that hydrogenation has the effect of lowering the molecular weight, which suggests that there is some fragmentation at the temperature of refluxing trifluorotoluene ( $102^{\circ}\text{C}$ ). However, GPC data have to be considered with some caution. The traces were recorded in DMF using PEO standards. Some of the samples were not completely soluble in DMF; in general, the higher the fluorinated repeat unit

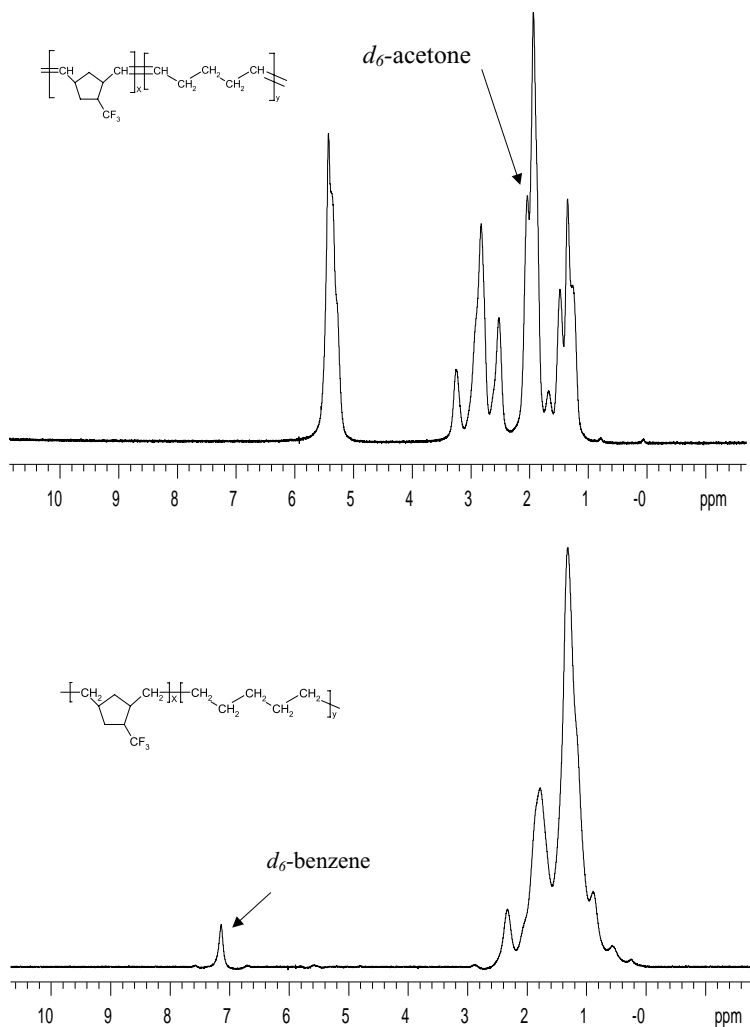


Fig. 7. Comparison of the  $^1\text{H}$  NMR spectra of polymers (III) (above) and (V) (below).

content the more soluble the material. The GPC results are consistent with the processes described in that the materials are definitely polymers, but because the GPC obtained is not always representative of the whole sample, the deductions that can be made are not particularly secure. While the main conclusions; namely, that we have polymers and that during hydrogenation some degradation occurs are reasonable. However, the absolute values of  $M_n$ ,  $M_w$  and polydispersity have to be treated with some caution; for example, the low values observed for the polydispersity of polymers (III) and (VI) almost certainly arise from fractionation effects in dissolving and filtering the sample prior to analysis. The TGA analysis indicates no variation in the thermal stability of the copolymers after the hydrogenation process and that, if any of these materials prove to be useful, the working temperature range will be quite broad.

#### 4. Conclusions

A series of unsaturated fluorinated copolymers prepared by ROMP were hydrogenated to give new fluorinated materials with new physical and chemical properties: the extent of hydrogenation was over 99%. The saturated polymers showed lowered  $T_g$  values when compared with their unsaturated analogues. Partially fluorinated elastomers were achieved from copolymers from *exo:endo* ( $\pm$ )-5-trifluoromethylbicyclo[2.2.1]hept-2-ene and cyclopentene. The saturated copolymer (VIII) with a  $T_g$  of  $-22^\circ\text{C}$  and 27 wt.% fluorine content (60 mol% of fluorinated monomer) is potentially interesting as an electrostrictive material and further investigations are in progress.

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